COST Action CA20129
MultIChem

The Second Conference
" Multiscale Irradiation and Chemistry Driven Processes and Related Technologies"

MultIChem 2023

BOOK OF ABSTRACTS

Vila Lanna
Prague, Czech Republic
April 26-28, 2023

https://www.jh-inst.cas.cz/multichem/

Preface

Dear colleagues,

We welcome all participants to the 2nd conference of the COST Action CA20129 “Multiscale Irradiation and Chemistry Driven Processes and Related Technologies” (MultIChem 2023). We are very pleased to host this meeting in Villa Lanna, a representative venue of the Czech Academy of Sciences in Prague.

MultIChem 2023 promises to be an exciting and stimulating conference with 30 oral and 30 poster presentations. It topically covers all areas that are of interest to the MultIChem COST action. At this meeting, in addition to academic partners, we have included contributions from industrial and clinical practice. The conference will also host the 2nd MultIChem Management Committee meeting which will happen in a hybrid in-person and online form.

We wish you a successful meeting and a pleasant stay in Prague!

Alexey Verkhovtsev
Juraj Fedor
(MultIChem 2023 chairs)

MultIChem Scientific Committee

- Alexey Verkhovtsev (MBN Research Center, Frankfurt am Main, Germany)
- Nigel Mason (University of Kent, Canterbury, UK)
- Andrey Solov'yov (MBN Research Center, Frankfurt am Main, Germany)
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Conference website

https://www.jh-inst.cas.cz/multichem/

Up-to-date information about the MultIChem 2023 conference and the COST Action MultIChem is available on the webpage http://mbnresearch.com/ca20129-multichem/main

Conference e-mail

multichem@jh-inst.cas.cz

General Information

Registration

The registration desk will be in the entrance hall of Villa Lanna on Wednesday, 26th April. In case of administrative questions, feel free to ask the organizers anytime during the conference.

Venue for Scientific Presentations

The talks will be given in the Apollo Hall, the main meeting room of Villa Lanna. Since we are approaching the capacity of the lecture room, we would like to ask you to also occupy places in the front rows, so that the rear seats are free for possible latecomers.

Poster Session

Poster session will be on Wednesday, 26th April at 18:00, in the entrance hall of Villa Lanna and in the back of the Apollo Hall. The poster panels will be set during the afternoon coffee break on Wednesday. The posters are not labeled, the participants are free to choose the panel according to their liking.

Conference Dinner

The conference dinner will be on Thursday, 27th April at 19:30, in the Restaurant and Brewery U Medvídků in the Old Town of Prague. The address of the restaurant is Na Perštýně 7. The dinner will be preceded by a beer tasting with a commentary from the brew master. The participants can get to the restaurant either by walking (3 to 5 km, depending on the chosen trajectory and on the amount of sightseeing) or by public transport. The fastest option is by green metro line A - start at station Hradčanská, exit at station Můstek. The local organizers will serve as guides for both of these options. Restaurant location may also be found by scanning the QR code or in the link below.

https://goo.gl/maps/p5ry3kxR6W87X4iF8

Management Committee meeting

The MC meeting will be on Friday, 28th April at 15:45. The meeting will take place in hybrid form in order to allow participation of MC members who do not attend the conference.

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Abstracts of Invited Talks

Abstracts for Poster Contributions

Scientific Program

Wednesday, April 26

10^{00} – 14^{00}	Participants registration
12^{30} – 14^{00}	Lunch
14^{00} – 14^{10}	**MultIChem 2023 Opening**
	Afternoon session I: Irradiation-driven transformations of molecular systems (Chair: Alexey Verkhovtsev)
14^{10} – 14^{40}	**Andrey Solov'yov**, MBN Research Center, Frankfurt am Main, Germany *The fifth release of MBN Explorer and MBN Studio: Advances and challenges in multiscale computational modeling*
14^{40} – 15^{10}	**Nigel Mason**, University of Kent, Canterbury, United Kingdom *Solid state chemistry in astronomy – A new age*
15^{10} – 15^{40}	**Brendan Dromey**, Queen's University Belfast, United Kingdom *Narrow energy spread proton beams from a laser driven accelerator for high precision spatiotemporal measurements of ion damage in matter*
15^{40} – 16^{00}	Coffee break
	Afternoon session II: Electron interactions with nano- and biomolecular systems (Chair: David Field)
16^{00} – 16^{30}	**Miloš Hrabovský**, TESCAN, Czech Republic *Automation of FIB-SEM process and open-access control of nanopatterning*
16^{30} – 17^{00}	**Stefan Denifl**, Institute for Ion Physics & Applied Physics, University of Innsbruck, Austria *Exploring reaction pathways of electron induced DNA damage*
17^{00} – 17^{20}	**Felipe Ferreira da Silva**, Universidade NOVA de Lisboa, Caparica, Portugal *Electron interactions with astrochemical relevant molecules*
17^{20} – 17^{40}	**Mateusz Zawadzki**, Gdansk University of Technology, Gdansk, Poland *Experimental studies on electron collisions with fundamental molecular targets*
17^{40} – 19^{30}	**Roadmap discussion (ca. 20-25 min)** **Poster session**

Thursday, April 27

	Morning session I: Ion interactions with biomolecular systems (Chair: Hidetsugu Tsuchida)
09^{00} – 09^{30}	**Thomas Schlathölter**, Zernike Institute for Advanced Materials, University of Groningen, the Netherlands *Heavy ion collisions with gas-phase DNA*
09^{30} – 10^{00}	**Alicja Domaracka**, Centre de Recherche sur les Ions, les Matériaux et la Photonique, Normandie Université, Caen, France *Ions interacting with complex molecular systems: the effect of a surrounding environment*
09^{00} – 10^{30}	**Gérard Baldacchino**, Université Paris-Saclay, France *What chemistry in the Bragg peak of protons and carbon ions?*
10^{30} – 11^{00}	Coffee break

	Morning session II: Irradiation-driven transformations of nano- and biomolecular systems (Chair: Malgorzata Smialek-Telega)
11^{00} – 11^{30}	**Paola Bolognesi**, CNR-Istituto di Struttura Della Materia, Monterotondo, Italy *Photoionisation studies of dipeptides*
11^{30} – 12^{00}	**Aleksandar Milosavljević**, Synchrotron SOLEIL, Gif-Sur-Yvette, France *Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy of protonated adenosine triphosphate molecule*
12^{00} – 12^{30}	**Alexey Verkhovtsev**, MBN Research Center, Frankfurt am Main, Germany *Quantum mechanical inputs for irradiation-driven molecular dynamics*
12^{30} – 14^{00}	Lunch
	Afternoon session I: Irradiation-driven chemistry in nanofabrication processes (Chair: Matija Zlatar)
14^{00} – 14^{30}	**Ilia Solov'yov**, Institute of Physics, Carl von Ossietzky University Oldenburg, Germany *Stochastic dynamics simulation of the focused electron beam induced deposition process*
14^{30} – 15^{00}	**Petra Swiderek**, Institute of Applied and Physical Chemistry, University of Bremen, Germany *Electron-driven chemistry of NH_3: New insights from molecular synthesis and fundamental processes of nanofabrication*
14^{00} – 15^{30}	**Anne Lafosse**, Institute of Molecular Sciences of Orsay, Université Paris-Saclay, France *Quantifying non-thermal desorption from molecular ices - Comparative study of photon and electron irradiation in the valence- and core-shell energy ranges*
15^{30} – 16^{00}	Coffee break
	Afternoon session II: Nanofabrication with focused particle beams (Chair: Felipe Fantuzzi)
16^{00} – 16^{30}	**Jose Maria De Teresa**, University of Zaragoza, Spain *Metallic structures grown by focused ion beam decomposition of condensed precursor layers and of metallorganic films*
16^{30} – 17^{00}	**Lukas Seewald**, Institute of Electron Microscopy and Nanoanalysis, Graz University of Technology, Austria *Recent progress in functional nanofabrication via 3D Nanoprinting*
17^{00} – 17^{30}	**Lisa McElwee-White**, University of Florida, USA *(η^3-allyl)Ru(CO)$_3$X Precursors: From FEBID to photoassisted area selective deposition*
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Friday, April 28

	Morning session I: Biomedical and technological applications of radiation (Chair: Michael Hausmann)
09^{00} – 09^{30}	**Andrew Nisbet**, Department of Medical Physics & Biomedical Engineering, University College London, United Kingdom *Current challenges and future developments in photon beam treatment planning*
09^{30} – 10^{00}	**Richard Amos**, Translational Proton Therapy Physics, University College London, United Kingdom *Planning and delivery of ion beam cancer therapy: Limitations of contemporary clinical practice*
10^{00} – 10^{30}	**Revaz Shanidze**, Kutaisi International University, Georgia *New hadron therapy center in Kutaisi, Georgia*
10^{30} – 11^{00}	**Alexander Gerbershagen**, The University Medical Center Groningen (UMCG), Groningen, the Netherlands *UMCG - from radiobiology to treatment planning*
11^{00} – 11^{20}	Coffee break
	Morning session II: Mechanisms of nanoparticle radiosensitization (Chair: Marc Benjamin Hahn)
11^{20} – 11^{50}	**Martin Falk**, Institute of Biophysics, Czech Academy of Sciences, Brno, Czech Republic *Is there a simple explanation for metal nanoparticle-mediated cell radiosensitization?*
11^{50} – 12^{20}	**Olivier Tillement**, NH TherAguix, France *Chelating bio-polymer for metal extraction: from concept to clinic*
12^{20} – 12^{45}	**Cécile Sicard-Roselli**, University Paris Saclay, France *Do we always want nanoparticles to enhance radical production?*
12^{45} – 13^{00}	**Yasmine Sebti**, University of Sorbonne, Paris, France *Hafnium oxide nanoparticles as computed tomography contrast agent*
13^{00} – 14^{00}	Lunch
	Afternoon session I: Radiation-induced chemistry (Chair: Juraj Fedor)
14^{00} – 14^{30}	**Stanislav Kadlec**, Eaton European Innovation Center, Czech Republic *Radiation-induced effects in power distribution industry - switching arcs, streamers and breakdown in low and medium voltage devices*
14^{30} – 15^{00}	**Tomáš Homola**, Roplass, Czech Republic *Atmospheric pressure plasma sources for rapid treatment of nano and bio surfaces*
15^{00} – 15^{20}	**Majdi Hochlaf**, Université Gustave Eiffel, Champs-sur-Marne, France *Irradiation-driven formation of abiotic* O_2 *from* SO_2
15^{20} – 15^{30}	**MultIChem 2023 Closing**
15^{30} – 15^{45}	Coffee break
15^{45} – 17^{00}	**MultIChem Management Committee Meeting**

The fifth release of MBN Explorer and MBN Studio: Advances and challenges in multiscale computational modeling

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Understanding of structure and dynamics of complex molecular systems, their stability, self-organization and growth, transformation, their interaction with radiation, chemistry are very important for a broad spectrum of applications in nanotechnology, microelectronics, materials science and medicine. Many of the aforementioned research areas and open problems therein involve processes that happen on very different time and spatial scales and may have rather different nature, although often sequences of such processes and their interlinks constitute multiscale scenarios capable to explain and quantify complex phenomena manifesting themselves in such systems. Examples of such multiscale phenomena include most of the radiobiological case studies, irradiation driven technologies for nanofabrication, astrochemistry and many more. Computational modelling of such complex processes and phenomena became possible only recently through the development of the multiscale theories and related powerful computational techniques enabling to interconnect outcomes of theoretical analysis at different temporal and spatial scales. The talk will give an overview of the recent developments of the multiscale techniques and their realization in the advanced software packages MBN Explorer and MBN Studio [1,2].

The official fifth release of MBN Explorer and MBN Studio will be announced in this talk and the key advances and new features of the new release will be presented though the related case studies conducted recently [3,4]. Particular attention will be devoted to the modelling of phenomena arising in irradiated MesoBioNano (MBN) systems which have been studied by means of reactive and irradiation driven Molecular Dynamics (RMD and IDMD) [5,6] and multiscale simulation techniques based on the combined use of quantum methods (many body theory, collisions theory, DFT, TDDFT), molecular dynamics (MD) and MC (Monte Carlo) approaches (see [3,4] and references therein), as well as by means of stochastic dynamics [7]. The talk will demonstrate many unique features of MBN Explorer and a wide range of its applications in Physics, Chemistry, Biology, Materials Science, and related industries.

The selected case studies are in the core of currently running European Research Projects supported within the HORIZON 2020 (N-Light and RADON), Horizon Europe (TECHNO-CLS) and Deutsche Forschungsgemeinschaft (DFG) frameworks as well as the COST Action MultIChem, see www.mbnresearch.com/european-collaborative-research-projects

References:

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[2] G.B. Sushko, I.A. Solov’yov, A.V. Solov’yov, *J. Mol. Graph. Model.* 88 (2019) 247
[3] I.A. Solov’yov, A.V. Korol, A.V. Solov’yov, *Multiscale Modeling of Complex Molecular Structure and Dynamics with MBN Explorer* (Springer International Publishing, Cham, 2017)
[4] I.A. Solov’yov, A.V. Verkhovtsev, A.V. Korol, A.V. Solov’yov (eds.), *Dynamics of Systems on the Nanoscale* (Springer Nature Switzerland, Cham, 2022)
[5] G.B. Sushko, I.A. Solov’yov, A.V. Solov’yov, *Eur. Phys. J. D* 70 (2016) 217
[6] G.B. Sushko, I.A. Solov’yov, A.V. Verkhovtsev, S.N. Volkov, A.V. Solov’yov, *Eur. Phys. J. D* 70 (2016) 12
[7] I.A. Solov’yov, I. Friis, G. Sushko, A.V. Solov’yov, *J. Comput. Chem*. 43 (2022) 1442

Solid state chemistry in astronomy – A New age

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In recent decades, ground-based (e.g. ALMA) and spaceborne telescopes (Spitzer and Hubble) have revolutionised our understanding of the chemical nature of the universe, with almost 300 gas-phase species now observed in the interstellar medium and circumstellar shells, ranging from simple diatomics to >12 atoms including fullerenes (C60 and C70). Species containing elements such as Carbon, Hydrogen, Oxygen, Nitrogen, and Sulphur (CHONS) are important ingredients in both planetary atmospheres and prebiotic molecules (e.g. simple amino acids observed in meteorites and comets). Since these complex organic molecules are believed to be formed on the surface of ice grains in the Interstellar Medium (ISM), the physicochemical interplay between gas-phase species and ice covered (or bare) grains is key to unravelling the origin of molecular complexity in space and its delivery to planets like Earth. Thus it is necessary to explore solid state chemistry under astronomical conditions.

Exploring solid state chemistry requires a number of different parameters to be defined and probed including; different mechanisms for inducing such chemistry (See figure 1 and composites of such methods); temperature (from circa 270 to <10K); morphology (crystalline vs amorphous); ice composition and the role of different substrates upon which the ice is grown (for examples different minerals which may act as catalysts). Exploring such a wide parameter base requires the adoption of a systems chemistry approach over the more traditional One Factor At a Time (OFAT).
In this presentation I will present recent results on the study of solid state chemistry illustrating some of the new insights that they are providing on the probability of synthesizing more complex biomolecules within the ISM and during planet evolution.

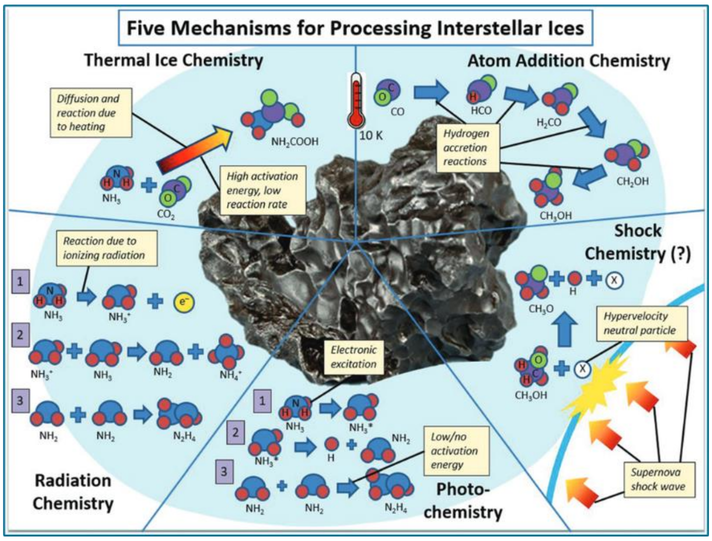

Figure 1: Different mechanisms of solid state chemistry identified as leading to molecular synthesis within ice mantles on surfaces of interstellar dust grains

Narrow energy spread proton beams from a laser driven accelerator for high precision spatiotemporal measurements of ion damage in matter

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Ionisation dynamics on the nanoscale seed the processes that govern pathways to macroscopic equilibrium in irradiated matter. Therefore, understanding the conditions that underpin this transition is critical in a wide range of applications from healthcare to radiation science. Recently we have demonstrated that laser driven ion accelerators can provide an ultrafast tool for studying this inherently multiscale regime with temporal resolution < 0.5 ps [1-3]. More generally speaking developing the techniques to study these phenomena in real time are becoming increasingly sought after for benchmarking the models and numerical approaches that seek to drill down into the relevance of these nanoscopic ultrafast processes for macroscopic radiation damage.

Here we discuss novel methods for improving the spatiotemporal resolution of these measurements by controlling the energy spread of the proton beam generated by the target normal sheath acceleration mechanism. Early estimates indicate a reduction from 100% to <10% energy bandwidth in the emitted proton beam while at the same time maintaining picosecond resolution for the interaction.

These new results indicate that the approaching horizon outlined above is coming into shaper focus as the tools and measurement techniques to tackle ultrafast nanodosimetry in a laboratory-based setting become increasingly more refined and streamlined.

References:

[1] B. Dromey, et al., *Nat.Comms*. 7 (2016) 10642
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Automation of FIB-SEM process and open-access control of nanopatterning

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One of the main challenges of full utilization of FIBSEM in current Nanoprototyping environment is automation of the process, to reduce downtime. Current portfolio of Tescan Essence software modules offer large variety for lamella prep, 3D tomography, automatic imaging, nanopatterning and depositions.

For highly demanding tasks, where the users require absolute freedom of parameters and steps in his workflow, we offer newly released SharkSEM Automation Toolbox SDK, based on python. Users get the possibility to program and develop their own patterning strategies based on their research in novel materials and patterning techniques. The biggest advantage are complex 3D depositions where precise patterning control is the key to a successful working prototype.

The users can also utilize Tescan Stream Files, for the definition of their own patterning strategy via the scripting interface, making it more compatible with already existing 3rd party tools within the community.

To fully utilize the microscope we allow the users to access the hardware and software controls to for example develop their own detector and test it in real world conditions.

Exploring reaction pathways of electron induced DNA damage

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Since more than two decades there has been a significant interest in the understanding of damage processes of DNA by low energy electrons (LEEs). Ionizing radiation releases a large number of LEEs in cells. In 2000, a pioneering study by Sanche and co-workers demonstrated that LEEs with kinetic energies between 3-20 eV can induce single strand breaks (SSB) and double strand breaks in a film of dry plasmid DNA [1]. They concluded from the measured profiles of strand breaks as function of electron energy that dissociative electron attachment (DEA) plays a significant role for the formation strand breaks. In the process of DEA, an electron attaches to a molecule and forms a transient negative ion which then may decay into a stable anion and neutral(s). Few years later, Sanche and co-workers extended the electron energy range in their studies with plasmid DNA downwards to about zero eV [2]. They only obtained SSB´s at very low energies, with major yields between ~0.8 and 2 eV. J. Simons modelled the SSB formation at such low energies and predicted in his computational studies that first the excess electron is captured in a π^* orbital of the base and subsequently the electron is transferred to the C-O σ^* orbital leading to the respective bond cleavage [3].

In this contribution I will present our recent DEA results for 5'-monophosphate of 2'-deoxycytidine (dCMPH), 5'-diethylphosphate of 2'-deoxycytidine (di-Et-dCMP) and 3',5'-tetraethyldiphosphate of 2'-deoxycytidine (tetra-Et-dCDP) [4]. To form the required molecular beam in the gas phase, significantly lower heating temperatures were sufficient for di-Et-dCMP and tetra-Et-dCDP, compared to dCMPH. The obtained results fully support the strand break model proposed by Simons. In addition, I will discuss intramolecular mechanisms competitive to DEA and implications for wet DNA.

References:

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Low energy electron interactions with molecules observed in the interstellar medium

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Polycyclic aromatic hydrocarbon (PAH) molecules, which are formed by fused aromatic rings, are ubiquitous in the interstellar medium (ISM). Based on the observation of unidentified infrared bands, it is estimated that PAH molecules hold up to 25% of all interstellar carbon. However, no particular PAH molecule has been unequivocally identified so far.[1] In 2018, McGuire and co-workers have detected the benzonitrile (c-C6H5CN) molecule in the Taurus Molecular Cloud 1 (TMC-1) via rotational spectroscopy.[2] Despite the discovery of benzonitrile in TMC-1, the abundance inferred by observations exceeds vastly the abundance predicted by astrochemical models. Propylene oxide was also identified in the gas phase in a cold massive protostellar clusters in the Sagittarius B2 star-forming region. This observation is representative of the earliest stage of solar system evolution in which a chiral molecule has been found [3]. The abundance of electrons in ISM, reveals the role of electron collisions in the formation of the universe, as well as their role in the star and planet formation, and whether they may play an important role in the molecular synthesis and growing in ISM, as precursors of life. These finding suggests that further formation or destruction routes of such compounds need to be included in the modelling. A possibility is associated with reactions initiated by secondary low-energy electrons, with a kinetic energy distribution below 100 eV, produced in large numbers from the interaction between primary cosmic radiation, e.g. high-energy particles (cosmic rays) or photons (UV up to x- and γ-rays) with interstellar matter.[4] In this presentation electron interactions with benzonitrile, leading to the negative ion formation as well as electron interactions with propylene oxide leading to the cation formation, will be presented and discussed.

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Experimental studies on electron collisions with fundamental molecular targets

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Collisions between electrons and molecules at low energy reveal unique quantum effects. Therefore electrons can be used as a powerful tool for testing quantum phenomena inside the matter. The scattering signal of electrons on different targets, in different range of incident energies, brings useful information about the quantum nature of processes occurring in electron-matter interaction. Our recent experimental work deals with the interactions of electrons with fundamental molecular targets. The simplest neutral molecule H_2 and CO are the subject of investigation.

Accurate data for molecular hydrogen dissociation is of crucial importance [1-3]. The great advantage of a recently built time-of-flight (TOF) system [4,5] is that it is not susceptible to transmission effects and can accurately give inelastic to elastic ratios for (in this case) electron excitation of H_2 and CO.

We report TOF cross section (DCS) measurements for the electron impact excitation transition in H_2 and CO. In this work, agreement between the available Converged Closed-Coupling (CCC) theory and experiment is excellent overall, and marks a transition in electron molecule scattering where differential scattering of excitation is found to be in such precise agreement. We also prove that the newly built apparatus can be used for accurate measurement of the mass stopping power for low energy electrons for H_2 for which agreement between theory and experiment is also found to be excellent [6].

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Heavy ion collisions with gas-phase DNA

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Heavy ion interaction with molecules of astrophysical interest

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Ion interaction with complex molecular systems rises a variety of phenomena of importance for our understanding in different fields, e.g. tailoring material properties, radiation damage at the molecular level of biological tissues, the formation and ageing of aerosols in the atmospheres of planets/moons, as well as the origin and evolution of molecules in space.

The collision of ions with matter leads to energy deposition via interaction with electrons and nuclei. These mechanisms are referred as electronic and nuclear stopping processes, respectively. The importance of this processes and the ratio depend on the projectile mass and velocity. The nuclear stopping, due to its localized character, can open specific fragmentation channel (non-statistical fragmentation). Such non-statistical process - knockout - has been observed in collisions with fullerenes and polycyclic aromatic hydrocarbon (PAH) molecules and produce reactive molecular species on the fs time scale. These react with other molecules of the cluster and intra-cluster growth processes drive the formation of a wide range of new large molecular species [1].

In this talk, I will give an overview of results on ion-induced fragmentation and ion-induced molecular growth processes of carbon containing clusters colliding with slow ions in the context of bottom-up approach to investigate formation of molecules in astrophysical environments. For example, formation mechanisms of large carbonaceous nanoparticles via ion single collision with fullerene/PAH clusters as well as a peptide bond formation in He^{2+} collision with β-alanine amino acid clusters (see Fig. 1) [2] will be discussed. Examples of ion processing of astrophysical ice analogues and condensed complex organic molecules (like nucleobases) will be also presented [e.g.: 3].

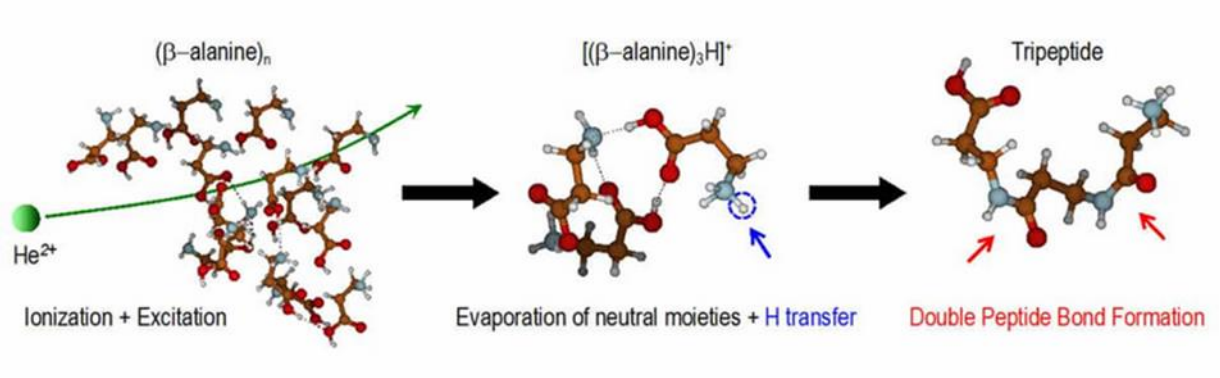

Figure 1 Polypeptide formation in clusters of β-alanine amino acids induced by low-energy He^{2+} ions.

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What Chemistry in the Bragg peak of protons and carbon ions?

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The reactivity of Fricke dosimeter solution was analyzed in the track-end of 25 MeV protons. Using a bundle of 20 optical fibers, we carried out an original optical setup to describe the absorbance changes of the solution under continuous irradiation over the ion-propagation axis with a sub-millimeter resolution. The differential primary yields were determined from the initial slope of the absorbance as function of time and with the constant dose rate provided by TRIM and GEANT4 program, for every bundle's fiber.

The results show an expected minimum value of the yield at the Bragg peak of 5 molecules/100eV. The yields are not null, which proofs the chemistry is still active in the peak and damages occurring in hadrontherapy for example might be also caused by indirect effects.

In addition, the broad Bragg peak observed for protons revealed a rise of yield beyond the peak, over 1 mm, which was attributed to the proton beam straggling providing high-LET protons but having low dose rates. Since a dose rate effect is ruled out [1], a few-keV electron effects are hypothesized [2] as they can produce an intermediate LET effect [3].

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Photoionisation studies of dipeptides

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Since the well-known Miller's experiment [1] in the 50s, the origin of biologically relevant compounds in abiotic conditions has attracted a lot of interest. Several investigations on the synthesis of early Earth organic compounds have been reported and the concept of a 'prebiotic soup', where some kind of activation triggers the spontaneous formation of such species, has been proposed as a likely milieu for the first appearance of complex molecules necessary for life.

In this work, we propose a new and alternative synthetic route for the formation of peptide chains that does not require a catalyst or an aqueous environment. In a collaboration among the groups at CNR- ISM, University Autonoma Madrid, Stockholm University and Elettra Sincrotrone Trieste state-of-the-art experiments and extensive simulations have been combined to show that VUV ionizing radiolysis of cyclo(alanine-alanine) [2,3], one of the simplest 2,5-Diketopiperazines (DKP) produces reactive cationic and neutral fragments such as oxazolidinones intermediates. Theoretical simulations have shown how the reaction among these fragments may lead to the reconstruction of the original cyclic dipeptide, that would then survive rather hostile ionizing environments, or to the formation of longer linear peptide chains, thus playing a key role in the early stages of the chemical evolution of the life.

The study of other cyclic dipeptides like cyclo(glycine-alanine) and cyclo(glycine-glycine) provides the opportunity to probe the generality of the proposed mechanisms [4]. The results show complex fragmentations far from trivial or generalisable from one species to another.

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Near-edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy of Protonated Adenosine Triphosphate Molecule

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We will present results of action Near-edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy of isolated singly protonated adenosine 5′-triphosphate (ATP) molecule, performed by coupling an ion trap to the soft X-ray synchrotron beamline PLEIADES [1]. We will compare the fragmentation of the singly protonated ATP from collisional induced dissociation (CID) and photon induced dissociation for the photon energies that correspond to valence (Figure 1) and core ionisation around P2p, C1s, N1s and O1s ionisation edges. Also, we will compare present NEXAFS spectra for C1s and N1s with previously published spectra for solvated ATP at different pHs [2]. We have performed DFT/TDDFT calculations [3] to investigate the protonation site of ATP and differences in resonant K-shell excitation when passing from a simple adenine to a neutral ATP and further to a protonated ATP, for C, N and O K-edges. Therefore, we could understand better the structure of the ATP by combining the experimental and theoretical results. The present study sheds light on ATP molecule, which is found in all life forms and represents the most important energy storage of a cell.

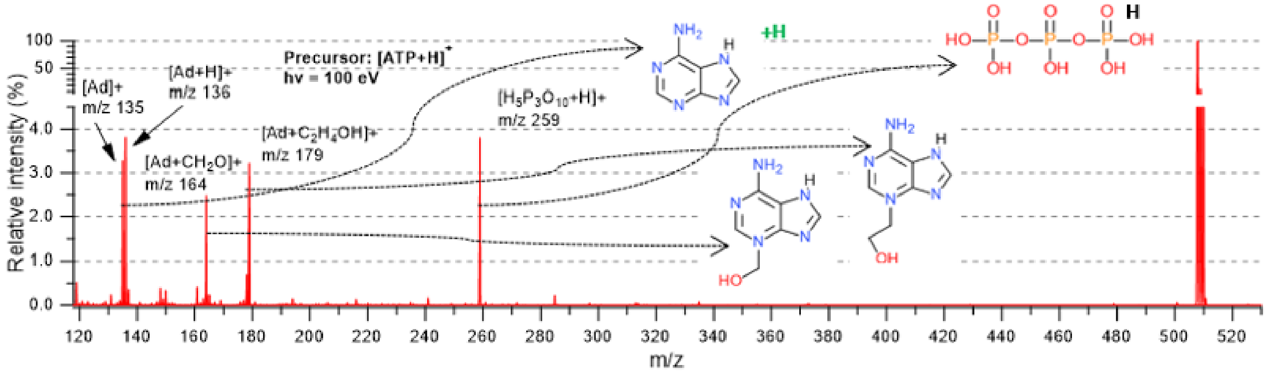

Figure 1. Tandem mass spectrum of $[ATP+H]^+$ recorded at the photon energy of 100 eV.

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Quantum mechanical inputs for irradiation-driven molecular dynamics

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Irradiation-Driven Molecular Dynamics (IDMD) [1] is the novel computational methodology implemented in the MBN Explorer software package [2], which enables atomistic simulations of irradiation-driven transformations of complex Meso-Bio-Nano (MBN) systems exposed to various radiation modalities (photons, electrons, ions). Within the IDMD framework, various quantum processes occurring in irradiated systems (e.g. ionization, electronic excitation, bond dissociation via electron attachment, or charge transfer) are treated as random, fast, and local transformations incorporated into the classical MD framework in a stochastic manner with the probabilities elaborated on the basis of quantum mechanics [1].

IDMD relies on several input parameters, such as the bond dissociation energies, molecular fragmentation cross sections, as well as the amount of energy transferred to the system upon irradiation and its spatial distribution. These characteristics originating from smaller spatial and temporal scales can be obtained (i) from accurate quantum mechanical calculations, e.g. by means of density functional theory (DFT) and time-dependent DFT [3], (ii) from experiment, or (iii) using analytical models [4-6].

Due to the limited number of parameters entering IDMD and the stochastic way of their implementation into molecular dynamics, the approach opens unique possibilities for modeling irradiation-driven modifications and chemistry of complex molecular systems beyond the limits of quantum mechanics-based computational schemes and pure classical MD.

This presentation will highlight several case studies illustrating the utilization of IDMD and its validation through the comparison with experiments. Particular examples include simulations of the formation of metal-containing nanostructures during the Focused Electron Beam-Induced Deposition (FEBID) process [1,4-6] and irradiation-induced fragmentation of biomolecular systems [3].

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Stochastic dynamics simulation of the focused electron beam induced deposition process

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Stochastic dynamics describes processes in complex systems having a probabilistic nature. They can involve very different dynamical systems and occur on very different temporal and spatial scales. This talk will discuss the concept of stochastic dynamics and its implementation in the popular program MBN Explorer [1-6]. MBN Explorer is a multi-purpose software package developed for advanced multiscale simulations of complex molecular structure and dynamics [1] by the MBN Research Center in Frankfurt (www.mbnresearch.com). It has many unique features and a wide range of applications in Physics, Chemistry, Biology, Material Science, and related industries.

Stochastic dynamics in MBN Explorer relies on the Monte Carlo approach and permits simulations of physical, chemical, and biological processes [5,6]. Stochastic dynamics can be used to describe many-body systems, where all their constituent elements can move stochastically and may experience transformations and reactions. These include different diffusion modes, dissociation and attachment (decay, fission and fusion), uptake and injections (creation and annihilation) processes, reactive transformations and particle type alteration. The system's constituent elements may have different nature, scale, properties, and a set of interactions with other components within the system that affect their stochastic dynamics.

The talk will present the basic theoretical concepts underlying stochastic dynamics implementation and demonstrate how it can be used to study focused electron beam induced deposition (FEBID). It will be shown that the FEBID process could be described through step-by-step transformations occurring to particles, representing intact and fragmented precursors, ligands, metal atoms, and substrate. The probabilities of the underlying processes occurring in the system will be discussed and strategies for their determination, relying on atomistic molecular dynamics and the track structure calculation, will be presented.

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Electron-driven chemistry of NH_3: New insights from molecular synthesis and fundamental processes of nanofabrication

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The electron-driven chemistry of ammonia (NH_3) has been a subject of research in our group for over a decade. Initially, projects aimed at the fundamental question how the synthesis of larger molecules from smaller building blocks, including NH_3, can be controlled by electron irradiation [1-3]. Exploiting the results obtained thereby, novel approaches to the functionalization of carbonaceous materials have been demonstrated [4-6]. Based on the fact that NH_3 can also act as a reducing agent under electron irradiation, the favorable effect of NH_3 as ligands or process gas in electron beam induced deposition (EBID) was investigated for the example of the potential precursor molecules cisplatin [7,8] and η^3-allyl ruthenium tricarbonyl chloride [9]. As a further step towards better control over nanofabrication processes, a recent study has revealed that NH_3 may be also a suitable reagent to impede autocatalytic surface reactions of $Fe(CO)_5$ on Fe deposits made by EBID [10].

This contribution reviews the examples summarized above and highlights the most recent findings. Our current mechanistic understanding of the underlying electron-induced chemistry of NH_3 will be presented and open questions as well as unexpected new results will be discussed.

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Quantifying non-thermal desorption from molecular ices - Comparative study of photon and electron irradiation in the valence- and core-shell energy ranges

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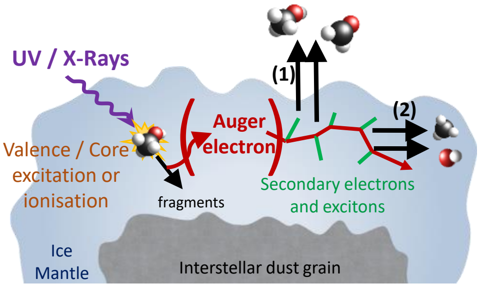
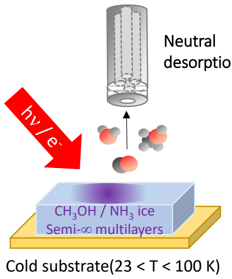
Chemistry in the interstellar medium (ISM) takes place both in the gas phase and on the surface of interstellar dust grains, where films of physisorbed molecules build up. These ices undergo processing by photons, cosmic rays, and by the large number of secondary electrons produced through their interaction with the ice. This chemistry feeds the medium with new molecular species. Desorption is the key step in this interplay between gas phase, solid phase and radiation, and is central in the interpretation of the most recent observational data obtained by the latest generation of telescopes (ALMA, NOEMA, JWST). Desorption can be induced thermally (by heating) or non-thermally (by radiation, including the promoted chemical processes.)

In order to quantify the non-thermal desorption from cryogenic molecular films and to gain insights into the processes at play, we have conducted comparative measurements of photo- and electron-induced desorption (PSD and ESD). Two setups were used for these experiments, the SPICES setup of the LERMA group, and the E/SOLID setup at ISMO. In both setups, model molecular ices of methanol (CH_3OH) [1,2] and ammonia (NH_3) [3,4] were vapour deposited onto gold and the desorption of neutral species was measured by mass spectrometry. Thermal desorption analysis (TPD) was used to calibrate the mass spectrometer signal, determine the ice thickness and morphology, and chemically analyse the processed layers. The SPICES setup was coupled to two SOLEIL synchrotron beamlines: (i) DESIRS in the valence-shell range (6-12 eV) and (ii) SEXTANTS in the core-shell range (O and N-K edges). The electron irradiation twin experiments were performed using the E/SOLID setup, in the low-energy range (typical for secondary electrons < 20 eV) and at several hundreds of eV in order to mimic the secondary Auger electrons. Desorption yields per incident/absorbed particle are compared for photon and electron irradiation either as a function of the incident energy in the low-dose regime (spectroscopic study), or as a function of the cumulated dose at a fixed irradiation energy (kinetic study).





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Metallic structures grown by focused ion beam decomposition of condensed precursor layers and of metallorganic films

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Focused Ion Beam (FIB) techniques are very relevant to pattern materials down to the nanoscale. In combination with precursors, they gives rise to the growth of nanomaterials, a technique known as Focused Ion Beam Induced Deposition (FIBID). Unfortunately, FIBID is a slow technique, which limits its applicability. In my contribution, I will discuss two strategies that improve the throughput of FIBID by a few orders of magnitude. Binary-collision-approximation simulations have provided theoretical support to some of the experimental findings.

The first strategy is based on the condensation of precursors delivered through a gas injection system onto a cooled substrate (Cryo-FIBID). By using a cryogenic module based on liquid N_2, we have applied Cryo-FIBID to grow W-C [1, 2], Pt-C [3] and Co [4] deposits, observing a-few-hundred-times enhancement in the growth speed compared to room-temperature FIBID. Following this approach, we have grown electrical contacts on micro-structures will be discussed. In addition, its successful implementation at -60°C, making use of a thermoelectric plate, will be highlighted [5].

The second strategy is based on the ion-induced dissociation of spin-coated metalorganic films, in particular Palladium Acetate films [6]. Remarkably, the usage of a Ga^+ dose as low as 30 $\mu C/cm^2$ is sufficient to fabricate structures with a high metallic Pd content and a low electrical resistivity. Three applications have been explored: (i) creation of electrical contacts to nanowires, (ii) fabrication of small gaps between large metallic contact pads, and (iii) fabrication of large-area metallic meshes. On the other hand, the use of focused electrons is less efficient to decompose these films [7].

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Recent Progress in Functional Nanofabrication via 3D Nanoprinting

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The ongoing trend towards ever smaller spatial dimensions in many fields of science and technology raises a demand on reliable processes to fabricate structures at such dimensions. Although traditional technologies, such as resist-based lithography, matured in that respect, there are situations in which additive direct-write manufacturing would be the method of choice due to minimized requirements on the substrate and the possibility of true 3D nanofabrication. Amongst the very few techniques in that context, Focused Electron Beam Induced Deposition (FEBID) has matured to a level of controlled mask-less direct-write fabrication, which is currently unique when aiming on nanoscale structures. In essence, a typically organometallic precursor is injected into an electron microscope, adsorbs on a substrate and is locally decomposed and immobilized by interaction with the focused electron beam. Precise control over pixel dose and lateral position allows the controlled spatial stacking of individual nano-volumes to produce even complex 3D nano-architectures with individual feature sizes down to the sub-20 nm regime under optimized conditions [1]. Cooperative efforts between experiments, theory and simulation identified the major contributions in 3D-FEBID[2] and enabled a predictable upfront design[3]. These possibilities are used in our workgroup for the development of novel 3D nano-probe concepts for advanced atomic force microscopy (AFM) [4] in collaboration with industry, while new possibilities are explored to expand the 3D nano-printing toolbox. In this contribution, we start with a brief FEBID introduction and then give an overview of recent progress with respect to novel 3D nano-probes for advanced AFM modes, including conductive-AFM (CAFM), electrostatic force microscopy (EFM), Kelvin force microscopy (KFM) and magnetic force microscopy (MFM). Additionally, we discuss currently ongoing activities, which focus on the controlled local functionality tuning of multiscale FEBID structures to pave the way for yet unknown possibilities. Thereby, the contribution spans a bridge from fundamentals to scientifically but also industrially relevant applications, rounded up with a view on pending questions.

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(η^3-allyl)Ru(CO)$_3$X Precursors: From FEBID to Photoassisted Area Selective Deposition

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Precursor choice for any deposition method requires consideration of the reaction conditions and possible decomposition mechanisms for the particular method. This talk will compare precursor design and deposition of Ru thin films and nanostructures from the same (η^3-allyl)Ru(CO)$_3$X precursors by two different methods: Focused Electron Beam-Induced Deposition (FEBID) and Photo-Assisted Chemical Vapor Deposition (PACVD). For the FEBID application, the electron-induced precursor chemistry was studied by UHV surface science modeling [1] and gas phase electron-molecule interactions [2] before it was used in FEBID [3].

Photoassisted chemical vapor deposition (PACVD), or photochemical CVD, is a technique that can be used for metallization of thermally sensitive substrates such as patterned self-assembled monolayers (SAMs), providing a potential route to area selective deposition (ASD) through different reactivity with the terminal functional groups of the SAM [4, 5]. In PACVD, photochemical dissociation of the precursor occurs in the gas phase and is dependent upon the photochemical and subsequent thermal reactivity of the precursor. The reactivity is controlled by the excited state properties and bond dissociation energies of the precursor and can be assessed by determining quantum yields for starting material disappearance and appearance of ligand loss products [6, 7]. Screening for the decomposition efficiency of potential precursors for PACVD can be used in a down selection process before deposition experiments begin. Precursor design, electronic structure, and photochemical reactivity of the complexes will be discussed in the context of the results of PACVD of Ru on functionalized SAMs.

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Current Challenges and Future Developments in Photon Beam Treatment Planning

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The development of computerised photon beam radiation therapy planning can be traced to the 1950s (1). Within the same decade beam modulation using physical absorbers was proposed (2). With the development of computerized tomography in the 1970s 3D treatment planning become possible. The first proposal for beam intensity modulation using rotational therapy was published in the 1980s (3). Today volumetric modulated radiotherapy and image guided radiotherapy is widespread (4,5), with automatic treatment planning (6) and adaptive radiotherapy (7) beginning to be implemented routinely. However, challenges still remain in photon beam radiotherapy treatment planning. Global access to advanced radiotherapy is still an issue, although remote radiotherapy treatment planning support is possible. Motion management and plan robustness remain challenging for some clinical sites. The calculation of dose to medium, rather than water, is a relatively recent recommendation. The use of biological optimisation has not been adopted routinely and inconsistencies are still present in target volume delineation. Against this background the current status, challenges and future developments in photon beam treatment planning are reviewed and presented.

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Planning and Delivery of Ion Beam Cancer Therapy: Limitations of Contemporary Practice

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The application of protons and heavier-ion species to clinical radiotherapy continues to grow and develop worldwide. However, we are yet to fully exploit the physical characteristics of charged-particles for radiotherapy. Precise control of particle range within patients’ anatomy and accurate quantification of variable biological effectiveness along particle tracks remain challenging. A lack of adequate data to reduce uncertainty in calculated particle ranges *in vivo* and to accurately model linear-energy transfer (LET) and its correlation to relative biological effectiveness (RBE) hinders progress with solving these issues with contemporary practice.

Despite these challenges, technological advances are presenting new opportunities for charged-particle radiotherapy. The application of ion-beams to the delivery of ultra-high dose rate (UHDR) radiotherapy is received significant attention globally; the first in-human UHDR proton therapy clinical trial has recently been completed in the United States. The delivery of spatially-fractioned radiotherapy with ion-minibeams is also being investigated and hitherto shows promise as a clinically efficacious technique. Understanding the underlying mechanisms for pre-clinical observations made with these new delivery techniques is paramount for their safe clinical translation.

This presentation will summarize the limitations of contemporary clinical practice and the challenges associated with emerging techniques for delivery of ion-beam radiotherapy.

New hadron therapy center in Kutaisi, Georgia

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New Hadron Therapy Center (HTC) at the Kutaisi International University in Georgia, which is currently under construction, will be equipped with 2 superconducting synchrocyclotrons IBA S2C2, providing proton beams, with maximum kinetic energy of 230 MeV. One of these accelerators is a part of IBA single gantry Proteus©ONE system for the proton therapy, while the other one is the main device for this new research infrastructure at Kutaisi International University. The HTC is funded by the International Charity Foundation Cartu, the largest charity foundation in Georgia. Opening of HTC is planned in 2025. Research with the proton beams in 70-230 MeV energy range is foreseen in multiple disciplines, including basic and applied nuclear physics, radiation biology and medicine as well as material sciences and detector development and testing. As the only cyclotron-based treatment and research facility in Georgia and South Caucasus, HTC will become a research hub for international projects. The research projects at HTC will be selected by the dedicated International Advisory Board.

UMCG - from Radiobiology to Treatment Planning

A. Gerbershagen, P. v.d. Luijk, P. Pisciotta, F. Romano, A. v.d. Scaaf, S. Both

The present contribution summarizes the long path from radiobiological experiments to patient treatment optimization. UMCG in Groningen, Netherlands, uniquely combines the operation of a research laboratory PARTREC, which provides proton and ion beams for fundamental research in radiobiology and medical physics, and GPTC, a proton therapy treatment center treating hundreds of patients per year. The presentation summarizes diverse research activities performed at UMCG and, with help of specific examples, delineates the path from radiobiology to human treatment planning.

Is There a Simple Explanation For Metal Nanoparticle-Mediated Cell Radiosensitization?

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Metal nanoparticles (NPs) represent a promising tumor cell sensitizer for radiotherapy. However, the mechanism of radiosensitization by NPs remains a subject of intense research. Initially, it was thought that irradiated NPs emit secondary electrons and ROS, which thus amplify the radiation dose in their immediate surroundings and enhance nuclear DNA damage. However, it has been shown that NPs do not penetrate the cell nucleus, calling this hypothesis into question. Thus, cytoplasmic organelles, particularly mitochondria, which have their own DNA, and lysosomes, which contain NPs, are suggested as additional / alternative targets for NP-mediated radiosensitization. In this presentation, we will compare the effects of different types and sizes of irradiated and non-irradiated NPs on the cell nucleus (DNA fragmentation, chromatin architecture), cytoplasmic organelles (mitochondria and lysosomes) and the overall state of the cell as a system. Taken together, our results to date suggest that NP-mediated radiosensitization is caused by an integrative involvement of multiple mechanisms rather than a single mechanism, which together with the effects of radiation stimulate the cellular system towards cell death.

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Chelating bio-polymer for metal extraction: from concept to clinic

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Metallic dysregulations of endogenous metals and metal overloads have long been known to be tightly correlated with diseases like Wilson disease (copper) or hemochromatosis (iron). During the last decades, metal dyshomeostasis with small overloads of endogenous redox active metals like copper or iron have also been suspected to be correlated with pathologies where oxidative stress is recognized to have an important role. In particular, important levels of unbound iron in plasma have been associated with lower vital prognosis for patients in intensive care units (ICU) for different pathologies where free iron or copper can be released either by hemolysis and/or different cell deaths.

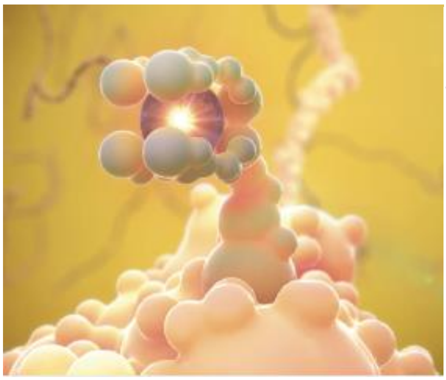
Clinical studies have shown that higher plasma concentrations of catalytic iron are correlated with significantly greater risk of deaths. Likewise, elevated free iron and transferrin saturation in serum have also been associated with an increased mortality in patients. The impact of iron has also been emphasized in chronic liver diseases with higher iron levels for patients: for ACLF, higher incidence of multi-organs failure and consequent mortality is observed for patients with dysregulated iron homeostasis. Kidneys are other at-risk organs for iron dysregulation. Level of catalytic iron is an important factor during cardiac surgery.

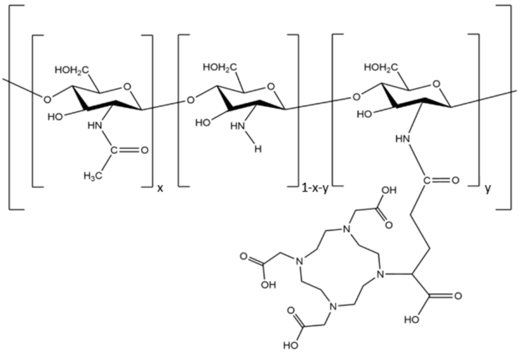
We report the development and the use of a dialysis-based medical device for the extraction of metals in critical cases. The medical device is an additive to the dialysate composed of a functionalized chitosan that can chelate endogenous metals like iron or copper. This water-soluble polymer is obtained after controlled reacetylation and grafting of DOTAGA. Due to the high mass of chitosan, the polymer cannot cross through the membrane and the metals are trapped in the dialysate during hemodialysis.

Metal extraction has been evaluated in vitro using a hemodialysis protocol.

Feasibility studies have been performed on healthy sheep showing no acute toxicity throughout the entire dialysis procedure and first insights of metallic extraction even on healthy animals.

The first clinical trial is in progress.





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Do we always want nanoparticles to enhance radical production?

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A major application of metallic nanoparticles is expected in medicine and more specifically for radiotherapy and imaging. For radiotherapy, nanoparticle benefit is their additional radical production when submitted to ionizing radiation, leading to enhanced cancer cell death [1, 2]. Another asset of metallic nanoparticles is that they can act as enhanced contrast agents and could have an important role for early stage detection of pathologies [4, 5]. Nevertheless, considering that imaging is often performed with radiation beams as such X-Rays, additional non-negligible dose delivered to the tissues is expected. Therefore, comparing gold and hafnium nanoparticles, we measured hydroxyl radical production when nanoparticles are submitted to ionizing radiation. We also compared the impact of different coatings to design an efficient nanoparticle for early diagnosis without inducing any deleterious radical production.

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Hafnium oxide nanoparticles as computed tomography contrast agent

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Computed Tomography (CT) is a widely used imaging system based on differences in the X-ray attenuation of tissues [1]. The primary limitations of CT are its relatively low soft-tissue contrast and sensitivity. The development of a multicolored scanner, and the many significant side effects of iodine, currently used as a contrast agent, requires new candidates with high k-edge as contrast agents in X-ray imaging. Using nanoparticles (NPs) as contrast agents can enable the delivery of a greater mass concentration of the X-ray attenuating element per particle compared to molecular agents (i.e., iodine). Recent research has shown that hafnium oxide (HfO_2) nanoparticles are biocompatible. These inorganic nanoparticles have gained attention for their high X-ray attenuation, and thus can be used as potential contrast agents for computed tomography. Herein, inorganic NPs made of hafnium oxide had been synthesized as nanocarriers and potential CT contrast agent. The synthesis of hafnium oxide NPs was optimized using a sol-gel method associated to microwave irradiation [2]. The analysis of several synthesis conditions allowed the selection of an optimal condition for the synthesis and stabilization of surfactant-free nanoparticles. The obtained stable, and reproducible HfO_2 NPs were surface functionalized with fucoidan, a sulfated polysaccharide and citrate ions as a control ligand. The nanoplatforms were then characterized with several physicochemical techniques.

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Radiation-induced effects in power distribution industry - switching arcs, streamers and breakdown in low and medium voltage devices

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An overview of radiation-induced effects in power distribution devices is given, especially those effects related to atmospheric plasmas. Both hot (switching arc) and cold (streamers) atmospheric plasmas are important phenomena occurring or used in devices of the power distribution industry.

Switching arcs are established during the opening of electrical contacts in devices like circuit breakers or contactors. During switching, a high current of several kA can flow through the contacts and is ionizing the surrounding gas, leading to the formation of an electric arc. This arc carries high power with a significant part being transferred by radiation.

The heat transferred to the contacts results in contact erosion. The evaporated metal modifies the plasma itself and its properties (conductivity, specific heat, viscosity etc.). Apart from contact erosion, plastic ablation effects are also important for the switching arcs. Such ablated vapors interact with the arc and alter its chemical composition and its behavior. Examples of numerical arc models for a miniature circuit breaker are shown and compared with experimental results [1, 2].

Next part is related to simulation of streamer propagation and breakdown in gases, where photoionization is important, especially in air. However, also other gases are of high technical importance, especially SF_6 and other fluorinated gases as alternatives to SF_6, e.g. fluoronitrile C_4F_7N. The authors and their partners have been looking for properties of C_4F_7N like cross sections of electron impact ionization, attachment, photoionization and photoemission [3-5].

Finally, comparison of two approaches to radiative transfer and photoionization in streamer simulations are presented: Eddington approximation and method of Discrete Ordinates. While the Eddington approximation has been frequently used in streamer simulations, using the Discrete Ordinates method allows to capture shadows, leading to much lower photoionization and delays in streamer propagation.

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Atmospheric pressure plasma sources for rapid treatment of nano and bio surfaces

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Surface and interface treatment using low-temperature plasma presents an intriguing opportunity for a diverse range of applications, spanning from textiles and automotive to advanced optoelectronics such as flexible and printable solar cells and batteries. ROPLASS focuses on creating novel plasma technologies that enhance the value of various materials, including glass, fabrics, polymers, metals, and even 2D nanomaterials such as graphene and graphene oxides, for surface treatment purposes. The flagship and primary technology utilized by ROPLASS is the Diffuse Coplanar Surface Barrier Discharge (DCSBD), an exclusive form of dielectric barrier discharge. DCSBD can rapidly alter the surface properties of various materials while preserving their bulk properties. DCSBD is capable of producing cold, diffuse, and uniform plasma (<70 °C) in ambient air as well as in technical-grade gases such as nitrogen, argon, methane, hydrogen, carbon dioxide, and pure water vapor (as illustrated in Fig. 1). ROPLASS' DCSBD technology owes its success to the unique electrode arrangement and advanced alumina ceramics, which enable it to generate cold surface plasma at temperatures lower than 70 °C, with an incredibly high-power density of up to 100 $W.cm^{-3}$. This power density is among the highest ever reported for open air plasma. The DCSBD plasma units can be seamlessly integrated into existing roll-to-roll lines [1], allowing for swift surface treatment of functional films and interfaces in thin film devices, such as perovskite solar cells [2]. Additionally, due to the low plasma temperature, the DCSBD is ideal for effectively treating biological materials, such as plant seeds (plasma agriculture) or other biologically relevant materials (plasma medicine).

Figure 1. a) A roll-to-roll setup featuring 25 RPS400 planar plasma units, each with a plasma area 8 cm × 19 cm, operating in ambient air conditions, b) portable plasma unit RPS40+ (5 cm × 2 cm), utilized in [3].

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Irradiation-driven formation of abiotic O_2 from SO_2

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Molecular oxygen, O_2, is vital to life on Earth and possibly also on exoplanets. Although the biogenic processes leading to its accumulation in the Earth's atmosphere are well understood, its abiotic origin is still not fully established.

In the present work, SO_2 has been investigated experimentally by multi-particle coincidence detection using the well-established TOF-PEPEPIPICO technique where the target species were irradiated by 40.81 eV photons (HeIIα) from a pulsed helium discharge lamp, mimicking an intense component of the solar spectrum and of many stellar spectra. In addition, ion-ion coincidence measurements on SO_2 were carried out at the synchrotron radiation facility BESSY-II where photon energies of several more solar X-ray lines were available. We find experimental evidence for electronic-state-selective production of O_2^+ from SO_2, a chemical constituent of many planetary atmospheres and one which played an important part on Earth in the Great Oxidation Event. These experimental findings are analysed with the aid of advanced ab initio computations resulting in the following model: First, the single photon double ionisation of SO_2 forms the SO_2^{2+} dication. The O_2^+ production involves isomerization of SO_2^{2+} by a roaming mechanism leading to efficient formation of the O_2^+ ion in form of dissociative double ionisation of SO_2, which can be converted to abiotic O_2 by electron neutralisation. This formation process may contribute significantly to the abundance of O_2 and related ions in planetary atmospheres, such as the Jovian moons Io, Europa and Ganymede. It represents an alternative to and may compete with the well-established abiotic O_2 production pathways via the photodissociation of water vapor by extreme ultraviolet (XUV) light [2-4] or the near ultraviolet (NUV) photochemistry of titanium (IV) oxide (titania) [5]. We suggest that this sort of ionic pathway for the formation of abiotic O_2 involving multiply-charged molecular ion decomposition may also exist for other atmospheric and planetary molecules. This work is just published in Science Advances [5].

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Abstracts for poster contributions

Electron beam effects on neuromorphic nanocluster networks during electron microscopy experiments

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Brain-inspired (neuromorphic) computation has the potential to overcome certain inherent limitations of conventional silicon technology, offering – ultimately – a new generation of faster, low-power computing.[1,2] Networks of atomic clusters near the electrical percolation threshold display fascinating physics such as voltage switching behaviour like that found in the brain. They are one candidate of particular interest for the emerging field of neuromorphic and reservoir computation.[3–8] Electron microscopy is employed in such studies in order to assess the morphology of the nanocluster networks.[5–8] Little attention has been given to the effects of the electron beam on the nanocluster network under electron irradiation, e.g., via beam-induced heating.[9,10]

In this contribution, I will present our observations of electron beam induced effects on nanocluster networks during electron microscopy experiments performed at different instruments, and employing various imaging modes in order to reduce these effects.

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Atomistic Modelling and Structural Characterisation of Coated Gold Nanoparticles for Biomedical Applications

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We present the results of atomistic structural characterisation of 3.7 nm gold nanoparticles (NPs) coated with polymer polyethylene glycol (PEG)-based ligands of different lengths (containing 2-14 monomers) and solvated in water. The system size and composition are selected in connection to several experimental studies of radiosensitisation mechanisms of gold NPs [1]. We characterise the coating structure and distribution of water close to the NP surface by means of molecular dynamics simulations using the MBN Explorer [2] software package. The results of simulations carried out in this study, combined with the results of our recent study [3], and those from the field of polymer physics, are used to calculate key structural parameters of the coatings of radiosensitising gold NPs. On this basis, connections between the coating structure and distribution of water are established for different NP sizes as well as lengths and surface densities of coating molecules. The quantitative analysis of water distribution in the vicinity of coated metal NPs can be used to evaluate the radiosensitising effectiveness of a particular NP system based on the proximity of water to the NP metal core, which should impact the production of hydroxyl radicals and reactive oxygen species in the vicinity of metal NPs exposed to ionising radiation [4].

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Freezing and thawing cells to radio-sensitize tumour cells

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In this work, we shed new light on the highly debated issue of chromatin fragmentation in cryopreserved cells. We describe replicating cell-specific DNA damage and higher-order chromatin alterations after freezing and thawing. We identified DNA structural changes associated with the freeze-thaw process and correlated them with the viability of frozen and thawed cells. And simultaneously evaluated DNA defects and the higher-order chromatin structure of frozen and thawed cells with and without cryoprotectant treatment. We found that in replicating (S phase) cells, DNA was preferentially damaged by replication fork collapse, potentially leading to DNA double strand breaks (DSBs), which represent an important source of both genome instability and defects in epigenome maintenance.

This induction of DNA defects by the freeze-thaw process was not prevented by any cryoprotectant studied. Both in replicating and non-replicating cells, freezing and thawing altered the chromatin structure in a cryoprotectant-dependent manner.
Freezing and thawing efects are tested to radio-sensitize the tumour cells.

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Collision-Induced Transformation of Graphene Nanoflakes into Carbon Nanotubes: A Reactive Molecular Dynamics Investigation

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Graphene [1] is a 2D planar structure consisting of a single sheet of sp^2 carbon atoms arranged in a honeycomb-like pattern. It has exceptional properties such as high carrier mobility and capacity, high electron transfer rate, outstanding fluorescence quenching ability, high thermal conductivity, maximal surface-to-volume ratio, excellent robustness and flexibility, and zero-band gap. Graphene is expected to play a significant role in the development of the next generation of high-performance electronic and spintronic applications. It is also a base material for the advancement of carbon-based electronics. However, structural modifications are required to overcome graphene's semi-metallicity after incorporating a finite band gap. This can be achieved by creating new edge states and corner states by cutting graphene into various finite shapes. Graphene nanoflakes (GNs) or graphene quantum dots [2,3] are created through this strategy. Initially, it was believed that GNs would transform spontaneously into carbon nanotubes, but they are thermally stable and do not undergo significant structural changes upon heating [4]. The underlying nucleation and growth processes responsible for carbon nanotube formation are still largely unknown. To investigate whether finite pieces of graphene can be basic building blocks of other carbon allotropes, we conducted reactive molecular dynamics simulations to study the collision-induced transformation of graphene nanoflakes into carbon nanotubes. We utilised the MBN Explorer [5] computational package to perform calculations involving one colliding projectile (C_n fullerene, $n = 20,60$) and a graphene nanoflake with varying collision energies and angles. We considered different nanoflake shapes and sizes and used the reactive empirical bond order Brenner potential in all simulations. We incorporated thermal effects through inclusion of a Langevin thermostat. Our simulations revealed evidence that collision-mediated transformation of graphene nanoflakes into carbon nanotubes can occur under certain collision conditions. We identified two transformation mechanisms: through bouncing and through attachment, which are dependent on the fullerene angle incidence and the relative masses of the nanoflake and the fullerene.

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Synchrotron-based VUV spectroscopy of solid methanol and water ice as a diagnostic tool

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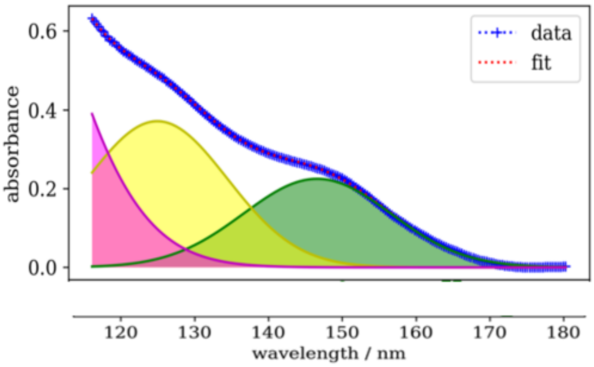
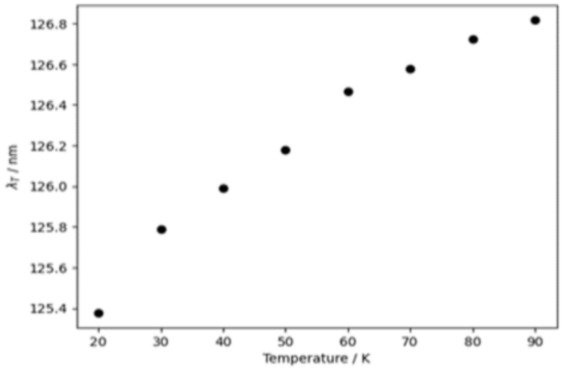
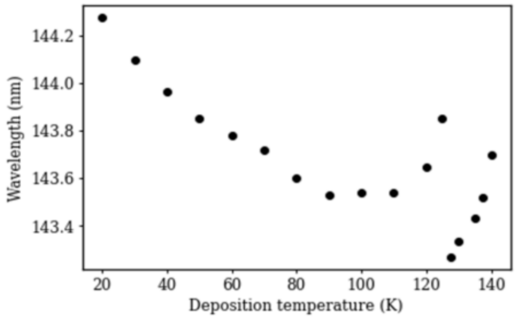
The extraordinary temporal stability of the ASTRID2 synchrotron storage ring, of better than 0.1% over many hours, yields very high signal-to-noise (S/N) VUV spectra of ices. Such spectra lack sharp features, but the S/N is such that one can assign wavelengths to better than 0.025 nm in peaks of width 20 nm. A typical spectrum of a 7.5 nm methanol film is shown below, plus the variation with temperature of deposition of the peak absorption wavelength, in the ${}^1A' \leftarrow X\,{}^1A'$ transition. Data for the A ${}^1B_1 \leftarrow X\,{}^1A_1$ transition for water ice films, of similar thickness, are also shown.



VUV absorption spectrum of solid methanol, showing a 3 gaussian fit. 20K data



Solid methanol: peak absorption wavelengths at ~125 nm as a function of deposition temperature



Amorphous solid water: peak absorption wavelengths at ~143 nm as a function of deposition temperature

Results may be used to demonstrate that these films harbour electric fields in the region of 10^7 to 10^8 Vm^{-1} as described in [1]. Note that methanol and water ice behave quite differently and also that a phase transition at 125K is evident in water ice. These data have implications for astrophysical ices.

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Extending Bio-SAXS measurements of Single-Stranded DNA-Binding Proteins: Radiation Protection of G5P by Cosolutes

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Small-angle X-ray scattering (SAXS) can be used for structural determination of biological macromolecules and polymers in their native states. To improve the reliability of such experiments, the reduction of radiation damage occurring from exposure to X-rays is needed. One method, is the use of scavenger molecules that protect macromolecules against radicals produced by radiation exposure.In this study we investigate the feasibility to apply the compatible solute, osmolyte and radiation protector Ectoine (THP(B)) as a scavenger throughout SAXS measurements of single-stranded DNA-binding protein Gene-V Protein (G5P/GVP). Therefore we monitor the radiation induced changes of G5P during bio-SAXS. The resulting microscopic energy-damage relation was determined by particle scattering simulations with TOPAS/Geant4. The results are interpreted in terms of radical scavenging as well as post-irradiation effects, related to preferential-exclusion from the protein surface. Thus, Ectoine provides an non-disturbing way to improve structure-determination of proteins via bio-SAXS in future studies.

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An XPS study on the influence of water on radiation damage: Chemical changes to Gene-V Protein

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Single-stranded DNA-binding proteins such as Gene-V Protein (G5P) play a crucial role in DNA replication, recombination and repair of Bacteriophage F1. These processes are responsible for the cell response to and survival of the cell after exposure to ionizing radiation, i.e. during radiation therapy in cancer treatment.

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical damage of ionizing radiation to G5P itself. Direct and indirect damage was detected through combined vacuum XPS and near-ambient pressure (NAP) XPS measurements under water and nitrogen atmosphere. The x-ray irradiation leads to degradation i.e. via dehydrogenation, decarboxylation, dehydration and deamination. A strong increase of protein damage was observed in water as compared to vacuum.

In situ monitoring of the influence of water on Gene-V Protein radiation damage by NAP-X-ray photoelectron spectroscopy

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X-ray photoelectron spectroscopy (XPS) was used to analyze the influence of water on radiation damage to a single-stranded DNA-binding protein: Gene-V Protein (G5P/GVP) and its most abundant amino acids (Alanine, Arginine, Cysteine, Glycine, Lysine, Methionine, Tyrosine). This protein plays a crucial role in maintaining the DNA replication and repair within Bacteriophage F1. G5P serves as a model protein for ssDNA-binding proteins.

Vacuum (UHV) measurements were combined with near-ambient pressure (NAP) XPS measurements under water and nitrogen atmosphere to detect the effects of water on radiation damage to G5P protein and selected aminoacids. The corresponding damage pathways of both direct and indirect radiation damage were examined. The exposure of proteins and aminoacids to x-rays lead to degradation i.e. via dehydrogenation, decarboxylation, dehydration and deamination. Furthermore, reactive neutral or ionic radicals derived upon protein fragmentation. A strong increase of protein damage was observed in water as compared to vacuum.

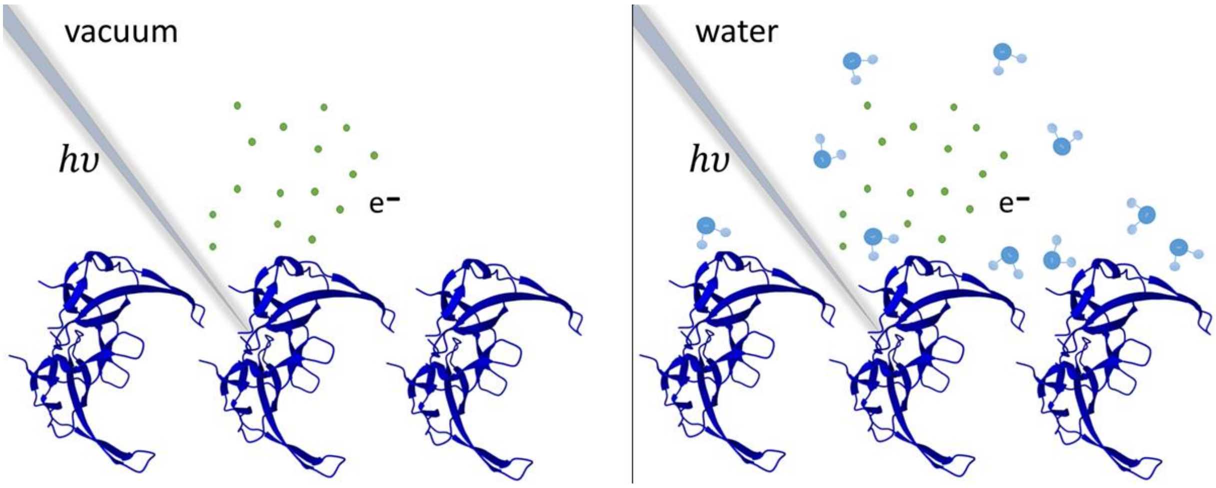

Figure 1: X-rays pass through vacuum (left) or water atmosphere (right), scatter at the Gene-V Protein (G5P) and eject photoelectrons.

Topology and geometry of chromatin radiation damage response

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The cell nucleus is a complex biological system in which simultaneous reactions and functions take place to keep the cell as an individualized, specialized system running well. The cell nucleus contains chromatin packed in various degrees of density and separated in volumes of chromosome territories and sub-chromosomal domains. Between the chromatin, however, there is enough "free" space for floating RNA, proteins, enzymes, ATPs, ions, water-molecules etc. which are trafficking by super- and supra-diffusion to the interaction points where they are required. It seems that this trafficking works somehow automatically and drives the system perfectly. After exposure to ionizing radiation causing chromatin double-strand breaks (DSBs), the whole system "cell nucleus" responds, and repair processes are starting to recover the fully functional and intact system. In molecular biology, many individual epigenetic pathways of DNA damage response or repair of single and double-strand breaks are described. How these responses are embedded into the response of the system as a whole is often out of the focus of consideration. By means of super-resolution fluorescence localization microscopy we have measured the spatial organization of γH2AX around DSBs, DSB attached repair proteins, and ALU regions and heterochromatin of the whole cell nucleus after exposure to external ionizing radiation or internally incorporated electron emitter (β decay).The application of Ripley statistics, persistent homology, persistent imaging and principal component analysis showed defined geometric conditions of the components analysed and revealed a cyclic movement in the topological space of the two major principal components. Systematic changes in the mesh sizes of chromatin networks indicate chromatin organization rearrangements associated with repair activities. The presented data give hints that verify the hypothesis of chromatin architecture's impact on epigenetic pathways and vice versa. Based on the assumption that chromatin acts like an "aperiodic solid state within a limited volume", the functionally determined networks and local topologies seem to drive and control the appropriate repair process at given damage sites.

Electron Attachment to Butadiene Clusters

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Interaction of low energy electrons with isolated butadiene results in the formation of transient negative anion with 100% decay probability via autodetachment or dissociative electron attachment. On the other hand, butadiene clusters with sizes above 9 molecular units attach electrons forming stable cluster anions.[1] Usually, such behavior is attributed to the polarizability of the medium and attachment via electron bound states of a dielectric nanostructure. Our study combining theory and experiment demonstrates that the butadiene case is different. The dielectric sphere model requires much higher size of the cluster for attachment to occur, what was confirmed by classical molecular dynamics simulations. Reproduction of the electron attachment to small clusters consisting of 9 molecular units is enabled only using quantum path integral MD involving nuclear motion. More surprising, the simulation also shows that electron is not delocalized over the cluster but localized on a single molecular unit. Supported by electron energy loss spectroscopy, we show that this behavior is linked to high efficiency of butadiene vibrational excitation by incoming electrons and strong intermolecular vibrational couplings. The results have consequences for our current understanding of charging of nanostructured dielectrics.

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Complex Aberrations Produced by Therapeutic Proton Beams

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Multicolor Fluorescent In Situ Hybridization (mFISH) has been successfully introduced for advanced study of cytogenetic damage induced by high LET radiation [1] to recognize complex aberration which are not visible using standard staining. It enables estimation of long-term consequences of tumor radiotherapy particularly carbon ion therapy [2,3] as well as of genetic stability and radiosensitivity of embryonic human and mammalian stem cells [4].

Here we use the the 24-colour FISH analysis to determine the complexity of chromosome aberrations induced in human lymphocytes of healthy donors after exposure to Co60-γ-rays, 150 MeV and spread out Bragg peak (SOBP) proton beams. Recorded structural aberrations were subdivided into chromosome and chromatid breaks, simple and complex exchanges. The data from mFISH have been compared to values that would be obtained using routine cytogenetic analysis.

In both cases (mFISH and Giemsa) we have evaluated biological efficiency of proton beams at given dose (isodose effect) by means of the relative dose effectiveness (RDE) [5]. The RDE values were determined for several radiobiological outcomes: the number of aberrations per cell, the number of breakpoints per cell, the percentage of breaks participating in total breakage and from mean number of breaks per complex. Aberration spectra for 3 Gy protons revealed that ~20% of aberrations is of complex type. While routine metaphase analysis resulted in similar aberration spectrum for photons and fast protons (RDE at 3 Gy ~1.1), it has increased significantly (1.51±0.08) for SOBP protons when the mean number of breaks per cell was taken into account.

Higher RDE values obtained using the mFISH for therapeutic proton beams show that biological efficiency of particle ionizing radiation may be underestimated by routine cytogenetic analysis, and the extent of this underestimation depends on the number and complexity of complex aberrations.

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UV and visible-light photodegradation of Methylene Blue and Diazepam using laser synthesized black TiO_2 nanoparticles

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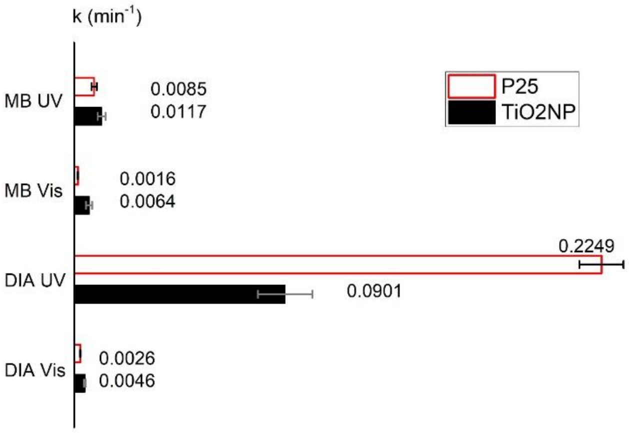
In this work we examined the photocatalytic efficiency of a laser-synthesized colloidal solution of TiO_2 nanoparticles synthesized by laser ablation of titanium target in water [1,2]. Pulsed laser ablation in liquid (PLAL) is method which allows synthesis of nanoparticles with very high purity compared to chemically synthesized nanoparticles. Due to its ecological acceptability PLAL is often referred as "green method".   Photocatalytic photo-degradation rate of Methylene Blue and Diazepam under UV-Visible and visible irradiation is measured using crystallized ‘black’ TiO_2 nanoparticles as photocatalyst and compared with photocatalysis using commercial Aeroxide P25 TiO_2 nanoparticles of the same amount. TiO_2NP have shown by far largest photocatalytic activity in visible than P25 for both MB and Diazepam.It was found that photocatalysis using TiO_2NP shows 57% and 4 times higher degradation of MB under UV and visible irradiation, respectively, than when P25 was used. Moreover, the degradation of MB under visible irradiation is noticeable as it reaches a value of 55% of degradation under UV irradiation. Diazepam is degraded 2.5 times more efficient when P25 was used under UV-Vis irradiation while using visible irradiation the degradation is two times more efficient when TiO_2NP were used as catalyst. Visible degradation of both model compounds is promoted with the presence of Ti3+ sites in black TiO2NP catalyst and with the absorption increase of visible photons from the lamp. This work was supported from HrZZ-IP-2019-04-6418 project.



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Accumulation and Thermal Annealing of Radiation Defects in Single Crystals of Mineral Spinel

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High tolerance to harsh radiation environment and low swelling after heavy fast-neutron-irradiation encourages the use of mineral spinel crystals ($MgAl_2O_4$) in various nuclear technologies connected with fission reactors and allows considering $MgAl_2O_4$ in a priority list of optical window materials suggested by EUROfusion consortium for projected D-T fusion devices. In the present study, a special attention is paid to the accumulation of lattice defects in $MgAl_2O_4$ single crystals exposed to 156-MeV ^{132}Xe and 2.25-GeV ^{197}Au ions with varying fluence. Subsequently, the recovery of radiation damage has been analyzed via a stepwise thermal annealing of different radiation defects. Similar to the case of fast neutrons, the displacement (collision) mechanism of Frenkel defect creation is mainly responsible for radiation damage at metal oxides irradiation with ~GeV swift heavy ions.

Radiation-induced optical absorption (RIOA, absorption of a pristine sample is subtracted) was decomposed into elementary Gaussians, each of which served as a measure of a certain defect type in $MgAl_2O_4$ crystals with (100), (110) and (111) orientations exposed to varying ion fluence. The Gaussians peaked at 4.8- and 5.3-eV correspond to the F^+ and F centers (an oxygen vacancy with one or two trapped electrons, respectively); the ~7-eV Gaussian we ascribe to the exciton-like states nearby antisite defects (swapped cation positions – $Mg|_{Al}$ and $Al|_{Mg}$) and more complex defect associations (see [1-3]); tentative origin of the 5.9-, 6.6-eV elementary bands is considered as well. The concentration of all defects continuously enhances with ion fluence (up to 2×10^{12} cm^{-2}) without any mark of saturation thus confirming the radiation-induced origin of all these defects. Note that RIOA spectra coincide for all three orientations of the samples exposed to isodose irradiation.

Using a stepwise (isochronal) thermal annealing procedure, the annealing kinetics of the defects connected with relevant elementary bands of RIOA has been measured and analysed. The general trends in the annealing kinetics of the F^+ and F centers and the defects responsible for the 5.9-eV, 6.6-eV and ~7-eV RIOA bands do not depend on the type/energy of swift ions used – the temperature regions of the multistage defect decay remain the same. However, different values of mean energy loss along the ion path – 13.45 and 30.4 keV/nm, for Xe and Au ions, respectively, change the ratio between annealing stages of the same radiation defect. The low-temperature stages of the defect annealing are more pronounced in the Xe-irradiated crystals, while the decay of a main part of Au-ion-induced defects occurs via a high-temperature annealing stage. Based on our previous results [1-3], the features of the annealing kinetics of these defects are discussed.

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Dissociative ionization of $MeCpPtMe_3$: Formation of methane and ethane at single-collision conditions with electrons

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This study aims to understand chemical reactions that are fundamental to the dissociative ionization of trimethyl(methylcyclopentadienyl)platinum(IV) ($MeCpPtMe_3$), o common FEBID precursor of Platinum. Previous studies which probed electron-driven chemistry of this precursor using surface-science technique [1, 2] revealed a surprising phenomenon, namely that is not the methyl radical which is primarily released upon electron irradiation, but rather the methane molecule. The gas-phase study of Engman et al. [3] provided a large number of interesting data, however, it did not address this question.

In the present work, gas-phase $MeCpPtMe_3$ was irradiated with electrons of controlled energy, and the positive product ions were analyzed in a reflectron time-of-flight mass spectrometer (RTOF). By fitting complex isotope patterns, we identified the contributions of specific fragment ions to peaks in the mass spectrum. Additionally, the appearance energy for the parent molecule and selected groups of peaks corresponding to the loss of one and two methyl groups were determined. To support the experimental data, quantum calculations were performed using the B3LYP method with LANL2DZ basis and Empirical Dispersion correction GD3. The comparison of the experimental and calculated appearance energies suggests that methane and ethane are formed already in the binary collisions of the precursor with electrons at electron energies close to the ionization threshold.

The next step in these studies will be simulating irradiation process of $MeCpPtMe_3$ using a reactive molecular dynamics approach.

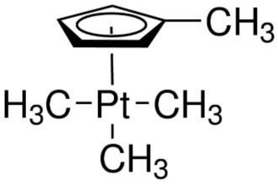

Figure 2: Trimethyl(methylcyclopentadienyl)platinum(IV) ($MeCpPtMe_3$)

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Study of elastic electron scattering by aneasthetic molecules in the gas phase

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We have investigated elastic electron scattering cross sections from anesthetics molecules in the gas phase for intermediate impact energies. Measurements of the elastic differential cross sections (DCS) have been performed with a crossed electron-target beam apparatus UGRA [1], settled at the Institute of Physics in Belgrade. Relative DCSs were put on the absolute scale by using the relative flow technique [2]. Calculations are based on the Independent Atom Model (IAM) by using the screening corrected additivity rule (SCAR) technique and including interference effects. Measurements have been carried out for anesthetics molecules, such as sevoflurane [1], isoflurane and desflurane. Absolute DCSs for elastic electron scattering from isoflurane at 100 eV are presented in Figure 1.

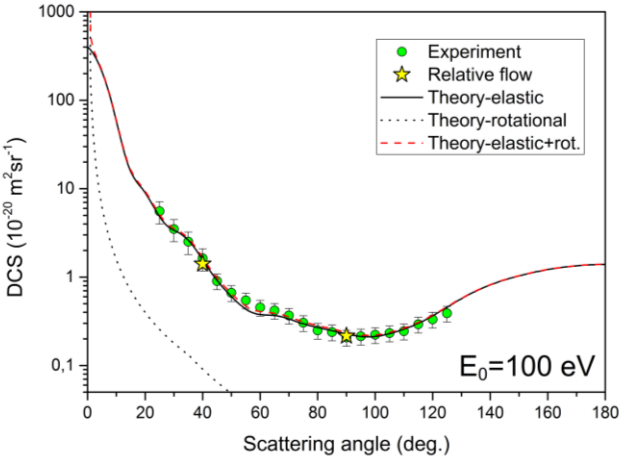

Figure 1: Angular dependence of the DCSs for elastic electron scattering from isoflurane at 100 eV. Circles represent absolute experimental differential cross sections; stars represent absolute values obtained by relative flow method and lines represent calculations.

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The Impact of Gold Nanoparticles on the Irradiation-Induced Damage of DNA Nucleobases

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Despite significant advancements and evolution in cancer treatment techniques and therapies, the development of more effective methods remains a major concern for the scientific community [1,2]. Photothermal therapy is an emerging treatment modality that exploits the optical surface plasmon resonance of gold nanoparticles (AuNPs) integrated in cancer cells to induce cell death by increasing local temperature, among other secondary effects [2,3]. In this study, we explore the degradation of DNA nucleobases, specifically 5-Bromouracil (5BrU) and Uracil (U), in the presence of AuNPs when exposed to 8 mJ Nd:YAG ns-laser pulses at 532 nm. The selection of these nucleobases was based on the potential radiosensitizing properties of 5BrU in cancer therapy, aiming to understand the effect of the laser light on 5BrU by studying U as a reference [4,5]. The observed kinetics of the decomposition and absorption processes during irradiation were described by a theoretical model based on Langmuir assumptions. Furthermore, we were able to experimentally correlate the measured reaction rates with the Langmuir model, suggesting a strong influence of nucleobase-specific absorption. Our results demonstrate a slight modification of the decomposition rates between U and 5BrU, with 5BrU exhibiting the fastest decomposition rates. These findings are consistent with the relative adsorption rates determined from the aggregation kinetics of AuNPs, which consider the effects of an inhomogeneous surface and modified (non-spherical) shapes.

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Reactor for probing electron-induced chemistry in liquid micro-jets

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We present a recently developed experimental setup for studying electron beam induced reactions with molecules solvated in the liquid phase. One of the motivations for this work is to understand the radiation induced damage to living cells and biologically important molecules in their natural environment – i.e. in aqueous solvated form. The experimental results will also enable us to understand the effect of liquid environment in the event of electron beam induced reactions.

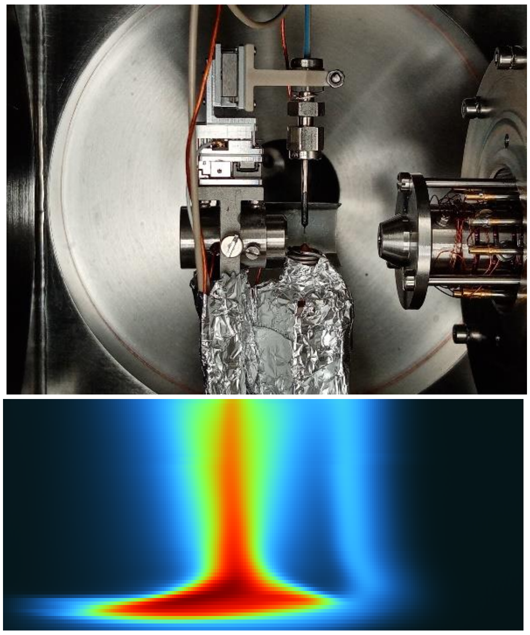

Fig.2: (a) The experimental setup (b) the scattered electron beam profile from the liquid jet is shown here.

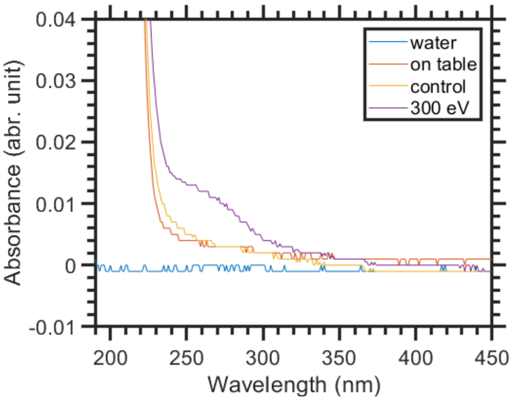

Figure 2: The uv-vis spectra of TRIS water solution before and after electron irradiation.

The experimental setup is equipped with a high-vacuum compatible liquid micro-jet source and an electron gun producing an electron beam with tenable energy in between 100 to 1000 eV. The experimental setup and the scattered electron beam profile are shown in Figure 1 (a) and (b) respectively. The liquid jet is produced by flowing the sample liquid, with 0.7 to 1.5 ml/min flow rate, through a small quartz nozzle with either 30- or 50-micron inner diameter using an HPLC pump producing around 50 to 120 bar pressure. Around 3 mm long liquid beam is exposed inside the high vacuum (of 10^{-5} mbar range) and then collected back either for recycling or for further analysis using standard analytical techniques such as UV-VIS spectroscopy or gel electrophoresis.

Recently we studied electron-beam induced reactivity in water solvated TRIS (2-Amino-2-(hydroxymethyl) propane-1,3-diol) molecule. Around 19.3 mM aqueous solution of TRIS was irradiated with 300 eV electron beam, and the irradiated solution was collected and analysed using UV-VIS spectroscopy. The results are shown in Fig 2.

Electron Induced Emission Spectra and Cross-Sections: Reference Data for Emission Spectroscopy

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Emission spectroscopy is a tool often used to analyze systems such as electrical discharges, atmospheric processes or various interstellar objects. The emission from these objects is often very complex as many different processes producing emission can be active at once and local conditions can affect the shapes of spectral features. Such a complex spectrum contains many valuable information on its source but can be difficult to analyze. In many of these environments the electron induced processes play an important role. Even in astrophysical conditions it was shown that slow secondary electrons generated by photoionization induce significant portion of radiation emitting particles [1]. Therefore, the laboratory experiments aimed at electron induced fluorescence can provide the reference data, since they work in controlled environment repeatably studying individual compounds. The figure 1 shows the example of the spectral electron energy map of nitrogen emission induced by electron impact. The main output are the reference emission spectra determined at range of electron energies providing the possibility to extract absolute emission cross-section values for all the detected transitions at any energy.

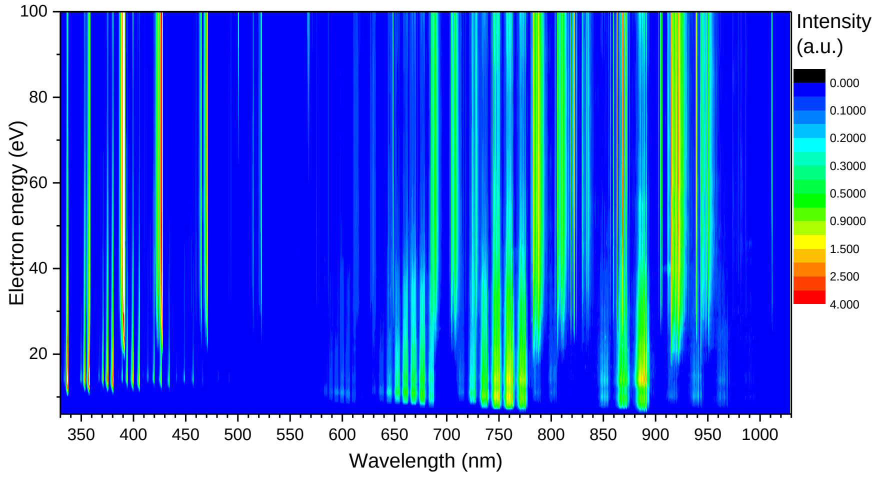

Fig. 1. Spectral electron energy map of nitrogen emission.

Acknowledgments: This work has received support from Slovak Research and Development Agency under the projects nr. APVV-19-0386 and APVV-15-0580, Slovak grant agency under projects nr. 1/0489/21 and 1/0553/22. This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 871149.

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Proton Transfer Reactions Studied by Ion Mobility Spectrometry/Mass Spectrometry and Quantum Chemistry - Phthalates

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The experimental studies using Ion Mobility Spectrometry (IMS), and its combination with Mass Spectrometry (IMS-MS), are combined with theoretical Density Functional Theory (DFT) calculations to reveal the proton transfer reaction to different phthalate molecules. The experiment was built in the past at the Comenius University in Bratislava [1,2], and is based on atmospheric pressure chemical ionisation (APCI) technique [3]. Positive corona discharge (CD) is used to generate the reactant ions (RI) – hydronium ions H_3O^+ and their different size of water clusters $H_3O^+.(H2O)_{n=1...4}$, or ammonium ion NH_4^+. IMS is generally used in analytical chemistry and in different analytical applications to detect a trace amount of substances, however can be used for decomposition of the measured substances via charge transfer reactions as well. These reactions from RI to the analysed substances were interpreted with DFT quantum-chemical calculations for dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DIP), dibutyl phthalate (DBP). Except the dominant proton transfer reactions, the products can be either ionised, protonated, attachment of hydronium and even larger water clusters to the measured molecules (M) or their fragments can be detected. This has been successfully applied to study the APCI of different kind of DMP isomers as well; the DMP and its dimethyl isophthalate (DMIP) and dimethyl terephthalate (DMTP) isomers [4]; as well as the DEP and its isomers DEIP, DETP, dipropyl (DPP, DIPP) and dibutyl phthalates (DBP, DIBP, DBTP) [5]. DFT conformational and isomer studies were performed, theoretically evaluated proton affinities (PA), possible reaction mechanisms for the proton transfer reactions, even for H_3O^+ attachment to the studied compounds were assigned to interpret the measured IMS spectra.

This research was supported by Slovak Research and Development Agency project nr. APVV-19-0386 and Grant Agency VEGA project nr. 1/0553/22. This work was supported in part through the Comenius University in Bratislava CLARA@UNIBA.SK high-performance computing facilities, services and staff expertise of Centre for Information Technology (https://uniba.sk/en/HPC-Clara) and Comenius University grant UK/211/2021.

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An *ab initio* study of PdTi nanocluster catalysts for the hydrogenation of 1-pentyne

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The hydrogenation of alkynes is an important reaction in the synthesis of both fine and bulk chemicals. Pd-based nanocatalysts are widely used for these reactions. However, Pd is a costly material. PdTi catalysts show promise: such nanocatalysts prepared via cluster beam methods have shown good activity for the hydrogenation of 1-pentyne and excellent selectivity to 1-pentene [1]. An investigation of the adsorption and desorption of the molecules involved in the reaction can shed light on the behaviour of these catalysts [2]. We firstly investigate the structure and mixing patterns of the PdTi nanoalloy catalysts employing Monte Carlo calculations. Then, we employ *ab initio* calculations to investigate the binding energies of 1-pentyne and 1-pentene on the (100) facets of a comprehensive set 309-atom PdTi cuboctahedral nanoclusters of various mixing patterns and Ti contents. We extract the Ti content and NP structure dependance of these binding energies. We find that the binding energy of 1-pentyne on the PdTi catalysts does not change significantly compared to the pure Pd catalysts. However, the binding energy of 1-pentene on them is reduced by a large margin. Our results corroborate the previous experimental findings and suggest these reduced-cost nanocatalysts as an substitute for Pd nanocatalysts.

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Photocatalytic activity of TiO_2(110) nanofilm in seawater: NAMD simulations

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Our study investigates the photocatalytic activity of a TiO_2(110) nanofilm in seawater, specifically exploring the effects of the prevalent ion, chloride, on water dissociation. To this end, we use *ab initio* approaches to construct models of chlorine adatoms on the rutile TiO_2(110)/water interface [1]. We calculated time-dependent spatial charges, bond-lengths of water molecules, and Hirshfeld charges using real-time time-dependent density functional theory and the Ehrenfest dynamics theory to investigate the nonadiabatic dynamics of water dissociation taking into account the excited states. This study suggests two photoinduced water-splitting pathways related to chlorine and analyzes the photogenerated hole along the reactions. We report that chlorine at the surface with H_2O adsorbate could trigger the dehydrogenation of a water molecule from the thermal effect and photoexcitation, and that combining photoexcitation and thermal dynamics is a significant challenge due to the crossing time scales and different governing equations. Additionally, constructing more realistic atomic structures is another challenge to enhance the value of the computational results. By considering atomic motions and electronic structures, as well as photoexcitation and thermal dynamics simultaneously, this work helps guide the design inspirations for photocatalytic systems and their applications in photoinduced water-splitting.

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Laser synthesis of Ag, Au, and Pt doped ZnO nanoparticles and application in photocatalysis under UV irradiation

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One of the main environmental problems today is water pollution due to industrial development. Organic dyes used by various industries can be toxic and mutagenic for the environment and living beings, so there is a need for an efficient removal method. One of the approaches is photocatalysis, which is based on oxidation-reduction reactions, which can further decompose any organic pollutant into environmentally friendly products such as carbon dioxide and water [1].

Nanoparticles have an important role in nanotechnology thanks to their unique magnetic, electrical, mechanical, optical, and electronic properties compared to their bulk counterparts. Zinc oxide (ZnO) is one of the most widely used photocatalysts in the photodegradation of various organic dyes [2]. Implementing a new element in the ZnO crystal structure leads to the enhancement of the electrical and optical properties extending the area of its application in photocatalysis [3]. Pulsed laser ablation in liquid (PLAL) gained a lot of attention due to the simplicity, effectiveness, high purity, and fast production of nanoparticles compared to conventional chemical methods [4,5].

In this work, a simple two-step method for the synthesis of silver (Ag), gold (Au), and platinum (Pt) doped ZnO nanoparticles will be addressed [6]. Using the pulsed laser deposition (PLD) technique, we produced targets where thin layers of metals (Ag, Pt, Au) have been deposited on a ZnO substrate. Such two-layer materials were used for targets in the pulsed laser ablation process producing a colloidal solution of doped ZnO nanoparticles (ZnO: Ag, ZnO: Au, and ZnO: Pt). The optical properties, crystalline structure, elemental composition, morphology, and nanoparticle size distribution were studied using UV-VIS spectrophotometer, X-ray diffraction (XRD), X-ray spectroscopy (XPS), and scanning electron microscope (SEM), respectively. Furthermore, we will discuss the photocatalytic activity and mechanism of Ag-doped ZnO nanoparticles under UV irradiation.

Acknowledgment:

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Electron-energy loss spectroscopy and electron-induced fluorescence of liquid microjets

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In recent years, an increasingly large number of studies are focusing their attention towards understanding the radiation damage on a fundamental level. A vast majority of such studies are based on experimental techniques that isolate a biologically relevant molecule under well-known conditions in the gas phase and then probe it by energetic collisions with either photons or electrons. By examining relaxation channels from such reactions, one can gain more insight into fragmentation patterns, ionization energies, excited states, cross-sections and electronic structure of such a large system. However, bio-molecules are naturally found in an aqueous environment where the function of solvent plays a crucial role in their fundamental properties.

A very promising experimental technique which allows interactions with such target is a liquid micro-jet, where a liquid-vapor interface is maintained in vacuum. This technique is still in development and a lot of technical challenges must be overcome before it becomes a fully adopted experimental tool. These are, for example, a gradient of gas-phase around the liquid-phase jet that projectiles must first penetrate in order to reach the liquid-phase as well as micro-jet stability.

We present our preliminary results obtained recently from two new experimental setups where we coupled (100-1000) eV electron gun with a liquid micro-jet source in vacuum. The first experimental setup is located in Synchrotron SOLEIL near Paris and it features a hemispherical energy analyzer giving us the possibility to record electron energy loss spectra from a liquid-phase target molecule. One of the first results, the electron energy loss spectrum of water in liquid micro-jet, is presented in Fig. 1. The second recently designed experimental setup in Prague Fig. 2 is aimed at studying electron induced fluorescence from targets in liquid-phase. In Fig. 3 we present an image recorded with a camera that shows an emission of visible light from a micro-jet in vacuum as a result of electron induced fluorescence from a laser dye molecule DCM.

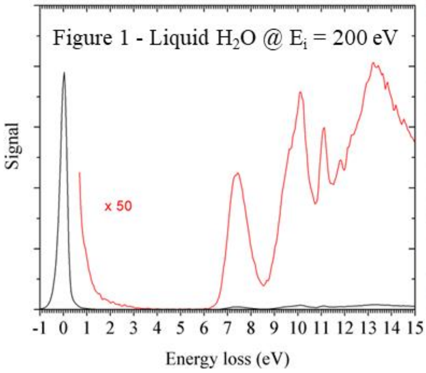
Figure 1 - Liquid H_2O @ E_i = 200 eV

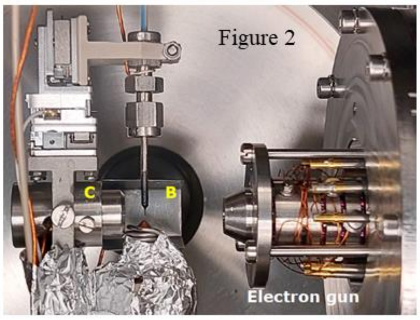
Figure 2

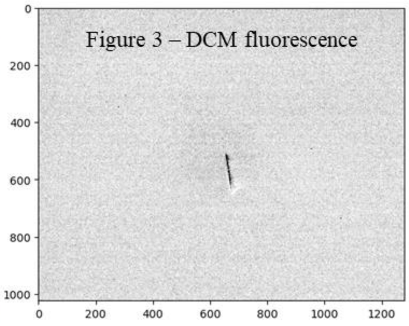
Figure 3 – DCM fluorescence

Direct writing fabrication of top-contact electrodes for molecular electronics

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Molecular electronic devices based on self-assembled monolayers (SAM) between two electrodes have been prepared. An oligo (phenylene ethynylene) (OPE) derivative, 4-(2-(4-(2-(4-aminophenyl)ethynyl)phenyl)ethynyl) benzamine, named in this work as NOPEN, has been used as the wire-like molecular component. Topography and packaging density of this monolayer are studied by Atomic Force Microscopy (AFM) and Cycle Voltammetry (CV), respectively. The device fabrication ends with the growth of a conducting structure of cobalt on the top of the organic monolayer by Focused Ion Beam Induced Deposition under cryogenic conditions (Cryo-FIBID). This versatile technique allows the direct writing of top electrodes with well-defined shape and well-controlled position. In addition, cryogenic conditions result in low ion-induced damage. In order to electrically characterize the final devices, *I-V* curves have been recorded with two electrical microprobes. These results represent an important step forward in the customization of molecular electronic devices based on self-assembled monolayers and conducting electrodes.

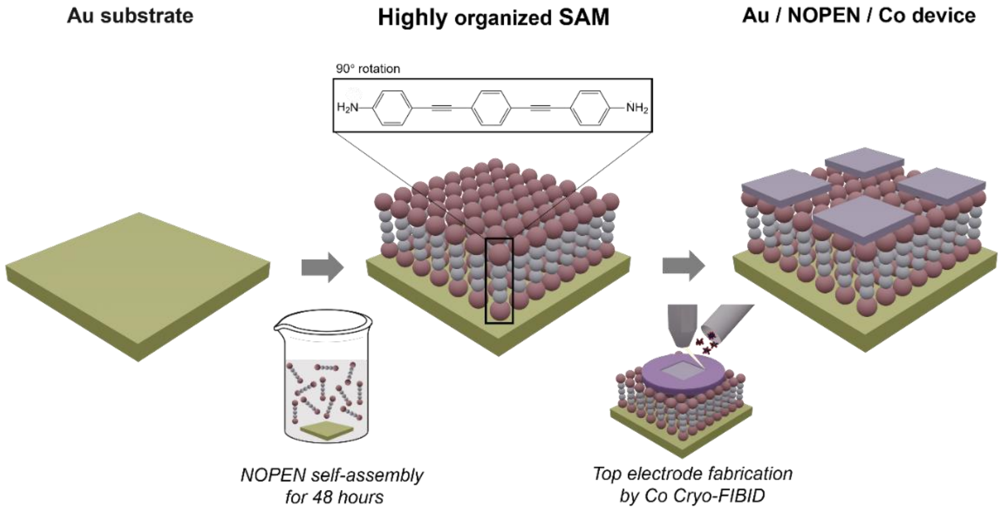

Figure 1. Illustration of the fabrication process of Au/NOPEN/Co electronic devices starting from the bare substrate. NOPEN molecules are oriented after 48 h in a THF solution and top-contact electrodes of cobalt are deposited by Cryo-FIBID using a gaseous precursor of $Co_2(CO)_8$.

Electrons in Liquid Ammonia and Water – from blue electrolytes to golden metallic solutions

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Metal–insulator transitions (MIT) describe the phenomenon when for example a metal loses its property to conduct electrons and becomes an insulator. This happens e.g. when a metal is oxidized and corrodes. Vice versa, non-conducting matter can become metallic by modulating ambient parameters such as pressure or temperature while maybe the most common and applied case is turning semiconductors into metals upon doping with impurity atoms. While MIT for solid-state materials has been investigated for decades already and thus the theoretical description is well advanced, MIT in liquids is scarcely understood. One reason is certainly that the experimental technique of photo-electron spectroscopy (PES) has become available for solids already end of 1950s which enables to directly investigate the electronic structure in general, thus allowing to map out electronic (band-) structure changes happening during MIT.

The advent of liquid micro-jets around the year 2000 in combination with PES enabled the direct access to electronic structure information of liquid systems [1]. In this poster presentation we show our recent experimental developments which enabled us to probe the changes of the electronic structure taking place during MIT in two different liquid phase systems: firstly, we mapped out electronic structure changes happening during the electrolyte-to-liquid-metal transition upon dissolution of alkali-metal in liquid ammonia [2]. Secondly, we observed the corrosion of a liquid sodium-potassium surface by adsorption of water vapour. Here, an interesting transition state of a metallic water solution has been identified [3]. We will also show future prospects on how we plan to investigate the mechanisms underlying MIT in liquids which is still unknown although different theoretical approaches have been proposed: i.e. is MIT merely a Mott-type, an Anderson-type or a percolation-driven transition [4][5].

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K-shell excitation induced fragmentation of DNA oligonucleotides revealed by near-edge X-ray absorption fine-structure (NEXAFS) action spectroscopy

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In the irradiation of biological tissue, the interaction of the DNA molecules with X-ray photons and low energy electrons is highly important. In this context, near-edge X-ray absorption fine-structure (NEXAFS) action spectroscopy is a powerful technique to study the interaction of biomolecules with ionizing radiation since it allows on the one hand to identify unoccupied molecular orbitals and on the other hand fragmentation pathways upon core-shell excitation and ionization are revealed.[1] In NEXAFS action spectroscopy measurements biomolecular ions are generated by electrospray ionization and stored in an ion-trap, which is aligned with a soft X-ray synchrotron-beamline (here: PLEIADES at SOLEIL). The fragmentation yield of the ions is recorded as a function the photon energy, so the role of certain resonances on individual fragmentation pathways can be elucidated.

Telomeric DNA is a repetitive single stranded DNA sequence (TTAGGG) at the end of chromosomes and plays a significant role in the therapy and generation of cancer. Here we present first-time NEXAFS action spectroscopy of a DNA-oligonucleotide (TTAGGG, m/z = 1847 a.m.u, telDNA) at ionization K-edges (N1s, C1s, O1s) to identify the unoccupied molecular σ- and π-states involved in electron transfer reactions and the fragmentation pathways following core-shell excitation and ionization. Following a controlled X-ray irradiation time, the yield of generated fragments have been recorded for the triple charged parent ion telDNA^{3-} with m/z=614 a.m.u.. Versatile reaction pathways as (multiple-) ionization, base loss and strand breaks, have been revealed. Moreover, since the individual atoms are only present in one or two of the DNA building blocks, namely nucleobase, sugar or phosphate group, conclusions about the location of the electronic states can be drawn. Such information about the X-ray induced dissociation of the telomeric DNA will be helpful for the understanding of DNA damage in the terms of cancer research.

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Comparative Analysis of Polymer Gels as Dosimetry Tools for High Dose Rate Brachytherapy using Monte Carlo simulations

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Polymer gels are widely used for dosimetry in radiotherapy and, to a lesser extent, in brachytherapy. However, their dosimetric properties and tissue equivalence vary depending on their composition. In this study, we compared the dosimetric properties of three types of polymer gels: MAGAS (methacrylic acid, gelatin, and ascorbic acid), MAGAT (methacrylic acid, gelatin and tetrakis (hydroxymethyl phosphonium chloride)), and AMPS (2-acrylamido-2-methylpropane sulfonic acid and gelatin). Monte Carlo package FLUKA was used to simulate the energy delivery/absorption processes during high dose rate brachytherapy procedures. Tissue equivalency of the gels was estimated by comparing them with ICRP soft tissue equivalent. The results of simulations were validated with experimental data obtained from the literature sources. Performed investigation revealed that FLUKA is a reliable tool for simulating dose distribution in irradiated polymer gels. These findings might be useful for clinicians who use polymer gels as dosimeters in high dose rate brachytherapy with Iridium-192 sources.

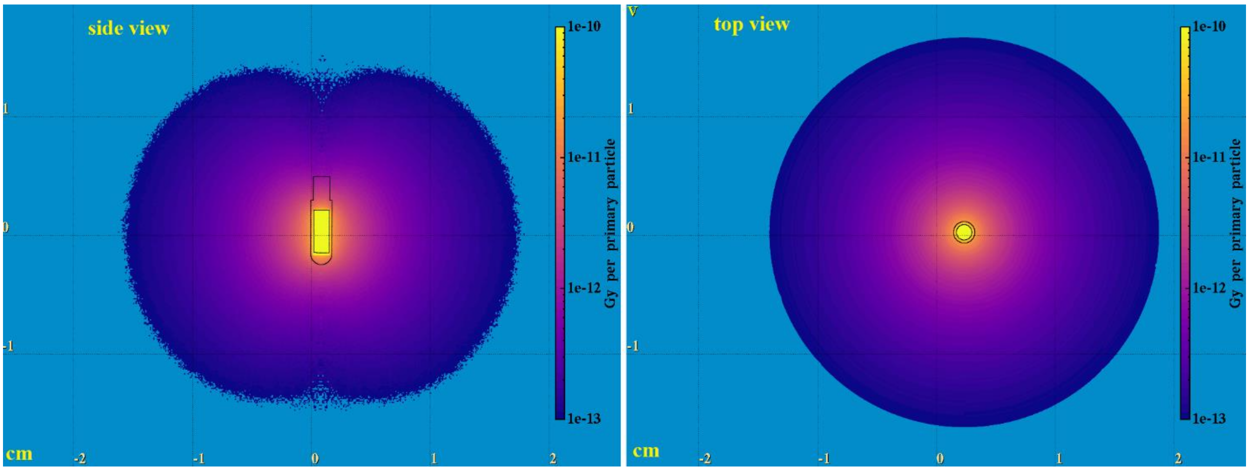

Fig.1 3D visualization of dose distribution around brachytherapy source in water model: simulated dose patterns in cylindrical coordinate system from side view (left) and top view (right)

DNA origami nanoblocks modified by cisplatin

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DNA origami is a folding technique of DNA strands into precisely defined 2D and 3D nanoscale structures that can be functionalized. DNA has a huge potential to be used as a material for construction in fields such as nanotechnology or pharmacy. In our group, we use DNA origami as a unique substrate to study radiation damage to DNA [1][2].

The present study focuses more on applied direction towards DNA origami for cancer treatment and theranostics. The results of our pilot *in vitro* experiments with 2D structures demonstrate promising use of cisplatin loaded origami in cancer treatment.[3] 3D structures are predicted to be more stable in biological environment than 2D structures and therefore, here we focus on the adaptation of the 3D drug delivery platform introduced by Zhong and co-workers [4] for the use with our cisplatin loading technique.

3D structures, nanoblocks with a size corresponding to 12x12x22 nm were created and modified with cisplatin. Transmission electron microscopy (Jeol JEM-F200) images show the shape of structures (Fig. 1). Cisplatin modified nanoblocks show deformation or damage. The damage may occur during loading or during deposition phases of the operation, because during these stages concentration of Mg^{2+}, phosphate group counter-ions, is significantly varied. The details of the damage processes and optimization of the 3D structures are being investigated and will be presented.

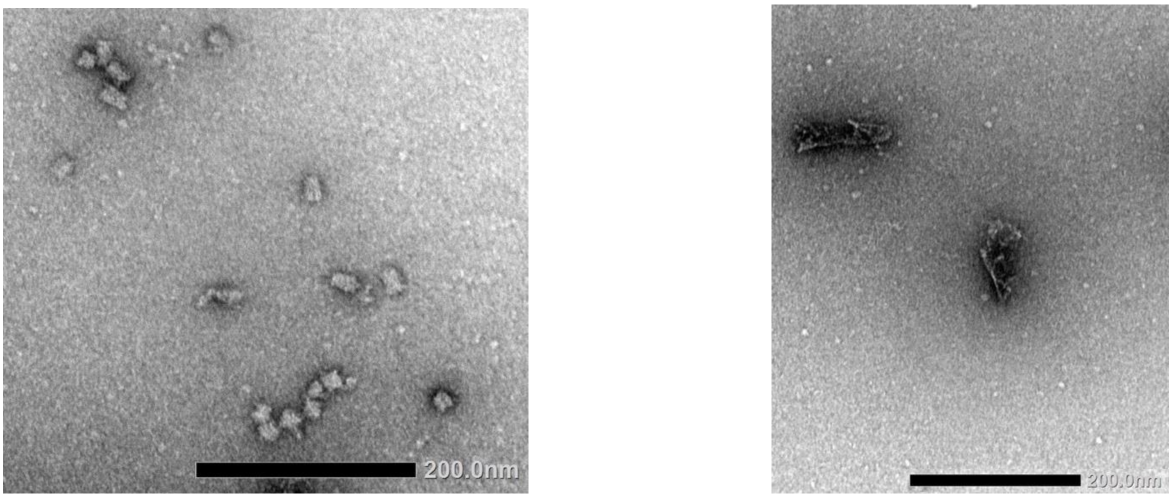

Fig. 1: Pure nanoblocks (left) and modificated nanoblocks by cisplatin (right), 30000x magnification.

References:

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Understanding the fate of electronically excited states by quantum chemical calculations

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The electronically excited states of transition metal complexes are classified into inter-configurational and intra-configurational metal-centered, ligand-centered, and charge transfer states. Different (de)localization of electron density in different types of excitations results in different geometry distortions. We use quantum mechanical calculations within the time-dependent density functional theory (TD-DFT) framework to describe and characterize the excited states of transition-metal complexes. From the shape of potential energy curves, we elucidate their fate.

Examples of our work on $Pt(PF_3)_4$, $Cr(CO)_6$, $Fe(CO)_5$, and $Cr(bpy)_3^{3+}$ will illustrate the differences between the fate of different types of excited states. The main aim of our work is to get chemical insight and control of metal-ligand bonding.

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