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1ST SYMPOSIUM ON ELECTRON, PHOTON AND ION COLLISIONS ON MOLECULAR & ATOMIC NANOSTRUCTURES

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ABSTRACTS
INVITED TALKS

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2D-MATERIALS IRRADIATED WITH SLOW HIGHLY CHARGED IONS

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When a solid surface is irradiated with slow highly charged ions, the deposited energy crucially depends on the ion's initial kinetic energy as well as on its charge state. Upon impact of the ion dozens of electrons are resonantly captured into highly excited states ($n \geq 20$) and rapidly decay into low-n shells ($n \leq 10$) via an Interatomic Coulombic Decay (ICD) process [1,2]. Thus, very efficient charge exchange already occurs at the target's surface. Utilizing 2D membranes as solid targets, allows to study explicitly charge transfer processes, since the ion's charge state is still in pre-equilibrium when interacting with only a monolayer. We perform ion transmission studies with slow (~1keV/amu) highly charged Xe^{q+} projectiles ($q<45$) on freestanding thin membranes such as single, bi- and trilayer graphene as well as monolayer MoS_2. In this contribution, we show the ion's exit charge states and scattering angles after their transmission. The results are compared to a recently suggested model, which for the first time includes charge state dependent stopping. A time-dependent scattering potential as a consequence of charge exchange via ICD is introduced [3]. For monolayer graphene we find an agreement in the exit charge states and maximum scattering angles but experimentally transmission in forward direction is present, not found in the simulations indicating vacancies in the membrane.

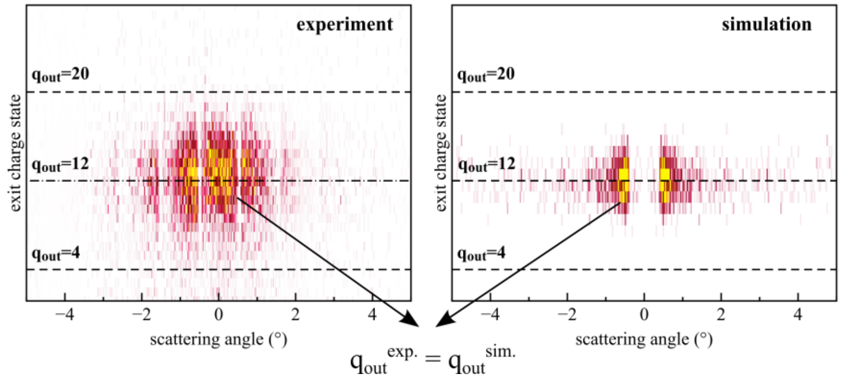

Figure 1: Exit charge states vs. scattering angle of 1.4 keV/amu Xe^{40+} ions transmitted through a single layer of graphene. Comparison between experimental data and simulation.

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MAGNETIC MOMENT GENERATION IN SMALL GOLD NANOPARTICLES VIA THE PLASMONIC INVERSE FARADAY EFFECT

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We theoretically investigate the creation of a magnetic moment in gold nanoparticles by circularly polarized laser light. To this end, we describe the collective electron dynamics in gold nanoparticles using a semiclassical approach based on a quantum hydrodynamic model [1] that incorporates the principal quantum many-body and nonlocal effects, such as the electron spill-out, the Hartree potential, and the exchange and correlation effects. We use a variational approach [2] to investigate the breathing and the dipole dynamics induced by an external electric field. We show that gold nanoparticles can build up a static magnetic moment through the interaction with a circularly polarized laser field, see Fig. 1. We analyze that the responsible physical mechanism is a plasmonic orbital inverse Faraday effect, which can be understood from the time-averaged electron current density that exhibits rotating surface currents, see Fig. 2. The latter are dramatically enhanced when the system is excited at the surface plasmon resonance frequency. The laser-induced magnetic moments are huge and increase with the intensity of the laser field, see Fig. 3. For a nanoparticle with a 2-nm diameter, the induced moments reach the value of 0.35 μ_B/atom for a laser intensity of 450 GW/cm^2 at the plasmon resonance. We thus predict a huge enhancement (~ 1000 times) compared to typical values obtained for bulk materials [3] where no surface plasmons are present. In addition to the induced magnetic moment, the gold nanoparticles become magnetic during the interaction with the laser pulse. We estimate that the magnetic field created at the center of the nanoparticle reaches values between 0.1 − 0.8 Tesla.

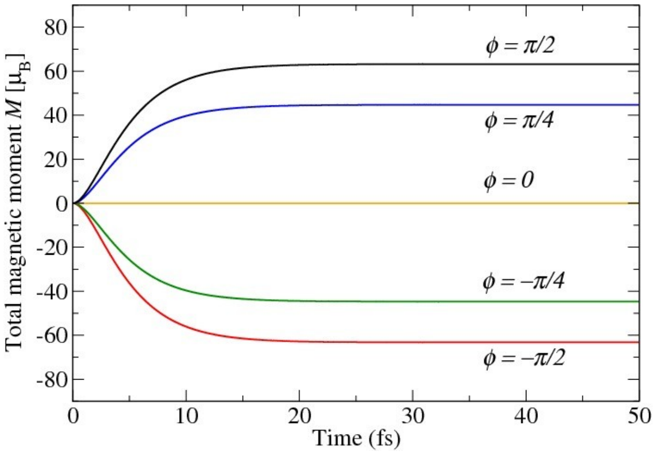

Figure 1: Calculated time evolution of the total laser-induced orbital magnetic moment in a Au nanoparticle with a diameter of 2 nm for different laser polarizations: circular right/left ($\varphi = \pm \pi/2$), linear ($\varphi = 0$) and elliptical ($\varphi = \pm \pi/4$). The laser is switched on at t=0.

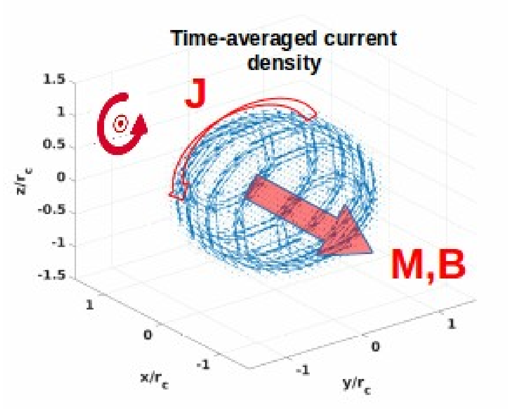

Figure 2: Three-dimensional plot of the calculated time-averaged current density vector field that is created at the surface of the nanoparticle through the interaction with a circularly polarized light.

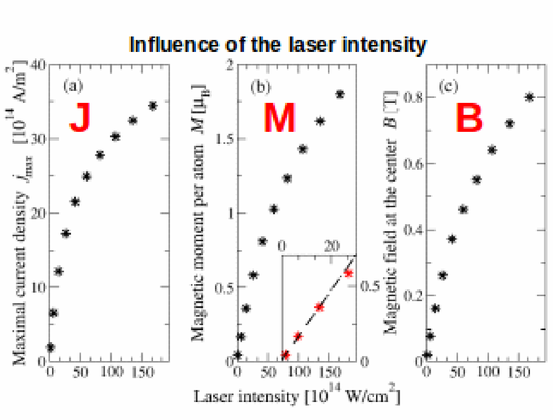

Figure 3: (a) Maximal current density, (b), magnetic moment per atom, and (c) magnetic field at the center of the nanoparticle, computed as a function of the laser intensity. The inset plot in (b) is a linear fit of the smallest values of the magnetic moment per atom. The investigated system is a gold nanoparticle with a 2-nm diameter interacting with a circularly polarized light-field.

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Small Carbon Nano-Onions Studied by Ion Mobility Mass Spectrometry

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It is known that carbon cluster ions, $C_n^{\pm}$, grow from linear to two-dimensional cyclic and then to cage-like structures typified by C_{60} in the small size range ($n < 100$) [1]. In contrast, carbon nano-materials form various structures. In this study, structural isomers of carbon cluster cations in the intermediate size range of $n = 100$–800 were investigated by ion mobility mass spectrometry [2].

In the experiments, carbon cluster cations generated by laser vaporization and supersonic expansion were injected into an ion-drift cell filled with 3.0-Torr He buffer gas. The ions reached a constant drift velocity with a balance of acceleration with an applied electrostatic field and deceleration by collisions with He in the cell. Thus, the ions exited the cell with different "arrival time" depending on their charges and collision cross sections (CCSs). Finally, the ions were analyzed by a reflectron-type time-of-flight mass spectrometer.

As a result, bilayer fullerene monocation series were observed as a continuous distribution for $n = 260$–700. Figure 1 shows the experimental CCSs of monolayer and bilayer fullerene cation series. Both CCSs increase monotonically with size, however, the slope of the bilayer series was smaller than that of the monolayer series. The difference indicated that the inner layer fullerene grows with the growth of the outer layer, and thus a variety of fullerenes could be present in the inner layer. The smallest bilayer fullerene at $n \approx 260$ ($[C_{30}@C_{230}]^+$) was reasonable from the fact that the inner layer of C_{30} was the smallest fullerene observed in this study and also in the previous report [1].

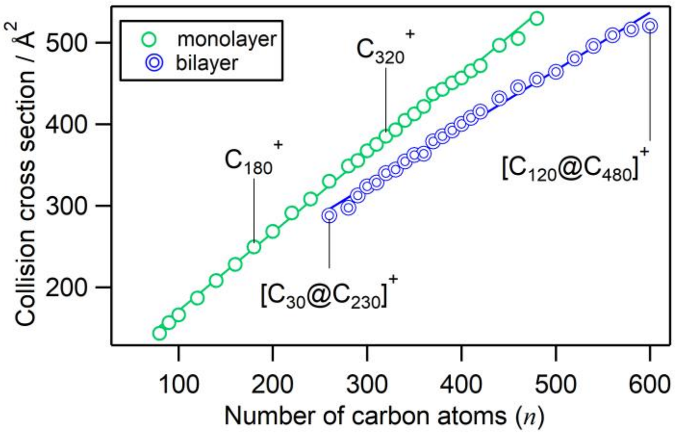

Figure 1: Plots of collision cross sections of monolayer and bilayer fullerene ions.

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DIMETHYL SULFIDE REACTION ON COLD GOLD SURFACE AND TRIGGERED BY LOW ENERGY ELECTRONS

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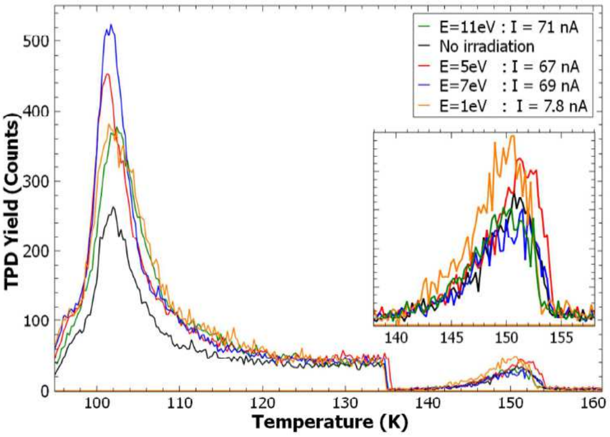
Dimethyl sulfide, a biogenic compound naturally synthesized by marine plankton, is the major source of sulfate aerosol that impact significantly the atmospheric chemistry. However, this molecule has a high potentiality in the fabrication of nanotubes, or even as a substituent of fossil feedstock, e.g., for the production of hydrocarbons that requires heavy transformation techniques and purification steps.

In this contribution, we will show that upon the deposition of the dimethyl sulfide on cold polycrystalline substrate, the surface reaction already decomposes the precursor molecule for the production of ethylene. Furthermore, this reaction depends on the surface of the gold substrate[2]. We will also show and discuss that upon the irradiation of the dimethyl sulfide film by low energy electrons, the production of ethylene is enhanced, and acetylene can be generated too. Finally, we will show that by controlling the electron energy, we are able to trigger selectively the production of a given hydrocarbon[3].



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Temperature desorption spectra of ethylene and acetylene

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URACIL CLUSTER INVESTIGATION BY PHOTOEMISSION SPECTROSCOPY

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The study of biomolecules in gas phase represents a powerful approach to investigate their intrinsic physical and chemical characteristics. In particular core level photoemission spectroscopy, XPS, is a perfect tool to probe the chemical environment of a specific atom. In this work XPS has been used to study the chemical environment of uracil molecules in homogeneous and nanohydrated clusters. Measurements have been performed at the Pleiades beam line [1] where a gas aggregation cluster source developed at CNRS-CIMAP [2] has been coupled to the end station equipped with a Scienta photoelectron spectrometer. The C, O and N 1s XPS spectra have been measured in both uracil and nanohydrated clusters at about 60 eV above their respective thresholds. XPS spectra of the clusters display a shift towards lower binding energy with respect to isolated Uracil molecules [3] as shown in Fig.1 for the case of C 1s. To disentangle the effects of the different intermolecular interactions, which lead to the observed shift, DFT-based simulations have been performed by using the Quantum ESPRESSO suite of programs in a plane wave/pseudopotential framework [4] as detailed elsewhere [5]. Our simulation strategy is based on the selection of aggregates (2-6 molecules) cut out from the uracil crystal structure and fully optimized as molecular clusters, where the effect of different interaction patterns (H-bond, π-stacking, side interaction) can be separately evaluated. The results shows significant agreement with experiments.

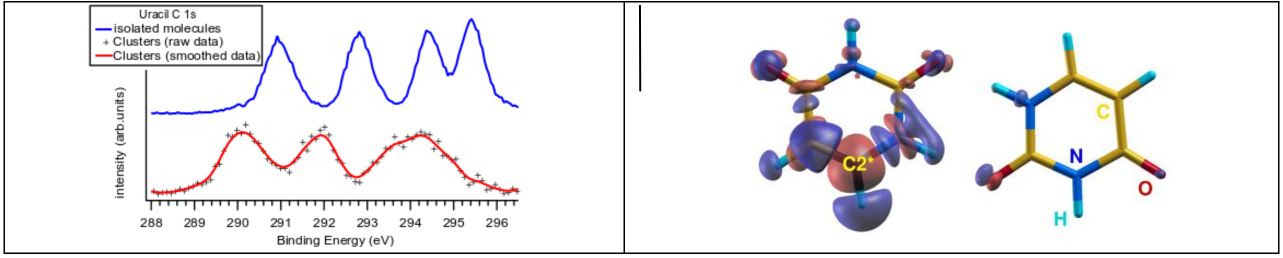

Figure 1: **(left)** C1S XPS spectra of Uracil isolated molecules [3] and homogeneous clusters**, (right)**. Examples of the simulation of charge displacement induced by a core-hole in the C2 position of a uracil dimer. Electronic density flows from blue zones to red zones.

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DYNAMICS OF ISOLATED BIOMOLECULAR IONS IN THE GAS PHASE

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In this presentation I will give an overview of the theoretical methods which we use to study different processes in molecular collisions. Especially, I will report on our recent study of mechanism of fragmentation process taking place in neutral and charged furan molecules in the gas phase. This heterocyclic compound is often taken as an elementary analogue system of deoxyribose, a fundamental component of the DNA backbone chain and it is used for the investigations of the action of ionizing radiation in biologically important material. It can also serve as simple model for verification of our approaches in order to give an extended description of the fragmentation process.

Our approach comprises of *ab initio* Molecular Dynamics using the Atom-Centered Density Matrix Propagation method [1] describing the evolution of the system following deposition of the energy from 5 to 30 eV, and exploration of the Potential Energy Surface (PES) studied at high level of theory. Extensive statistical analysis of the obtained trajectories allows us to identify most abundant dissociation channels. Therefore, the dynamical and energetic considerations of the studied process are expected to create a complete picture of the fragmentation mechanism [2]. The calculated PES and MD suggests the prevalent products differ in composition for different charge states. Particularly, for the case of furan ions, I will present the results of the MD simulations which leads to significant processes like: isomerization, skeleton fragmentation, H^+/H_2^+ loss and H/H_2 loss. With the increasing energy many body fragmentation processes become progressively more relevant. The study of the order of events and their average times provides further details on the fragmentation of furan ions. Moreover, I will present the statistical method-Microcanonical Metropolis Monte Carlo [3], based on the maximum entropy assumption as an alternative and a less computationally expensive than the AIMD. The recently performed experiments: coincidence time-of-flight (TOF) mass spectrometry and photoelectron-photoion coincidence (PEPICO) spectroscopy were employed and provided a great opportunity in order to compare with theoretical results. I will discuss in details how applied methods allow for determination of the energy deposition functions based on the comparison between reproduced theoretical and measured spectra.

This work benefits from the collaboration between research groups initiated through the COST *XUV/X-ray light and fast ions for ultrafast chemistry* action, which include the Gdansk University of Technology in Poland, Autonomous University of Madrid in Spain, Italian National Research Council in Rome in Italy and the University of Caen as well as GANIL in France.

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MODES OF ELECTRON-DENSITY OSCILLATION CORRESPONDING TO OPTICAL EXCITATIONS IN METAL CLUSTERS

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Within the framework of Time-Dependent Density-Functional Theory, the real-time (RT-TDDFT) propagation scheme of Yabana and Bertsch [1] gives direct access to the density dynamics and related quantities (dipole, absorption spectra…). However, in comparison with transition-based linear-response (LR-TDDFT) calculations the results of RT-TDDFT are relatively difficult to interpret due to the lack of direct information on the origin of spectral features. We analyze the time-dependent density from δ-kick time-evolution calculations using spatially resolved Fourier transformation [2,3]. In this way, we obtain spatial information about the origin of individual peaks in the spectra which are comparable to the transition densities obtained in LR-TDDFT calculations. Individual modes are recovered from the Fourier coefficients and can be identified using color maps and animations. This analysis is used to explicitly show the differences between collective plasmonic excitations and the excitations involving d-electrons, as well as the interplay between them. The method is applied to structure-determined monolayer-protected metal clusters to investigate the contributions of different chemical species to different features of the absorption spectrum.

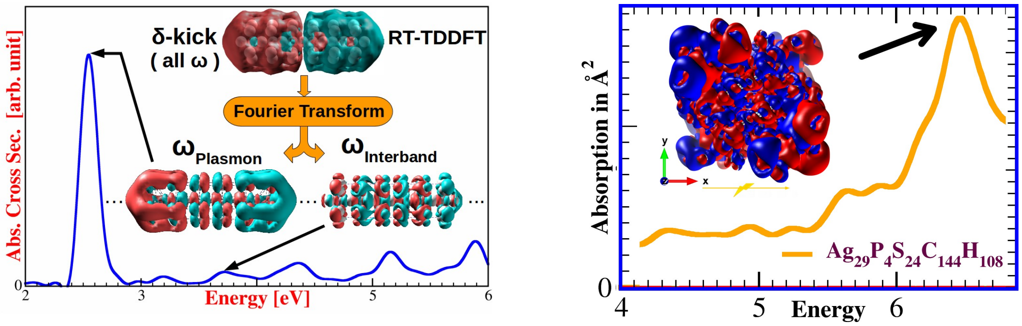

Fig.1: Left: schematic representation of the working of spatially resolved Fourier transform of the time-dependent density from δ-kick time-evolution calculation; Right: captured high-energy mode in $Ag_{29}(BDT)_{12}(TPP)_4$.

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DAMAGING INTERMOLECULAR ENERGY AND PROTON TRANSFER PROCESSES IN ALPHA-PARTICLE IRRADIATED ACETYLENE DIMER

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Although the biological hazard of alpha-particle radiation is well recognized, the molecular mechanisms of biodamage are still far from being understood. In this study we investigate the intermolecular relaxation processes of acetylene dimer, a biologically relevant system possessing an intermolecular hydrogen bond [1].

The experiment was performed with a reaction microscope mounted on the 320 kV platform at the Institute of Modern Physics, Lanzhou, China. After irradiated by alpha-particle with energy of 200 keV, the dimers break into pieces which were detected in coincidence with the scattered projectile. As shown in Figure 1, two fragmentation channels of the charged dimer are identified. The first is the already well-established intermolecular Coulombic decay (ICD) [2] of inner-valence ionized states. Its occurrence after ionization of the shallow carbon 2s levels has been identified for the first time here. The other is a novel relaxation mechanism of dicationic states involving intermolecular proton transfer. Both processes are very fast and trigger Coulomb explosion of the dimer due to creation of charge-separated states.

Important and new is the finding that like ICD the addressed proton transfer processes constitute a general phenomenon in hydrogen-bonded systems. They are expected to take place in alpha-particle irradiated DNA and thus cause damage to this biomolecule [1].

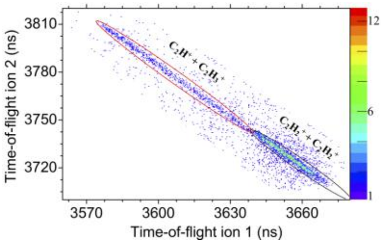

Figure 1. Time-of-flight coincidence map corresponding to the two-body breakups of acetylene dimers. The contribution of the $C_2H^+ + C_2H_3^+$ and $C_2H_2^+ + C_2H_2^+$ channels are indicated by the red and black ovals.

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TRIPLE DIFFERENTIAL CROSS SECTIONS FOR THE SINGLE IONIZATION OF BIOLOGICALLY RELEVANT MOLECULES BY ELECTRON IMPACT

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We present theoretical triple differential cross sections (TDCS) for the single ionization of biological molecules by electron impact, computed using a quantum approach which is based on the First Born approximation (FBA); the incident and scattered electrons are described by plane waves while the ejected electron is described by a distorted wave. The molecular electron wave function is generated using Gaussian 09 and converted to a single-center wave function thereby simplifying the multi-center problem encountered when dealing with complex biomolecules. This methodology is easily applicable to any molecular target [1-3] providing TDCSs within an acceptable computing time and is particularly interesting for biologically relevant molecules for which available TDCSs are very rare.

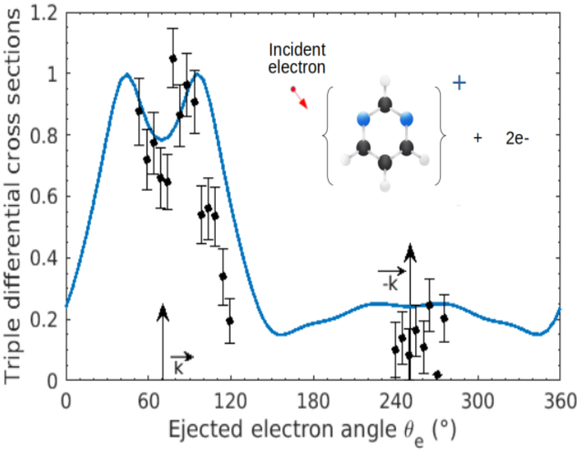

Figure 1: Ionization of the highest occupied and next highest occupied molecular orbitals of pyrimidine by electron impact. The summed triple differential cross section (blue line), computed using our model is compared to experimental data (black circles with error bars) from [4].

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X-RAY PHOTODESORPTION FROM WATER ICES

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In the colder parts of the interstellar medium, dust grains are covered with molecular ices, whose major component is water. They act as the main molecular reservoir of these regions and are therefore of high interest in astrochemistry. Among many radiative processes that occur into these icy mantles, the ones induced by X-rays may play an important role, for example in protoplanetary disks [1], but their effects remain poorly known. In particular, they can release molecules or radicals into the gas phase, by so-called photodesorption processes, and thus have an important role in the gas-to-ice abundance ratio measured by the most recent radiotelescopes. Besides this astrophysical context, X-ray induced desorption can also bring useful information on the physico-chemical properties of water ice, for example regarding the structure of the ice surface [2].

We irradiated H_2O ices between 520 and 600 eV using the SPICES 2 set-up connected to the SEXTANTS beamline. Following O 1s core excitation or ionisation, photodesorption of many species are detected and the efficiency of the photodesorption for each species is quantified. Neutral species are the most abundant, whereas positive or negative ions are much weaker [3]. The comparison between photodesorption spectra, ie the intensity of photodesorbed species as a function of the excitation energy, and absorption spectra measured in-situ gives information on the various processes involved in the photodesorption (Fig.1). Secondary electrons produced in the ice mainly lead to desorption of neutral molecules, whereas the dissociation of H_2O ejects protons for example. Measurement of the kinetic energy of desorbed ions gives valuable insights on the photodesorption processes but also on the ice structure at the surface.

All these data show the complexity and the richness of processes linked to core excitations, from chemical to structural ones, for physical-chemistry or astrophysics.

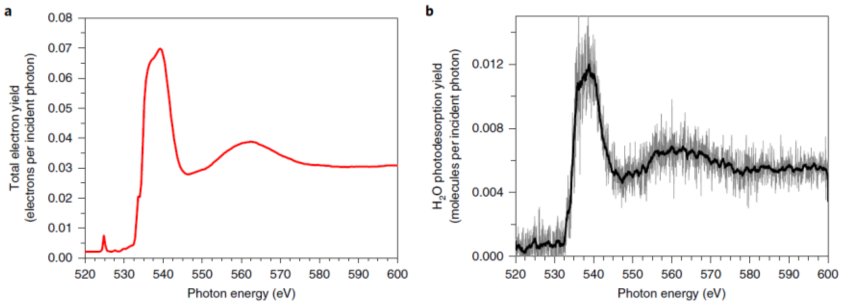

Figure 1 a. Absorption of an amorphous H_2O ice at 15 K ; b. Photodesorption of H_2O [3]

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PLASMON EXCITATION IN PAH MOLECULES AND ELECTON EMISSION UNDER FAST ION IMPACT

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Polycyclic aromatic hydrocarbon (PAH) molecules are of considerable interest because of its astrophysical relevance. From an astrophysical viewpoint, the interaction of these molecules with UV-radiation, as well as with ions over various energy ranges present in the stellar wind can shed light on the astrochemistry of these molecules. The unique electronic structure of PAH molecules draws attention of researchers from different fields. PAHs consist of fused benzenoid rings of sp^2-hybridized C atoms with certain number of H atoms. The remaining electrons from each C-atom forms a delocalized π -electron cloud over the C skeleton. For these large π -electron systems, it is expected to show multiparticle collective excitation like plasmon resonance, as in case of C_{60}-fullerenes [1-4]. While several studies exist for PAH interaction with UV photons, as well as with low-energy ions [5], the interaction of high energy ions with PAHs are quite sparse in the literature [1,2]. The impact of fast heavy ions (few MeV/u) can lead to multiple ionization and fragmentation of molecules as the dominant channel. The angular distributions of the electrons emitted from coronene show an unusually enhanced forward-backward angular asymmetry due to the collective excitation whereas in case of smaller PAH i.e. fluorene [$C_{13}H_{10}$] such plasmon peak is not clearly observed. It would be interesting to study the single, double and triple ionization of these PAH molecules in order to explore the influence of strong correlation inbuilt in many-electron excitation on the ration of double-to-single ionization. We will present a set of experimental results based on the electron and recoil-ion spectroscopic investigations with a few PAH molecules of different sizes and slightly different electronic structures under the collisions of fast highly charged C, O and F ions of energy tens of keV to tens of MeV obtained from an 14.5 GHz ECRIA [6] and 14MV tandem Pelletron accelerator.

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USING ADVANCED LIGHT SOURCES TO INVESTIGATE STRUCTURE AND RELAXATION MECHANISMS OF GAS-PHASE BIOMOLECULAR IONS

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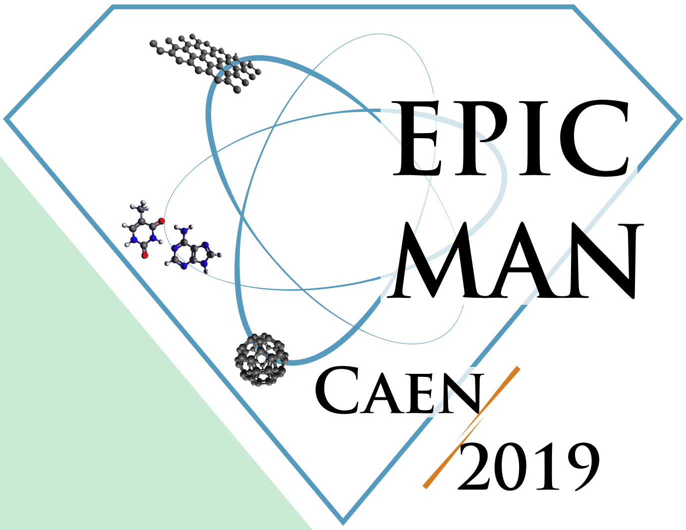
Macromolecules such as nucleic acids and proteins play functional and structural key roles for the metabolism of living organisms. Unveiling their tridimensional and electronic structures is crucial for the understanding of their interactions and the way energy is processed. Gas-phase experiments allow for such insights in a fundamental approach, without the influence of a solvent. Over the past decades, nucleic acids and proteins have been investigated in the gas phase using state-of-art electrospray ionization source, ion guiding in radiofrequency electric field and mass spectrometric techniques. In order to shed light on the electronic and structural properties of such biomolecules, VUV and soft X-ray photo-absorption experiments have been carried out on synchrotron facilities, offering a wide energy range and a high photon flux. While VUV allows probing the valence electrons, in the soft X-ray regime, the resonant photon absorption at the carbon, nitrogen or oxygen K-edges permits to selectively excite or ionize the system. However, due to the large amount of C, N and O in these molecules, the energy deposited upon photon absorption is not localized. Thus, the information retrieved is averaged and the fragmentation pathways appear similar. Getting a deeper understanding on the dissociation processes would require a controlled localization of the energy deposition.

Probing the inner shells of a single sulfur atom within a biomolecule as the only excitation site is a promising way to overcome this obstacle and could pave the way for the study of charge dynamics in such large systems. Among the natural amino acids that make up the proteins, the methionine and cysteine residues, both of which contain a sulfur atom, are ideally suited to investigate the processes following localized excitation in such biomolecular systems. To test this hypothesis, we recently investigated sulfur containing peptides, such as Met-Enkephalin, Cytochrome c protein and synthetic peptides to systematically study the influence of the Met residue position, using synchrotron light sources. The feasibility and outcome of such experiments as well as near edge X-ray fine structure (NEXAFS) studies and photo-fragmentation pathways around the sulfur L-edge will be discussed.



ABSTRACTS
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RESONANT ANIONIC STATES OF ORGANIC MOLECULES ADSORBED ON METAL SURFACES

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Scanning Tunnel Microscopy (STM) is a powerful technique widely used in the study of surfaces and nanostructures. It can be used to inject electrons, populating different molecular empty states. After this process, in the case of molecules deposited on surfaces, the extra electron can decay through the substrate, emitting a photon. This fluorescence has been measured recently in a single molecule [1]. In these systems, the lifetime of the electron on the molecule is a key factor, since these anionic states play an important role in chemical reactivity. They have also high interest for further applications such as nanodevices and optoelectronics.

In this work, we present a deep study of the anionic resonant states of molecules adsorbed on metal surfaces. We first obtain the adsorption geometry using Density Functional Theory, which allows the inclusion of the periodic boundary conditions that are required in order to have a correct description of the electronic structure of the metal. With these calculations, complementary studies are carried out and further information is obtained [2]. Then, through the use of Wave Packet Propagation (WPP) calculations we study the quantum dynamics of the active electron and thus, we are able to obtain information of the resonant states. This methodology has been used to study metal states [3] and nanostructures supported on surfaces [4]. In this communication we present results for three organic molecules (acrylamide, acrylonitrile and acrolein) adsorbed on a pristine Cu(100) surface, although our procedure can be generalized to more complex systems.

Our results show how the symmetry of the molecular state which couples with the surface affects the shape of the decay channel towards the bulk.

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ENERGETIC PROCESSING OF HYDROCARBONS MOLECULAR SPECIES BY IONIZING RADIATION TOWARDS THE FORMATION OF CYCLIC SPECIES

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Cassini-Huygens mission brought interesting results concerning one of Saturn's biggest satellites, Titan. In fact, it has been shown that this moon's typical orange-brownish haze layers could be due to the presence of aerosols. These aerosols are essential for Titan's climate, radiation balance and atmosphere chemistry. The formation of such aerosols is a complex process ranging from the molecular scale to large particles scale. Polycyclic Aromatic Hydrocarbons (PAHs) and their clusters are important components in terrestrial soot formation. Given this, their presence in Titan's atmosphere can be considered as a nucleation agent, which triggers aerosol formation in Saturn moon's low temperature atmosphere. However, since it is mainly composed of nitrogen, methane and a small amount of more complex hydrocarbons, understanding the way such PAHs are formed is mandatory[1].

Ionizing radiation sources (photons, electrons and ions) can trigger gas-phase polymerization, ion-molecule reactions and nanoparticle grain surfaces catalysis. These processes contribute to the formation of complex organic synthesis pathways in atmosphere and space. Simple ionization may induce chemical reactions and isomerization processes.

To understand them, simple linear hydrocarbons like butadiene (a non-aromatic molecule) have been chosen to study the formation of more complex cyclic species (aromatic). The irradiation of hydrocarbons clusters has been performed using different radiation sources (electrons, ions and UV photons) (Fig.1). This allowed the determination of the balance between ionization induced reactivity and collision induced one. The latter is the typical collision occurring in Titan's atmosphere involving slow and heavy ions (few keV O cations). It has been shown that this triggers reactivity, as observed in C60 clusters [2] or PAH ones [3].

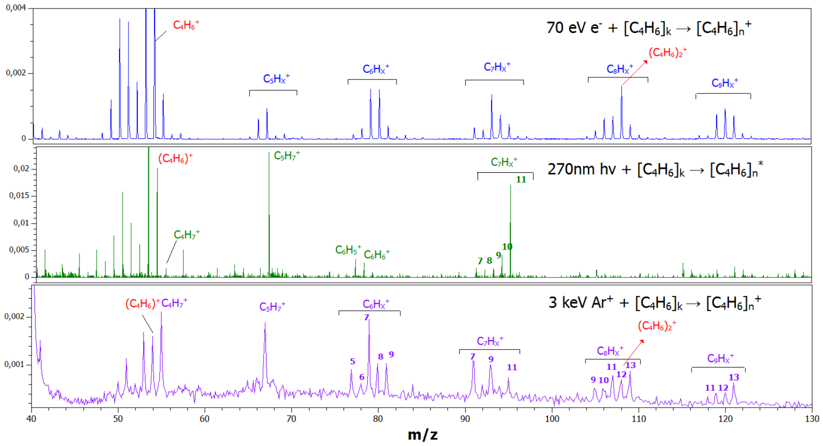

Figure 1: Mass spectra of butadiene clusters in collision with electron, photons and ions

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PHOTODISSOCIATION DYNAMICS OF THE DIAMONDOID ADAMANTANE INDUCED BY ATTOSECOND XUV PULSES

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Carbon is, by mass, the fourth most abundant element in the universe. In combination with its ability to form complex organic compounds, this makes it a major player for the evolution of the universe as well as all life. Diamondoids are a class of carbon nanomaterials based on carbon cages with well-defined structures formed by C(sp3)-C(sp3)-hybridised bonds and fully terminated by hydrogen atoms. All diamondoids are variants of the adamantane molecule, the most stable among all the isomers with formula $C_{10}H_{16}$. Today, diamondoids are attracting increasing interest for use as an applied nanomaterial [1]. In space, diamondoids have been found to be the most abundant component of presolar grains [2], and due to their high stability, they are expected to be abundant in the interstellar medium [3].

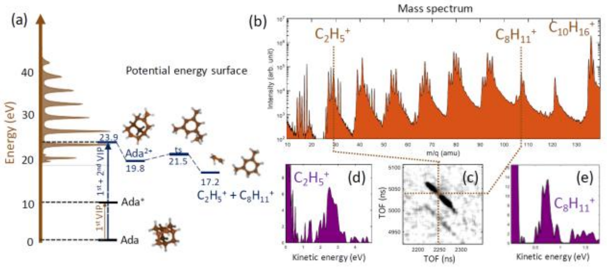

Figure 1. Example of experimental and theoretical

A recent experiment has been performed at Lund University using attosecond XUV pulses produced via high-order harmonic generation (Fig. 1a) to study the photodissociation of adamantane. The photoions were detected by a velocity map imaging spectrometer [4] recording the mass spectrum and the ion momentum distribution on a single shot basis, allowing for the use of covariance analysis to disentangle the dissociation dynamics. The mass spectrum (Fig. 1b) shows the production of a wide distribution of $C_xH_y^+$ fragments resulting from dissociation of singly and doubly charged adamantane molecules. The experimental data is currently being evaluated in detail and compared to the results of potential energy surface calculations and molecular dynamics simulations performed by the theory group in Madrid. These show that, in the dication, the available photodissociation channels have a common first step of cage-opening and hydrogen migration occurring within 500 fs via a barrier-less transition (Fig.1a). In Figure 1c,d and e, one of the possible fragmentation channels following the cage-opening, $C_{10}H_{16}^{2+} \rightarrow C_2H_5^+ + C_8H_{11}^+$, is highlighted as an example.

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Adamantane Dication Fragmentation Dynamics Following Ion Collisions

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Diamondoids are a class of carbon nanomaterials based on carbon cages with well-defined structures formed by C(sp^3)-C(sp^3)-hybridised bonds and fully terminated by hydrogen atoms. All diamondoids are variations on the adamantane molecule model, the most stable among all the isomers, with formula $C_{16}H_{16}$. Adamantane and diamondoids have proven to be of great interest under various points of view: from biomedical applications to nanomaterials and optoelectronics [1]. Another very interesting aspect is the interstellar abundance of these kind of molecules. In fact, in the interstellar medium, molecules are exposed to energetic particles, such as electron, photons, or ions [2]. In order to get a better insight of the behaviour of adamantane in such an environment, we have performed studies using ion collisions in the gas phase, which better resembles the interstellar medium. Under these conditions, the molecule is typically ionised, excited, and undergoes fragmentation. The produced charged molecular fragments are recorded with multicoidencident mass spectrometry. This allows us to infer the energy and charge redistribution processes after the collisions. Quantum chemistry simulations provided insights into the underlying fragmentation mechanisms.The two complementary approaches provided us with a deeper understanding on the complete picture of the fragmentation dynamics. In this communication, we will present results on the fragmentation dynamics of doubly charged adamantane cation produced in collision with 120 keV Ar^{8+} ions.

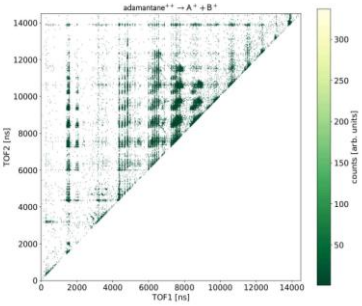

Figure 1: Adamantane dication fragmentation coincidence map produced in collision with 120 keV Ar^{8+}.

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LINEAR-RESPONSE RANGE-SEPARATED TDDFT FOR ATOMIC PHOTOEXCITATION AND PHOTOIONIZATION SPECTRA

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Photoexcitation and photoionization spectra are useful tools for probing electronic structure dynamics in atoms and molecules. However, a clear understanding of the mechanisms that control the electron dynamics in photoinduced processes requires interpretation by advanced theory. In the present work [1], the performance of the range-separated hybrid (RSH) scheme is explored [2]. Within this scheme, a short-range density-functional approximation (DFA) is combined with a long-range Hartree-Fock (HF) method for calculating the photoexcitation and photoionization spectra of the H and the He atoms. In order to correctly describe the continuum part of the spectra, a basis set of B-spline functions has been implemented. The study of these simple systems allows us to quantify the influences of errors coming from the short-range exchange-correlation DFA and from the missing long-range correlation in the RSH scheme. In addition, the differences between using a long-range HF exchange (nonlocal) potential and a long-range exact exchange (local) potential have been investigated. Contrary to the former, the latter supports a series of Rydberg states and reasonable spectra can be obtained, even without applying the linear-response theory. Finally, we show that the most accurate photoexcitation/photoionization spectra are achieved by using the linear-response time-dependent range-separated hybrid (TDRSH) scheme. In particular, for the He atom, we show that, at the optimal value of the range-separation parameter, TDRSH gives slightly more accurate spectra than the standard linear-response time-dependent HF method. More generally, the present work shows the potential use of the range-separated density-functional theory for calculating linear and nonlinear optical properties involving continuum states [3].

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MIGRATORY RESONANCES AND THE WIGNER ATTOSECOND TIMER IN PHOTOIONIZATION OF FULLERENES

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Empty fullerenes and atom-encaging endofullerenes are quintessential symmetric molecules exhibiting near stability in the room temperature. This property endows them with the quality of being tested for spectroscopic information which are otherwise inaccessible for regular atoms and molecules. Probing the response of these systems to electromagnetic radiations is one classic way to accomplish this.

Among varieties of resonances for such molecules, an exotic class of resonances, that will be presented, entail photoexcitation at one site of the endofullerene but its subsequent inter-Coulombic decay (ICD) at a different location [1], as well as a coherent admixture of this migratory mechanism with localized Auger processes [1,2] (Fig. 1). The other part of the presentation will connect to the contemporary attoseconds spectroscopy by evaluating the Wigner time-of-flight of the photoelectron at the energies of fullerene giant plasmon resonance [3]. Results are computed by a density functional methodology. The ground state is described in a local density approximation (LDA) [4], while its linear-response variant (TDLDA) is utilized to describe the interaction with the photon [4]. *The research is supported by the US National Science Foundation and US Department of Energy*.

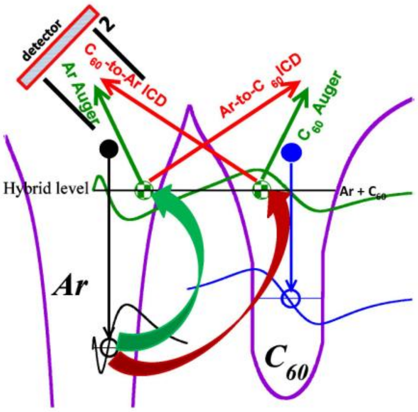

Figure 1: Schematic of coherence of one-center Auger and two-center migratory resonances in Ar@C_{60}.

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ELECTRON EMISSION DUE TO ION THRANSMISSION THROUGH FREESTANDING SINGLE LAYER GRAPHENE

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The rise of 2D materials offers new possibilities to study the neutralisation of (highly charged) ions since projectiles can still be detected after interacting with the target in transmission. For example, emission and capture of electrons from a surface can now be measured both for the same projectile. This makes it possible to disentangle the participating ion-deexcitation processes on a single ion basis [1].

In our experiment we use highly charged Xe ions (Xe^{20+} to Xe^{44+}) with various kinetic energies between 30 keV and 350 keV as projectiles to be transmitted through 2D materials such as single layer graphene (SLG). Primary emitted electrons are detected and serve as start signal for time of flight (ToF) measurements while transmitted ions impacting on a spatially-resolved detector provide the corresponding stop signals. Hence, coincidence measurements of transmitted ions and emitted electrons can be performed [2]. We find a high number of primary emitted electrons per incident ion (~70 for Xe^{40+}, c.f. fig. 1). A set of retarding grids was used to estimate the electrons' energy.

Another approach to study the energy of electrons emitted due to ions interacting with 2D materials was performed employing the ToF-MEIS (Medium Energy Ion Scattering) setup at Uppsala University [3]. Different from the setup in Vienna, singly charged, light ions such as H^+ and He^+ are transmitted through SLG. Information on the energy of emitted electrons is obtained via the flight times of detected electrons. Measurements from both facilities will be compared and discussed.

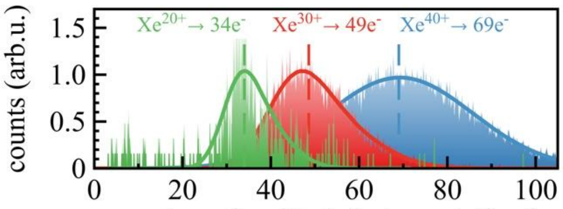

Figure 1: Ion-induced electron emission from SLG measured with 87 keV Xe^{q+} ions as projectiles.

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UNRAVELING ENERGY-LOSS PROCESSES OF LOW ENERGY HEAVY IONS IN 2D MATERIALS

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In order to use ion beams for defect engineering of 2D materials, a model for energy deposition is needed, which takes the ion charge state and charge exchange into account. In the first monolayers of a material impinging keV ions capture electrons and reduce their charge state until charge equilibrium is reached in less than 10 fs (about 1 nm) [1,2].

We present here a new model [3] for charge state and charge exchange dependent ion stopping force calculation, which shows that heavy ions in charge states greater than 1 deposit a substantially larger amount of their kinetic energy in a 2D material than predicted by standard tools as e.g. SRIM. This holds true for electronic and nuclear energy losses, whereas especially the latter causes sputtering and therefore structural defects.

Our model relies on a time-dependent scattering potential (TDPot), which changes due to charge exchange and electronic de-excitation of the projectile during collision. We compare our model results with experimental values determined by heavy highly charged ion transmission through freestanding single layer graphene and find very good agreement in energy loss, charge state distributions, and scattering angle-dependent charge exchange.

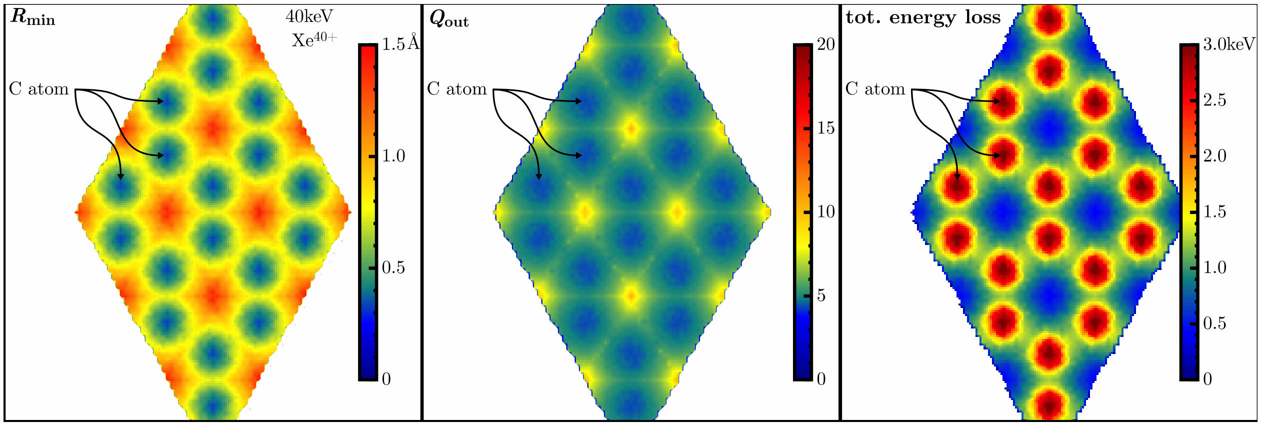

Figure 1: Results of our TDPot model for the distance of minimal approach $R_{\min}$, the exit charge state Q_{out}, and the total energy loss ΔE for 40 keV Xe^{40+} ions impacting a single layer of graphene.

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RADIOLYSIS OF ORGANIC MOLECULES IN CONDENSED PHASE

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Ices are omnipresent in cold regions in space. Examples include comets, dust grains, transneptunian objects, surfaces of planets and their satellites. Although such ices are mainly formed from small molecules (e.g. water, carbon oxides, nitrogen, methane) also larger, complex organic molecules (COMs) may be present. The temperatures of objects on which COMs occur cover a wide range, from 10 K in dense molecular clouds, through 25 K to 150 K in the outer Solar system, up to 300 K (or higher) in the inner Solar system. Ionizing radiation (UV photons, electrons, ions from cosmic rays or solar wind) induces several physicochemical processes such as radiolysis and subsequent formation of new molecules. At CIMAP (Caen, France), using different beam lines (ARIBE, IRRSUD, SME) of the GANIL facility, and at UNILAC of GSI (Darmstadt, Germany), the interaction of swift highly charged heavy ions with astrophysical ices was studied in a wide projectile energy range from keV to GeV [1]. We present results on the radiolysis and radiosensitivity of nucleobases (adenine, cytosine) at different temperatures (15-300 K). We also discuss the (still open) question if the presence of water (omnipresent in space environments), has a protective effect or, on the contrary, enhances radiosensitivity.

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Ion radiation in icy space environments:Synthesis and Radioresistance of Complex Organic Molecules
Low Temperature Physics/Fizika Nizkikh Temperatur **45** No. 6, 692–700 (2019) doi: 10.1063/1.5103250.

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CHARGE EXCHANGE OF HEAVY IONS TRANSMITTED THROUGH A SINGLE LAYER OF MOLYBDENUM DISULFIDE

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2D materials offer extraordinary optical, electronic and mechanical properties, which make them interesting for future applications. Modification techniques, like ion irradiation, allow to alter their properties to specific applications. However, because of their atomic thickness applied techniques have to address mainly the surface region. Highly charged ions are a novel tool for nanostructure formation. They carry potential energies up to tens of keV, which trigger the process of nanostructure formation due to the energy deposition in shallow depths in close vicinity of the surface region. Recently, HCI impact induced nanoholes in carbon nanomembranes [1] and in suspended monolayer MoS_2 [2] have been observed despite their atomic thickness limiting the amount of potential energy to be transferred. Here, we investigate the charge exchange of highly charged xenon ions passing a monolayer of MoS_2 (Fig. 1 a), from which we can obtain an upper estimate of the deposited energy. The exit charge states of transmitted ions are measured simultaneously with their scattering angle depicted in Fig. 1 b as well as their time-of-flights [3]. Two distinct distributions at high and low charge states are visible (Fig. 1 b). The different scattering angles indicate the existence of two impact parameter regimes leading to two (exit charge state) distributions. Our experimental results are supported by computer simulations using the Monte-Carlo code TDPot [4].

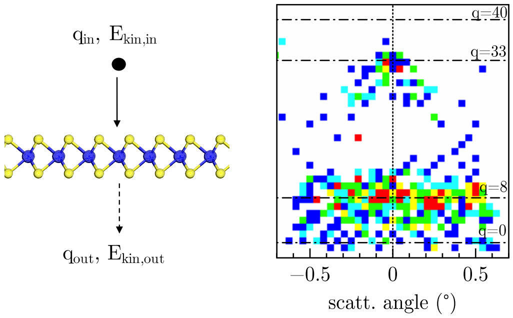

Figure 1: (a): Transmission of a highly charged ion through a suspended monolayer of MoS_2. (b): Two-dimensional charge state and scattering angle resolved spectrum of outgoing Xe ions with initial charge state of q=40 and kinetic energy of E=175 keV.

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EVEN HIGH-HARMONIC GENERATIONS BY ULTRASHORT PULSES IN INHOMOGENEOUS FIELDS

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We have studied the high-order harmonic generation (HHG) of hydrogen atoms within an inhomogeneous field by solving reduced-dimensional time-dependent Schrödinger equation [1]. Due to the symmetry property of atomic hydrogen, it is hard to generate even order high harmonics in the interaction between hydrogen atoms and femtosecond pulses [2]. While in the interaction between laser pulses and nanostructures, a highly enhanced inhomogeneous electric field can be generated [3]. By applying such highly enhanced inhomogeneous field to the HHG, we find that, not only the HHG can be enhanced by the inhomogeneous field [3], but also that the even order HHG can be observed, as shown by Fig.1 (a). We analyze results from classical trajectories (Fig.1 (b)) and the mechanism of enhancement and enabling of even HHG in such an inhomogeneous field. By analyzing the symmetry of system [2] and classical trajectories [3], we reveal that even harmonics are originated from the breaking of symmetry by inhomogeneous field.

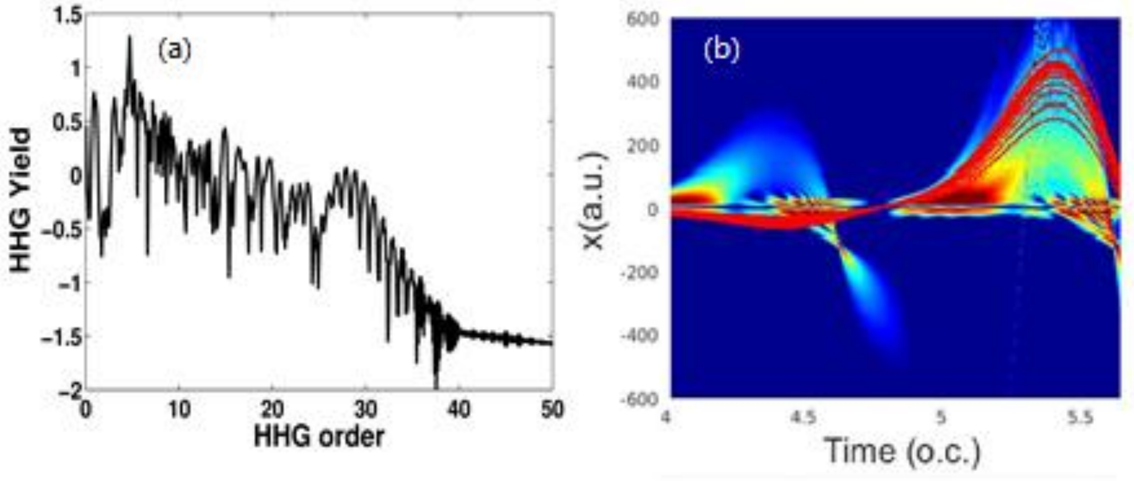

Figure 1: (a) HHG spectrum and (b) time evolution of wave function density of hydrogen atoms and classical trajectories analysis.

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Fragmentation dynamics of positively charged amino acids in the gas phase: Does methylation have a protective effect?

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A good understanding of the ionizing radiation effects in molecules could help us to correctly comprehend the mechanisms that lead to damage in biological tissues, proteins and DNA [1], or even, from a more astrophysical point of view, to study the formation of prebiotic molecules in the interstellar media [2] which could be understood, in a poetic way, as the origin of life.

This work have been focused on the first point of view mentioned and will be centered in the "fingerprint" of the structure of the proteins, the amino acids. Other amino acids like glycine [3] or β-alanine [4] have been previously studied by the group. This time, in order to study a possible 'protective effect' caused by N-methyl groups, a theoretical study of the fragmentation dynamics of two doubly-ionized amino acids *N*-methylglycine (*sarcosine*) and *N,N*-dimethylglycine, in the gas phase is presented.

State-of-the-art quantum mechanics methods like *ab initio* molecular dynamics (AIMD) were performed to expedite the exploration of the potential energy surface (PES) obtaining all possible exit channels at the femtosecond timescale. The main exit channel for both doubly-charged amino acids is the Coulomb explosion leading to the $C_\alpha - C_{carboxilic}$ bond cleavage leading to $COOH^+$ and the iminium fragment, but a much more colorful palette of exit channels was observed for the sarcosine, where, in competition with the Coulomb explosion, ultra-fast hydrogen and OH migrations, the formation of molecules like radical methyl reported as damaging to human health [5] and the emission of neutral molecules like CO, H_2O and H_2.

This work has been performed in close collaboration with experimentalists at the Grand Accélérateur National d'Ions Lourds (GANIL) in Caen (France), who simultaneously study the fragmentation of the biomolecules after collisions with atomic ions in the gas phase. It thus implies the combination of theoretical and experimental results to understand the dynamics of excited and ionized biomolecules.

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IRMPD spectroscopy and QC calculations on functionalized gold nanocluster ions

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Synopsis Many studies are devoted to functionalized metallic nanoparticles, for many applications: in Physics, due to their localized surface plasmon resonances; in Chemistry, due to their specific catalytic properties that depend on their surface nature; in Biology, due to their optical or magnetic properties coupled to their potential for targeting and vectorization of bioactive molecules within living cells. In this last domain, gold and silver nanoparticles are especially of interest and, for the control of their biological effects, it is very important to have a fine knowledge of the structural properties and the chemical stabilities of their functional ligands.

Indeed, many studies are devoted to the characterization of the nanoparticle – ligand interface, especially with NMR or IR methods [1]. However, data interpretations are somewhat difficult because of the relative lack of control in solution of the nanoparticle stoichiometry and of their ligand coverage.

With a bottom-up approach, we here report on a work in progress to study sub-nanometer metallic nanoclusters (few to few tens of metal atoms, few tens to few hundreds of ligand atoms) that allow for a size selection with mass spectrometry and hopefully for a precise characterization in the gas phase. Even if these functionalized nanoclusters do not display the same structural characteristics as the larger nanoparticles, their specific chemical-physical properties are more and more studied because they are very dependent from their size and structure and they are intermediate between those of the isolated metal – ligand and those of the nanoparticles in solution [2][3][4].
Moreover, the recently developed production methods for the synthesis of size-controlled functionalized nanoclusters in solution allow for efficient mass spectrometric experiments with rather high ion currents on a selected mass, either using FAB, MALDI or ESI techniques [5][6]. It is thus possible to consider now IRMPD experiments directly on these mass-selected ion species and to use these nanoclusters as model systems for understanding the effects of structures and of metal – ligand interactions. To our knowledge, this kind of experiments has been only very limited to few organometallic compounds containing only one metal atom [7][8] but, up to now, nothing has been published on IR spectroscopy studies of mass-selected functionalized gold or silver nanocluster ions in the gas phase.

First IRMPD spectroscopy experiments and Quantum Chemistry calculations have deal with gold clusters protected by phosphine ligands (Nanoprobes) and gold-sulfur hybrid clusters [9] (Dugourd's team). Preliminary results with their successes and difficulties will be presented in this contribution.

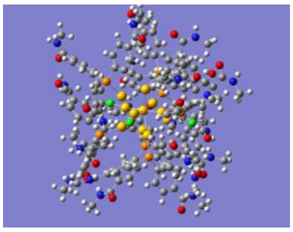

Figure 1. Gold – glutathion cluster anions synthesized in Philippe Dugourd's group.

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Experimental alternative to investigate the radiation-induced radical chemistry at the molecular level

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Synopsis This project aims to develop an original approach to investigate the damage at the molecular level on biomolecules from the indirect irradiation effects. We will construct a new device to put biomolecules in the gas phase, based on the soft laser desorption from microdroplets directly into vacuum, and this source will be coupled with an irradiation platform.

Biologically relevant material is usually associated with considerable amounts of water; e.g. the living cell contains about 70% water. When ionizing radiation interacts with such material one must consider two main modes of energy deposition: the *direct effect* (ionizing radiation is directly absorbed by the biomolecule) and the *indirect effect* (ionizing radiation is absorbed by the surrounding molecules). In the *indirect effect*, radical cations, electrons and slow ions (essentially oxygen ions) are formed. These reactive intermediates interact also with the biomolecules.

The radiation damage, usually obtained from studies where the living cells are directly irradiated with ionizing particles, is consequently the sum of these different effects. In this case, the only contribution of the radical chemistry in the global damage is reasonably impossible to extract. However, the radical species playing an important role in the formation of lesion clustering at the end of the Bragg peak, the understanding of the radical chemistry at the molecular level becomes crucial with the advent of cancer treatments by ionizing radiation [1].

We propose here an alternative to study separately the part of damage due to the radial species. We are currently developing an original source producing biomolecules in gas phase, which is based on the ultra soft laser desorption from liquid microdroplets under vacuum [2]. The desorbed biomolecules, initially present in the liquid, will thus be studied, in the gas phase by mass spectrometry, close to their native forms in solution. Upon irradiation by home-made mid-IR broad band laser pulses (centered on an absorption band of the solvent), analyte ions are ejected directly into high vacuum, with a minimum of perturbations. The possibility to irradiate the droplet with low energy ions gives then a unique access to the damage mechanisms linked with the radical species (see Fig. 1).

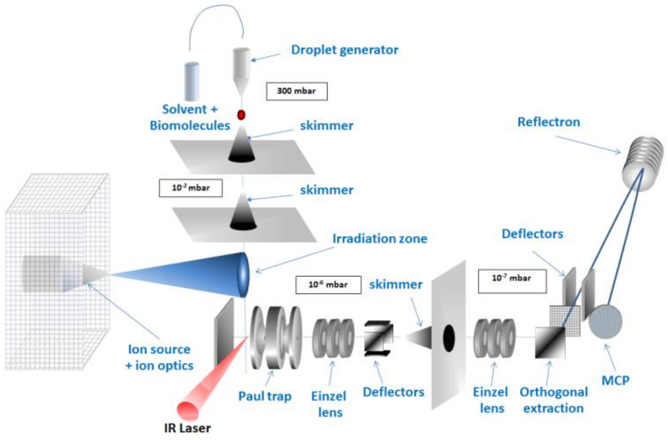

Figure 1. Schematic view of the experimental set-up.

The low energy ions cannot penetrate the microdroplet and create only water free-radicals (OH^{-} and solvated electrons) at the droplet surface, which interact later with the biomolecules included into the liquid droplet. This experimental method simulates, close to *real conditions*, the radical chemistry steps occurring during the irradiation.

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1st symposium on Electron, Photon, and Ion Collisions on Molecular and Atomic Nanostructures - EPIC-MAN

	Monday 22nd July 2019
08:00-09:00	Registration
09:00-10:00	Opening
	2D-Materials Irradiated with Slow Highly Charged Ions - Janine SCHWESTKA
	Magnetic Moment Generation in Small Gold Nanoparticles via the Plasmonic Inverse Faraday Effect - Jérôme HURST
10:00-11:00	Small Carbon Nano-Onions Studied by Ion Mobility Mass Spectrometry - Motoyoshi NAKANO
	Coffee Break
11:00-12:00	Dimethyl Sulfide Reaction on Cold Gold Surface and Triggered by Low Energy Electrons - Hassan ABDOUL-CARIME
	Uracil Cluster Investigation by Photoemission Spectroscopy - Jacopo CHIARINELLI
12:00-13:00	Dynamics of Isolated Biomolecular Ions in the Gas Phase - Marta ŁABUDA
13:00-14:00	Lunch
14:00-15:00	Meeting of the Electronic and Atomic Collision Section of the European Physical Society (EPSEAC)
	Modes of Electron-Density Oscillation Corresponding to Optical Excitations in Metal Clusters - Rajarshi SINHA ROY
15:00-16:00	Damaging Intermolecular Energy and Proton Transfer Processes in Alpha-Particle Irradiated Acetylene Dimer - Shenyue XU
	Triple Differential Cross Sections for the Single Ionization of Biologically Relevant Molecules by Electron Impact - Lena MOUAWAD
16:00-17:00	Coffee Break
	X-Ray Photodesorption from Water Ices - Géraldine FÉRAUD
17:00-18:00	Plasmon Excitation in PAH Molecules and Electron Emission under Fast Ion Impact - Lokesh TRIBEDI
	Using Advanced Light Sources to Investigate Structure and Relaxation Mechanisms of Gas-Phase Biomolecular Ions - Lucas SCHWOB
18:00-22:00	Poster Session and Cocktail