

Book of Abstracts

**1st annual meeting
of the MD-GAS COST Action**

organized in the framework of the
COST Action CA18212 “Molecular Dynamics in the GAS phase”



18th - 21st February 2020
Caen, France

About MD-GAS

Emerging highly advanced ion-beam traps and storage rings combined with synchrotrons, X-ray facilities, and high performance computers offer completely new ways to study Molecular Dynamics in the GAS phase (MD-GAS). Cryogenic traps and rings will allow studies of decay and reaction processes involving molecular ions in well-defined conformations and in single or narrow ranges of quantum states.

The MD-GAS COST Action aims to further develop and fully exploit the exceptional potential of the above range of tools to unravel the connection between the initial energy transfer in interactions between isolated molecules or clusters and photons, electrons, or heavy particles (ions, atoms, molecules) and the related molecular dynamics in unexplored time domains ranging from sub-femtoseconds to minutes and hours.

Furthermore, the Action aims to identify reaction mechanisms and routes that lead to the growth of new molecular species, clusters and aerosols. The new knowledge will be important for fundamental atomic and molecular physics, chemical physics, and for applications in radiation therapy and -damage on the nanoscale, astrochemistry, astrobiology, atmospheric science, and climate research.

The MD-GAS COST Action is organized in three Working groups:

- New high-performance instrumentation and experimental methods to study gas phase molecular dynamics at ion-beam storage rings and traps, at synchrotrons and X-ray facilities;
- Survival and destruction of molecules following their processing by heavy particles, electrons, or photons;
- Charge-, energy flow, and molecular growth processes in intermolecular and intra-cluster reactions.

Organisation

Chair

Alicja Domaracka

Scientific committee

Paola Bolognesi	Italy
Sergio Díaz-Tendero	Spain
Alicja Domaracka	France
Marta Łabuda	Poland
Thomas Schlathöller	Netherlands
Sanja Tosić	Serbia
Henning Zettergren	Sweden

Local organising committee

Suvasthika Indrajith
Chiara Nicolafrancesco
Patrick Rousseau

Programme

Tuesday 18th February 2020

08:15-09:15	Arrival of participants - Registration	
09:15-09:30	Opening - H. Zettergren & A. Domaracka	
09:30-10:00	<i>Action and luminescence spectroscopy of biomolecular systems in the gas phase</i>	S. B. Nielsen
10:00-10:30	<i>Electron transfer and molecular ion formation in cation-anion reactions</i>	X. Urbain
10:30-11:00	Coffee break	
11:00-11:30	<i>Large carbonaceous molecules in space: identification and photophysical processes</i>	C. Joblin
11:30-12:00	<i>The importance of H (and D) scrambling in astronomically relevant hydrocarbon species</i>	A. Candian
12:00-12:30	<i>Supernovae as "dust factories": grain composition, identifications, mechanism of formation</i>	E. Micelotta
12:30-13:00	<i>Surveying fragmentation to aggregation of polycyclic aromatic hydrocarbons in multiple radiation environments</i>	A. Steber
13:00-14:30	Lunch at the GANIL restaurant	
14:30-15:00	Working Group 2 Kick off Meeting - P. Bolognesi	
15:00-15:30	<i>Results and challenges of photofragmentation of molecules of biological interest</i>	L. Avaldi
15:30-16:00	<i>VUV/X-ray photoelectron spectroscopy of nanocrystals for solar cells absorbers isolated in vacuo</i>	A. Milosavljević
16:00-16:30	<i>Ion-molecule reactions of astrochemical and atmospheric interest</i>	D. Ascenzi
16:30-17:00	Coffee break	
17:00-21:00	Poster session	
17:00-21:00	Welcome Cocktail	

Wednesday 19th February 2020

09:00-09:30	<i>Electron induced processes in biologically relevant molecules</i>	J. Kopyra
09:30-10:00	<i>IRMPD spectroscopy and quantum chemistry calculations on metal-ligand cluster ions</i>	C. Desfrancois
10:00-10:30	<i>Proton mobility in water clusters</i>	E. Uggerud
10:30-11:00	Coffee break	
11:00-11:30	<i>Ionizing radiation influence on the fragmentation of glutamine and valine</i>	J. Tamuliene
11:30-12:00	<i>Ion-induced fragment emission from molecules: results, plans, new facilities</i>	B. Sulik
12:00-12:30	<i>Dissociation dynamics of the diamondoid adamantane upon photoionization by XUV femtosecond pulses</i>	S. Maclot
12:30-13:00	<i>Attosecond electron-nuclear dynamics in photoionized molecules</i>	A. Palacios
13:00-14:30	Lunch at the GANIL restaurant	
14:30-15:00	Working Group 1 Kick off Meeting - T. Schlathöler	
15:00-15:30	<i>Heavy ion storage rings: from magnetic to electrostatic and from room temperature to cryogenic</i>	H. Kreckel
15:30-16:00	<i>Electrostatic Ion Beam Trap: A versatile tool for studying gas phase molecular dynamics</i>	O. Heber
16:00-16:30	<i>Unravelling isomer-specific shape and photochemistry of complex molecular ions</i>	E. Carrascosa
16:30-17:00	Coffee break	
17:00-18:30	Poster session	
17:00-18:30	Management Committee Meeting	

Thursday 20th February 2020

09:00-09:20	<i>Inter- and intra-molecular interactions in uracil clusters studied by XPS</i>	J. Chiarinelli
09:20-09:40	<i>Fragmentation dynamics of ionized highly excited furan molecules: a combined theoretical and experimental approach</i>	E. Erdmann
09:40-10:00	<i>High radiative cooling rates of small clusters</i>	P. Ferrari
10:00-10:20	<i>The stability of the smallest carbon cluster dianion: C₇²⁻</i>	P. Najeeb
10:20-11:00	Coffee break	
11:00-11:30	Working Group 3 Kick off Meeting - M. Alcamí	
11:30-12:00	<i>Ion-collision induced reactivity in molecular clusters</i>	P. Rousseau
12:00-12:30	<i>Gas-phase molecules through the lens of time-resolved photoelectron spectroscopy</i>	A. Ponzi
12:30-13:00	<i>Interaction of low energy electrons with biomolecules and clusters of biomolecules</i>	J. Kocisek
13:00-14:30	Lunch at the GANIL restaurant	
14:30-15:00	<i>Highly charged helium nanodroplets</i>	M. Gatchell
15:00-15:30	<i>Creation and destruction of chemical species in liquids treated by atmospheric pressure plasmas - from gas phase chemistry to bulk liquid</i>	N. Skoro
15:30-16:00	<i>Resonant Inelastic X-ray scattering of chloromethanes</i>	M. Zitnik
16:00-16:30	<i>Elastic electron scattering on molecules in the gas phase in the middle energy range</i>	J. Maljković
16:30-17:30	Coffee break	
16:30-17:30	Laboratory visit	
19:00-21:30	Conference diner - Café Mancel, le Château Ducal, Caen	

Friday 21st February 2020

09:00-09:30	<i>Excited-state lifetime measurements of stored chromophore ions</i>	E. Gruber
09:30-10:00	<i>Automated discovery of chemical reaction mechanisms</i>	E. Martínez-Núñez
10:00-10:30	<i>Laser induced fabrication of 3D nanoparticle structures by femtosecond laser radiation</i>	E. Iordanova
10:30-11:00	Coffee break	
11:00-11:20	<i>Ultrafast laser fabrication of ion microtraps via multi-photon processing technologies</i>	B. Calin
11:20-11:40	<i>Energetic processing of biomolecular systems</i>	C. Nicolafrancesco
11:40-12:00	<i>Stability and IR signatures of carbonaceous molecules</i>	P. Pla
12:00-12:20	<i>MD study on reversible folding of tetrakisriazole catalysts and their binding with anionic substrates</i>	D. G. Piekarski
12:20-13:00	Closing remarks	
13:00-14:30	Lunch at the GANIL restaurant	

Abstracts of presentations

ACTION AND LUMINESCENCE SPECTROSCOPY OF BIOMOLECULAR SYSTEMS IN THE GAS PHASE

S. Brøndsted Nielsen^{(a)1}

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Spectroscopic properties of protein biochromophores often rely on the environment. For example, nearby amino acid residues or single water molecules could modulate the color, *i.e.*, shift the transition energy to the red or to the blue. This is seen for the oxyluciferin anion and the retinal protonated Schiff base, the chromophores of luciferase and rhodopsin proteins, respectively, while the chromophore of the green fluorescent protein (GFP) is much less sensitive to nearby electric fields. In general, spectral tuning is seen for chromophores that undergo charge-transfer (CT) transitions. Another important issue is the fluorescence quantum yield, and which chromophore-protein interactions that are responsible for high brightness. In this presentation, I will show how gas-phase ion spectroscopy reveals the true colors of biomolecular ions and uncovers the degree of CT.

Absorption spectra are recorded indirectly from ion dissociation or electron detachment (*i.e.*, action spectroscopy) as there are too few chromophore ions for traditional light transmission experiments. Unfortunately, our results also show that it is difficult to photodissociate the rather big systems on the instrumental time scale (up to 10 μ s). Another technique that does not rely on ion dissociation is luminescence spectroscopy where the photons emitted from the photoexcited ions are detected.

My group recently constructed an instrument, called LUNA (Luminescence iNstrument in Aarhus) where ions are photoexcited in the center of a cylindrical Paul trap followed by photon detection. One of our goals is to turn on light emission from GFP and oxyluciferin anions either by cooling to lq. N₂ temperatures or by the attachment of polar molecules.

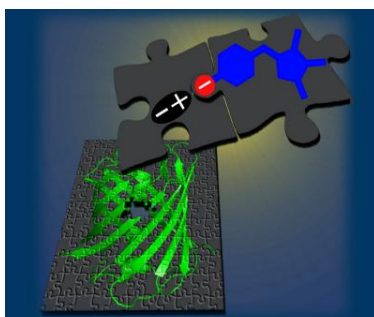


Figure 1: The picture shows the Green Fluorescent Protein as a jigsaw puzzle where one of the pieces adjacent to the buried chromophore provides a strong local electric field (100 MV/cm). We have added one piece to the puzzle and directly addressed how an electric field (of about 70 MV/cm) affects the absorption properties of the chromophore. .

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ELECTRON TRANSFER AND MOLECULAR ION FORMATION IN CATION-ANION REACTIONS

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In this talk, the vast amount of data collected with our ion-ion merged beam setup will be presented. The experimental constraints inherent to the study of beam-beam interactions will be explained, and ways to circumvent them, delineated. We shall discuss the extension of the present studies to the measurement of angular differential cross sections (for mutual neutralization) and rovibrationally resolved cross sections (for associative ionization).

The systematic study of total and partial cross sections for a wide variety of systems has allowed us to identify key parameters controlling the long range electron transfer [1,2] and the short range auto-ionization of the collisional complex [3]. This will be put in perspective with the most recent theoretical advances in the field.

References

- [1] N. de Ruelle, A. Dochain, T. Launoy, R. F. Nascimento, M. Kaminska, M. H. Stockett, N. Vaeck, H. T. Schmidt, H. Cederquist, and X. Urbain, *Phys. Rev. Lett.* **121**, 083401 (2018).
- [2] T. Launoy, J. Loreau, A. Dochain, J. Liévin, N. Vaeck, and X. Urbain, *ApJ* **883**:85 (2019).
- [3] A. Le Padellec, T. Launoy, A. Dochain and X. Urbain, *J. Phys. B: At. Mol. Opt. Phys.* **50**, 095202 (2017).

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LARGE CARBONACEOUS MOLECULES IN SPACE: IDENTIFICATION AND PHOTOPHYSICAL PROCESSES

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Polycyclic aromatic hydrocarbons (PAHs) and related large carbonaceous (C-) molecules such as fullerenes are the carriers of infrared emission bands in the 3-15 μm range, which are triggered by ultraviolet (UV) photons from stars. The study of the molecular processes involved in the spectroscopy, photophysics and chemistry of these large C-molecules requires considering the specific conditions of extreme isolation from the environment. This has motivated over the years the development of dedicated laboratory setups and theoretical simulations at the forefront of molecular physics. In particular, the astrophysical questions have fostered studies on the electronic spectra of cold gas-phase molecules, the relaxation pathways in energized PAHs, and the impact of anharmonicity on the IR emission spectra.

In this presentation, I will focus on two different aspects. The first one concerns the status of the identification of large C-molecules in astrophysical environments. I will emphasize the need to target relevant species, in relation with the question of their formation, which remains a complex problem (e.g. [1]). The second one concerns photophysical studies on long timescales [2]. Relaxation mechanisms including unimolecular dissociation, isomerization and radiative cooling can now be studied thanks to cryogenic ion traps and rings. I will describe how these experiments provide new constraints to evaluate the survival of large C-molecules in astrophysical environments [3].

References

- [1] L. Martínez, G. Santoro, P. Merino, et al., *Nature Astron.* **4**, 97-105 (2020).
- [2] C. Joblin, G. Wenzel, S. Rodriguez Castillo, et al., *J. Phys. : Conf. Series*, in press (2020).
<https://arxiv.org/pdf/1912.03137.pdf>
- [3] J. Montillaud, C. Joblin, D. Toubanc, *Astron. & Astrophys.* **552**, id.A15 (2013).

Acknowledgement

Support from the European Research Council under Synergy Grant ERC-2013-SyG, G.A. 610256 (NANOCOSMOS) is acknowledged.

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THE IMPORTANCE OF H SCRAMBLING IN ASTRONOMICALLY RELEVANT HYDROCARBON SPECIES

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Polycyclic Aromatic Hydrocarbons (PAH) and other large carbon-containing molecules such as fullerene, carbon chains and nanodiamonds are widespread in the Universe and understanding their lifecycle is of primary importance to constrain the inventory of organic molecules available in region of star and planet formation [1]. One of the processes shaping the population of organic molecules in space is the interaction with photons.

In this talk I will give an overview of our recent effort [2-5] to establish the behavior of large positively-charged hydrocarbon molecules upon interaction with photons that can be found in interstellar regions. Our main finding is that H atoms scramble around the molecular surface and their mobility is responsible of photodissociation products we observe.

References

- [1] A. Candian and A.G.G.M. Tielens and J. Zhen, *Phys, Today*. **71**, 11, p 38 (2018).
- [2] P. Castellanos, A. Candian et al, *Astron. Astrophys.*, **616**, A166 (2018)
- [3] P. Castellanos, A. Candian et al, *Astron. Astrophys.*, **616**, A167 (2018)
- [4] S.D. Wiersma, A.Candian et al, *Astron. Astrophys* (2020), accepted
- [5] A. Candian, A. Petignani et al, in prep.

SUPERNOVAE AS 'DUST FACTORIES': GRAIN COMPOSITION, IDENTIFICATIONS, MECHANISM OF FORMATION AND DESTRUCTION

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Observations have recently shown that supernovae are efficient dust factories, as predicted for a long time by theoretical models. The rapid evolution of their stellar progenitors combined with their efficiency in precipitating refractory elements from the gas phase into dust grains make supernovae the major potential suppliers of dust in the early Universe. However, the composition and morphology of dust grains formed in supernova ejecta, together with the mechanisms responsible for the formation and destruction of dust in such environments, is yet to be fully understood. In this talk, I will present the state of the art about these topics, in terms of theoretical modelling and comparison to observations.

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SURVEYING FRAGMENTATION TO AGGREGATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN MULTIPLE RADIATION ENVIRONMENTS

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The breadth of the role of polycyclic aromatic hydrocarbons (PAHs) in the interstellar medium is quite extensive. They impact the chemical morphology from the solid phase (ice grains) to the gas phase. As such, it is important to understand the photophysics and photochemistry of PAHs in the multitude of environments in which they can be found. A multi-spectroscopic approach has been employed to study PAH fragmentation upon interaction with high radiation fields, PAH homo-clustering and clustering with water, and the products from discharges of PAHs with organic molecules. The experiments utilized chirped pulse Fourier transform microwave (CP-FTMW) spectroscopy, IR-UV ion dip spectroscopy, and VUV-vis pump-probe spectroscopy to gain a better understanding of these phenomena. Where warranted, complementary experiments were done in multiple wavelength regimes.

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RESULTS AND CHALLENGES OF PHOTOFRAGMENTATION OF MOLECULES OF BIOLOGICAL INTEREST

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Tunable photon sources from the IR to soft-X ray regions combined with increasingly sensitive detection techniques enable energy and in some cases state selected studies of molecular dissociation in gas phase. Once applied to systems of biological interest these studies provide hints for example on the mechanisms of radiation damage at molecular level, the role of small molecules or nucleobase-substitutes as radiosensitizers in radiotherapy as well as the peptide bond formation and cleavage mechanisms. The basic science challenges consist of a better definition of the dissociation including the detection of all the particles in final state as well as the time dependence/control of the processes. As for the application, the limits to overcome in order to access the study of macromolecules or nanoaggregates relevant in the life sciences, are the possibility to produce beams of these systems dense enough to perform spectrometric and spectroscopic measurements and to investigate them in realistic environments.

Some examples of recent results on nitroimidazole compounds and dipeptides together with some perspectives will be presented.

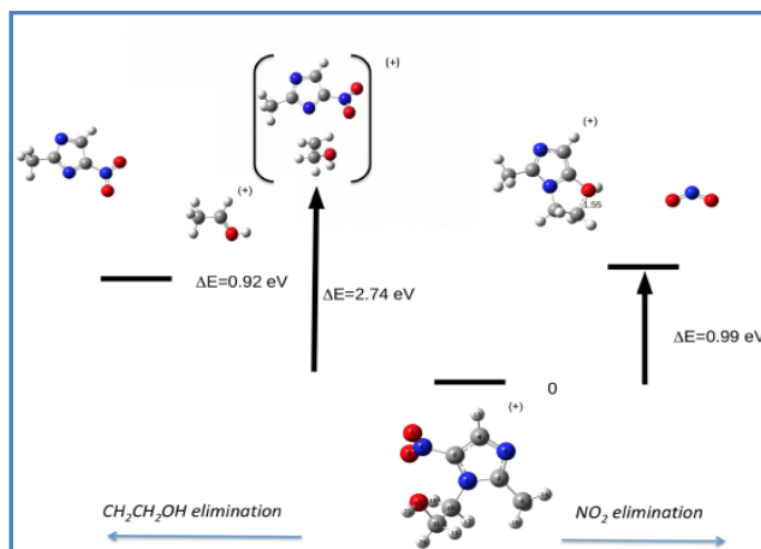


Figure 1: Fragmentation pathways in metronidazole leading to the NO_2 (right panel) and ‘tail’ $\text{CH}_2\text{CH}_2\text{OH}$ (left panel) losses [1].

References

- [1] J. Chiarinelli *et al.* *Front. Chem.* **7**, 329 (2019)

VUV/X-RAY PHOTOELECTRON SPECTROSCOPY OF NANOCRYSTALS FOR SOLAR CELLS ABSORBERS ISOLATED IN VACUO

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Following a breakthrough regarding lead halide perovskites materials, as potentially low-cost and unprecedentedly efficient solar cell absorbers [1], there has been an increased effort in recent years to develop more stable and environmentally friendlier lead-free perovskites [2]. The use of nanocrystals (NCs) can additionally increase the complexity and possibilities, due to the high importance of the surface with respect the bulk, size confinement effects, wider possibilities to tune the material properties etc. (see [3] and references therein). Recently, we have reported a new approach to study the electronic properties of perovskite NCs by combining laboratory-based X-ray photoelectron spectroscopy (XPS), as well as synchrotron-based ARPES/XPS on isolated NCs, produced by atomization of NC colloids, and then delivered and focused into the vacuum of the spectrometer by an aerodynamic lens. Furthermore, the experiential data are supported by DFT calculations of the electronic structure. Recently, by using such approach, we have investigated the electronic properties of silver bismuth iodide (Ag-Bi-I) nanocrystals.

In this talk, we will describe in details the setup to perform photoelectron spectroscopy of isolated nanoparticles, which presently exists on PLEIADES and DESIRS beamlines. We will give example results for the lead halide perovskite NCs and we will report some new results for lead-free Ag-Bi-I NCs.

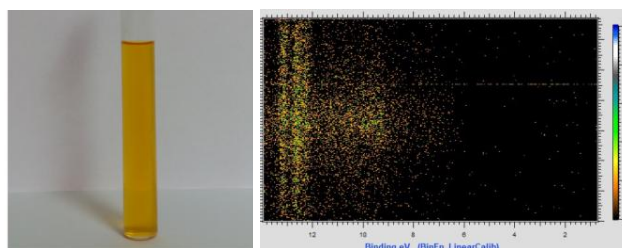


Figure 1: Ag-Bi-I NC sample dispersed in acetonitrile (left) and valence XPS image of such NCs (right).

References

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- [2] H. Fu et al., *Sol. Energy Mater. Sol. Cells* **193**, 107 (2019)
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ION-MOLECULE REACTIONS OF ASTROCHEMICAL AND ATMOSPHERIC INTEREST

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While being less abundant, and hence more difficult to detect with respect to neutrals, ions play a key role in the interstellar medium (ISM) and planetary atmospheres (including the Earth's one), either as intermediate steps in the build-up of complex molecules [1, 2] or as energy carriers for efficient fragmentation of neutrals [3, 4]. In fact, due to the long range attraction forces, ion-molecule reactions are usually barrierless and therefore efficient even in environments, such as the ISM, where low densities and temperatures apply.

Despite the ground-breaking discoveries made by space missions and astronomical observations, questions are still open on what are the most probable chemical pathways operative in such environments. Our contribution to the field is in the study of possible formation and destruction mechanisms lead by charged species [5, 6]. We approach the problem in a dual fashion by: *a*) measuring rate constant and branching ratios (BRs) of ionic reactions via tandem mass spectrometric techniques and RF octupolar trapping and *b*) performing theoretical calculations, at various levels of theory, of the energy hypersurface and possible formation mechanisms.

Here we review some of the most recent results obtained on the isomer-selective reactivity of small N-containing organic cations with saturated and unsaturated hydrocarbons. Experiments exploit photoionization of apt neutral precursors with VUV radiation from the DESIRS beamline @SOLEIL synchrotron radiation facility to ensure the selective production of specific isomers, namely *c*-C₂H₂N⁺ vs linear CH₂CN⁺ and HCNH₂⁺ (aminomethylene radical cation) vs H₂CNH⁺ (methylenimine radical cation). Our results can help in improving the reliability of chemical models predicting the abundances and distributions of complex molecules in astronomical environments.

References

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ELECTRON INDUCED PROCESSES IN BIOLOGICALLY RELEVANT MOLECULES

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Reactions initiated by electron attachment to molecules, including those which result in molecular dissociation, drive plenty of the important processes in many fundamental areas of (nano)technology, chemical engineering, radiation physics and chemistry.

Recent years have witnessed a remarkable growth in the scientific interest in studying the low energy electron interactions with biologically relevant molecules. Among them, a wealth of experimental and theoretical studies have been devoted to nucleic acids and their sub-units [1-3] in order to unravel the molecular mechanism how LEEs damage macromolecules.

In the present contribution I shall present experimental gas phase studies on dissociative electron attachment to heterocyclic organic compounds consisting of a six-membered ring which is fused with imidazole ring. Such chemicals are frequently used to mimic the behavior of purine nucleobases under reductive conditions. These compounds exhibit a remarkable phenomenon in DEA which is based on a site- and bond-selective formation of dehydrogenated parent anions (Fig. 1). In particular, emphasis will be placed on the description of the formation of the transient negative ions and the comparison of the fragmentation patterns for a series of biologically relevant compounds.

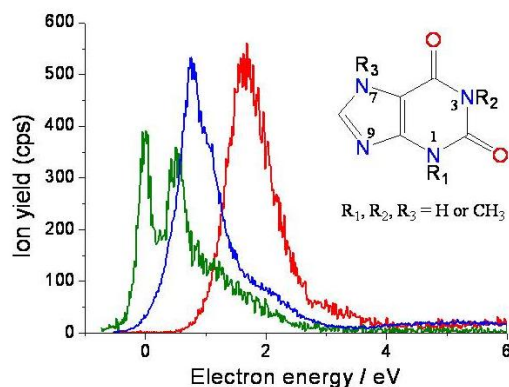


Figure 1: Formation of $[M - H]^-$ from xanthine (green), theophylline (blue), and theobromine (red).

References

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IRMPD SPECTROSCOPY AND QUANTUM CHEMISTRY CALCULATIONS ON METAL-LIGAND CLUSTER IONS

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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; in Biology, due to their optical or magnetic properties coupled to their potential for targeting and vectorization of bioactive molecules within living cells. In solution, the characterization of the nanoparticle – ligand interface, is often performed with NMR or IR methods but data interpretations are somewhat difficult because of the relative lack of control of the stoichiometry of nanoparticles and of their ligand coverage [1].

With a bottom-up approach, we here report on a work in progress to study sub-nanometer metallic nanoclusters (few metal atoms, few ligands) that allow for a size selection with mass spectrometry and hopefully for a precise characterization in the gas phase by IR spectroscopy. Even if these functionalized nanoclusters do not display the same structural characteristics as the larger nanoparticles, their specific chemical/physical properties 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].

We will present IR MultiPhoton Dissociation (IRMPD) spectroscopy experiments on isolated mass-selected metal-ligand ions which will be compared to Quantum Chemistry (DFT) calculations and vibrational spectra computed either at the static harmonic, static anharmonic, or molecular dynamics levels. Studied ions involve simple (Al), transition (Fe) and heavy (Ru) metals and different anionic ligands (Acetylacetonate, Cafeic acid, Alendronate). If time permitted, we will also present results on larger functionalized gold or silver nanoclusters [3].

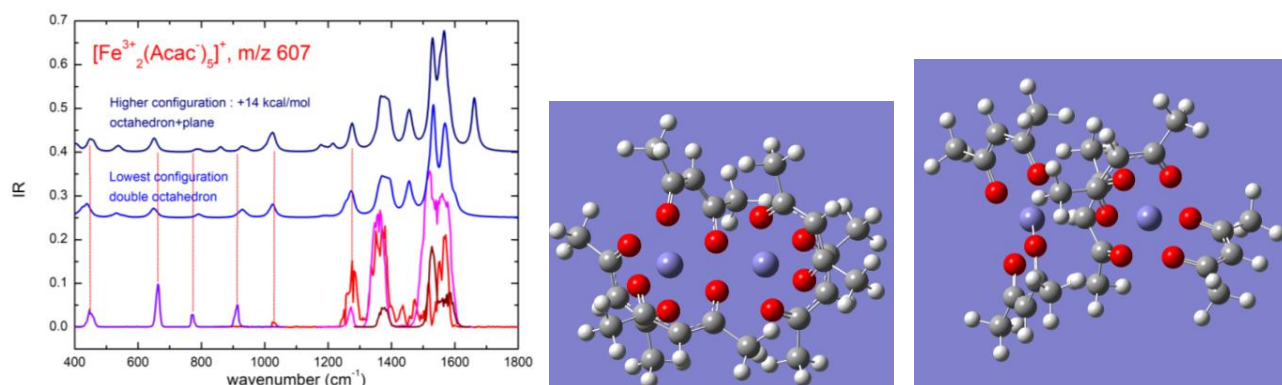


Figure: IRMPD spectrum and DFT calculations and structures of $[\text{Fe}^{3+}_2(\text{Acac}^-)_5]^+$ mass-selected cations.

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Proton mobility in water clusters

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Among hydrogen-bonded systems, water is unique and the basis for all known forms of life. Clusters of water molecules, $(\text{H}_2\text{O})_n$, constitute particularly attractive small-scale models for bulk water, and by introducing ionic or neutral molecules into a cluster, it becomes possible to investigate solvation in water at a fundamental level. The interaction between a small number of water molecules and polar or charged particles is in this respect essential. In the lecture it will be demonstrated how careful studies of H/D exchange upon reactions with D_2O provides direct insight into proton mobility and proton exchange as a function of cluster size. [1]-[5].

Furthermore, we present experimental and computational data on the uptake of CO_2 in small water clusters containing hydroxide ion, $\text{OH}^-(\text{H}_2\text{O})_n$ ($n = 2-12$) and suggest a general mechanism, also applicable to bulk water and thereby to CO_2 uptake in oceans.[6] This mechanism avoids intermediate H_2CO_3 by combining the CO_2 hydrolysis and the protolysis steps into one. The general mechanistic picture is consistent with low enthalpy barriers and that the limiting factors are largely of entropic nature.

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IONIZING RADIATION INFLUENCE ON THE FRAGMENTATION OF GLUTAMINE AND VALINE

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The influence of high (11.5 MeV) energy ionizing radiation on the fragmentation of the glutamine and valine amino acid molecules has been studied using the experimental mass spectrometric and theoretical density functional theory (DFT) techniques. The 11.5 eV energy electron beam was produced by the M-30 electron accelerator (microtron).

It has been shown that the above molecules undergo stable structural changes at different irradiation doses (i.e. 0, 5 and 20 kGy). It has been found that irradiation leads to destruction of some of molecules, the degree of which depends on the irradiation dose [1]. The influence of the electric field imposition on the molecules under study has also been analyzed.

The results of our investigations show that most of the valine and glutamine molecules remain intact. The analysis of the changes in the mass spectra of the valine molecules irradiated by high-energy electrons at the 5 and 20 kGy doses indicates that the interaction of the high-energy electrons with the valine molecule does not induce new peaks in the mass spectra, however, the intensity of some of them varies significantly with the irradiation dose. The amino group splitting off proceeds here, most likely, with a general tendency toward elimination of functional groups.

In contrary, in the case of glutamine some molecules undergo a pronounced structural transformation accompanied by the transition to the zwitterionic/deprotonated form, which causes a change in the fragment ion production yields at the interatomic distance variation. The results of our calculations show that the yield of the low-mass fragments from the zwitterionic glutamine molecular structure may increase due to the increase of the isobaric ion yield. This noticeably affects the efficiency of the dissociative ionization process, and the other reactions could also take place, resulting in the production of fragments with the same mass but different chemical compositions.

The DFT theory approach indicates also the possible pathways of the valine and glutamine molecules dissociation.

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ION-INDUCED FRAGMENT EMISSION FROM MOLECULES: RESULTS, PLANS, NEW FACILITIES

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Complementary ion-impact molecular fragmentation studies in gas phase targets have been performed at the accelerators of Atomki and at the beamlines of the Aribé facility in GANIL, Caen. I would like to tell a few words about selected topics of this long term collaboration, e.g, the fragmentation of water, methane and other small molecules by HCl and fast, single charged ion-impact [1-3], or the emission of negative fragment ions in keV energy collisions [4-8]. Our motivation here extends from the exploration of fundamentals to the understanding of radiation governed processes relevant for e.g., biology, astrophysics and astrochemistry.

Recently, we started two new projects in Atomki, in the latter directions. One of them is *studying radiation damage in polymers within an experimental multiscale approach*, by measuring related systems in solid and gas phase. We e.g., irradiate solid polyethylene and short alkane sequences (methane, ethane, propane...) in gas phase with the same ions. We attempt to find connection between the results from FTIR absorption spectroscopy of the irradiated solid and the ionization and fragmentation cross sections gained from the gas phase measurements. *The other project is laboratory astrophysics*. In a strong collaboration with the University of Kent and the Queen Mary University of London an experimental setup has been installed at the beamline of the new 2MV Tandatron accelerator of Atomki. The aim is to study chemical changes in low temperature (>15K) mixed ices by ion impact. Such kind of chemistry, undergoing in the ice mantle of space dust particles (or larger celestial bodies) by the impact of stellar wind and cosmic rays has been found to be the dominant channel of building organic molecules in space [9]. This new setup (already in operation) is open for the community in a transnational access framework within the new Europlanet (EP 2024-RI) project.

The lecturer is a witness of these collaborative works. The full list of many authors will be provided in the talk, together with the names of CIMAP members, who kindly helped us in our way to laboratory astrophysics. Support from Hungarian-French bilateral S&T projects, the Hungarian OTKA project (K128621) and from the European H-2020 EP 2024-RI project is gratefully acknowledged.

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DISSOCIATION DYNAMICS OF THE DIAMONDOID ADAMANTANE UPON PHOTOIONIZATION BY XUV FEMTOSECOND 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 C₁₀H₁₆. 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].

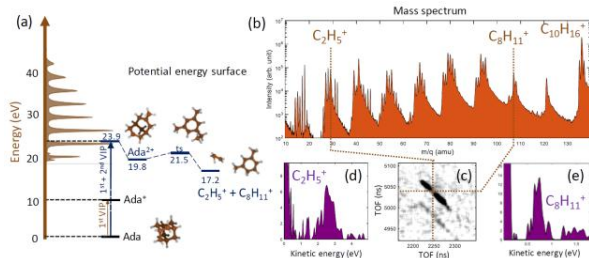


Figure 1. Example of experimental and theoretical

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 dissociation, 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, C₁₀H₁₆²⁺ → C₂H₅⁺ + C₈H₁₁⁺, is highlighted as an example.

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Attosecond electron-nuclear dynamics in photoionized molecules

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Coherent light sources producing femtosecond and sub-femtosecond laser pulses come with the promise of achieving an actual control on molecular excitation and ionization processes that govern a large extent of charge transfer reactions of interest not only in biology, but also in novel technological applications [1,2]. These sources allow for the real-time observation of the underlying electronic processes, which is the only path to attain a deep understanding of the chemical reaction in order to be able later to design control strategies. Attosecond pump-probe spectroscopy has been successfully employed in a manifold of recent experiments pursuing to trace and, eventually, manipulate molecular fragmentation paths [1]. Most of existing experiments available combine a single or a train of attosecond pulses in the VUV/XUV region to trigger molecular excitation or ionization, whose dynamics is then probed by the time-delayed interaction with an IR field. The ideally pursued scheme is that one using a second VUV/XUV pulse as a probe. This talk will discuss available theoretical methods for a reliable description of ultrafast electron dynamics in ionization processes [2]. Recent applications where electron dynamics is retrieved with sub-femtosecond resolution on molecular targets ranging from the hydrogen molecular ion to biomolecules.

The talk will focus on the role of electron-electron and electron-nuclei correlations in the excitation and/or ionization of molecular species. First, novel approaches, such those using single chirped VUV/XUV pulses or pairs of identical attosecond pulses, will be proposed in order to retrieve electron-nuclear dynamics with sub-femtosecond resolution in small molecules [3]. Second, recent applications of standard XUV/IR pump-probe protocols will be discussed. These approaches aim to explore molecular dynamics using protocols where the XUV pulse creates a coherent superposition of ionic states and an IR delayed field traces the dynamics into singly or multiple ionized species. The evolution of the ultrafast electron dynamics is then examined in distinct scenarios: i) the dynamics triggered by single or trains of attosecond pulses in molecules, where the time scales of electronic and nuclear motion are comparable and for which fully ab initio methods are available [4], and ii) the dynamics launched by an attosecond pulse in polyatomic and large molecules of biological interest, where ultrafast processes such that charge migration are predicted to occur prior nuclear rearrangement [1].

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Heavy ion storage rings: from magnetic to electrostatic and from room temperature to cryogenic

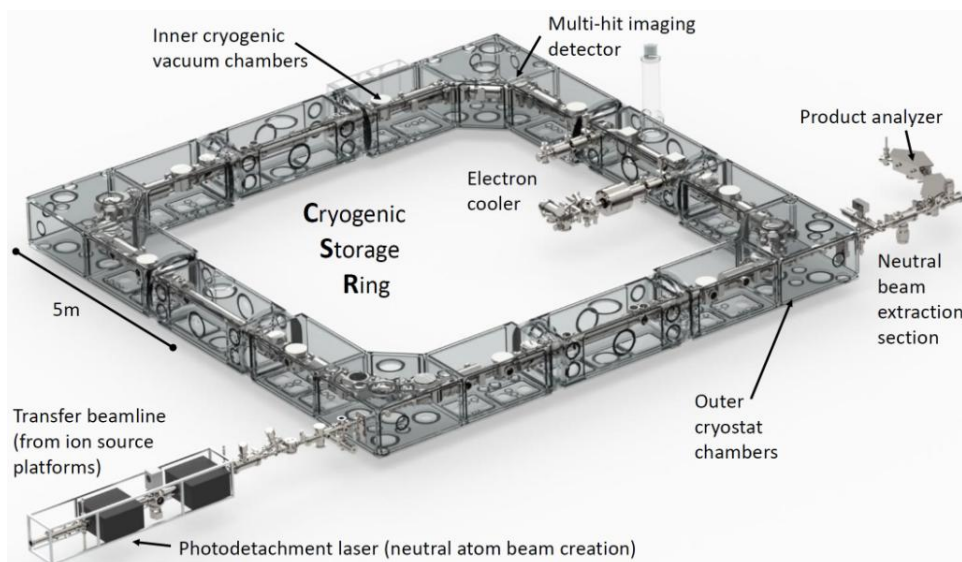
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Molecular ions play an important role in various fields, ranging from astrophysics to atmospheric chemistry and biophysics. However, studying molecular ions in the laboratory can be challenging, owing to the difficulty of preparing them defined internal states. In this context experiments at heavy ion storage rings have been remarkably successful, facilitating research with superior state definition.

While the use of *magnetic* storage rings is often without alternative in the field of nuclear and particle physics, a new generation of *electrostatic* storage rings, for experiments with atomic and molecular ions, has been commissioned in laboratories around the world. In these devices, the ion optics relies on static electrodes at high voltage [1], rather than strong magnetic fields. This allows for the storage of ions of almost arbitrary mass, from protons to bio molecules. Some of the more advanced instruments couple the electrostatic optics with cryogenically cooled vacuum chambers [2,3,4]. The low temperatures come with the added benefit of extremely low pressure – translating into long storage times – and an almost negligible blackbody radiation field.

We will give a quick outline of the heavy ion storage ring technique and the advantages of merged beams experiments, followed by an overview of recent developments, mainly using the example of the new Cryogenic Storage Ring (CSR) at MPIK in Heidelberg.



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ELECTROSTATIC ION BEAM TRAP: A VERSATILE TOOL FOR STUDYING GAS PHASE MOLECULAR DYNAMICS

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Electrostatic Ion Beam Traps (EIBT) have been used for molecular dynamics study since 1997. During these years many new techniques enabled (among other things) the study of gas phase molecular dynamics. In this review a few applications done at the Weizmann Institute will be explored. Few Techniques and examples will be presented from a “simple” lifetime measurement of a metastable electronic molecular level through clusters coupled dynamics using master equations and the road to full reaction microscope as well as molecule – molecule-controlled collision reactions.

Unravelling isomer-specific shape and photochemistry of complex molecular ions

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Over the last decades, gas phase chemists have directed efforts toward developing isomer-specific methodologies, such as multi-resonance spectroscopy schemes, that allow characterization and indirect structural deconvolution of isomerically congested samples. One alternative, unambiguous isomer discrimination method involves coupling of ion mobility mass spectrometry (IM-MS) with techniques such as action spectroscopy or collision induced dissociation (CID).

This presentation will describe the different types of IM-MS separation techniques commonly used in gas phase chemistry research, highlighting several studies where addition of IM-MS has provided unprecedented information on the structure and photochemistry of complex molecular ions such as bio-chromophores or molecular photoswitches [1].

Special emphasis will be put in introducing a novel instrument developed at the Rizzo Group that combines a cyclic high-resolution variant of travelling wave IM-MS and cryogenic IR spectroscopy, thus providing vibrational spectra of mass- and isomer-selected biomolecular ions with ultra-high mobility resolution [2]. I will present very recent results on the combination of this device with enzymatic digestion and CID to unravel the primary structure of large saccharides [3,4].

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INTER- AND INTRA-MOLECULAR INTERACTIONS IN URACIL CLUSTERS STUDIED BY XPS

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Core level photoemission spectroscopy, XPS, is a perfect tool to probe the chemical environment of a specific atom in a system. In this work XPS has been used to study the different molecular interactions (H-bond, π -stacking, dispersion interactions) at work in uracil clusters in gas phase. The 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 measured C, N and O 1s XPS spectra of the clusters display a shift towards lower binding energy with respect to isolated uracil molecules [3] (Fig.1). DFT-based simulations using the Quantum ESPRESSO suite of programs [4] to calculate the binding energy of each atom in the cluster and molecular dynamics simulations to define the structural properties have been performed. Our strategy is based on the selection of aggregates (2-50 molecules) cut out from the uracil crystal structure and fully optimized to disentangle the effect of different interaction patterns. The results shows significant agreement with experiments and a molecular dynamics simulation at finite temperature confirmed that the model used is able to reproduce connections and structures that can be found in realistic gas phase clusters.

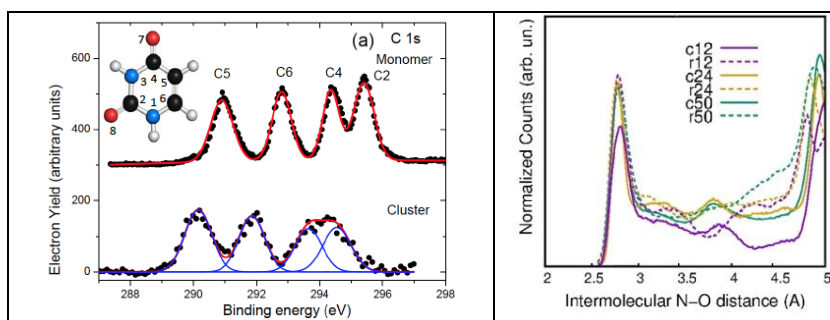


Figure 1: **(left)** C1s XPS spectra of Uracil molecules [3] and clusters, **(right)**. Distribution of the (N(H)...O) intermolecular distances in clusters of 12, 24 and 50 molecules starting from both the crystallographic structure (full lines) and a random distribution of molecules (dash lines).

Acknowledgements. CNRS PICS Project BiFace, International Associated Laboratory (LIA) DYNAMO.

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Fragmentation dynamics of ionized highly excited furan molecules: a combined theoretical and experimental approach

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The main aim of our work is to investigate and understand a complex problem of the evolution of a molecule following deposition of the energy in an ionizing collision with a photon or an ion. If the amount of energy is sufficient, the excited molecule can subsequently undergo fragmentation through a radiationless transition of energy to rovibrational degrees of freedom. The combination of theory and experiment gives a verifiable confirmation of the occurring processes. Furan molecule has been chosen as a target due to its model structure that can be seen as an elementary analogue of deoxyribose, fundamental component of the DNA backbone chain. Depending on the charge state, the furan molecule is expected to decompose in various ways [1].

Our theoretical approach consists of three complementary methodologies: (1) *ab initio* molecular dynamics simulations, (2) exploration of the Potential Energy Surface with Density Functional Theory, and (3) a statistical Microcanonical Metropolis Monte Carlo (M_3C) method [2]. The main result of M_3C technique are the probabilities of occurring fragmentation channels as a function of the excitation energy (breakdown curves), which are obtained with less computation cost than with molecular dynamics. Therefore, by considering the dynamical, energetical and entropic aspects of the studied process we expect to create a complete picture of the fragmentation mechanism.

The fragmentation mechanism varies depending on the energy deposited to the system (from 5 to 30 eV). More insight into three- and four-body fragmentation processes is obtained by investigation of the order of events occurring as the trajectory progresses. Calculated fragmentation pathways, presenting minima and transition states, indicate stability of intermediate steps and point out to energy barriers for specific fragmentation channels.

Due to an assumption of the ergodic hypothesis in the M_3C method, the direct comparison of M_3C probabilities with the experimental breakdown curves measured by the PEPICO technique is possible. Moreover, mass spectrometry has been employed to study the interaction of various ions (Ar^+ , O^{3+} , O^{6+} , Ar^{11+} , Xe^{25+}) with the furan molecule. As a result, we are able to evaluate the effect of the energy redistribution after electron capture at different impact parameters.

A good comparison between theoretical and experimental breakdown curves indicates the adequacy of the approximation of the fast redistribution of energy in the electronic ground state and efficient coupling between electronic and vibrational degrees of freedom.

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HIGH RADIATIVE COOLING RATES OF SMALL CLUSTERS

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The radiation from thermally populated excited electronic states has recently been recognized as an important cooling mechanism in carbon-based molecules and small metal clusters. Experiments have demonstrated that many of these systems radiate at surprisingly high rates, often with a distinct dependence on the precise size of the particles. There are several consequences of an active radiative cooling channel, as for example in the production of size-selected particles in an evaporative ensemble, where abundances of highly radiating sizes will be enriched. In an astrophysical context, radiative cooling provides a mechanism to dissipate internal energy in star-forming processes, which stabilizes molecules selectively in the circumstellar medium. Despite its relevance, there are several open questions about the fundamental mechanism responsible for the radiative cooling process of clusters. For instance, even though experiments provide strong evidence for photon emission via low-lying electronic excited states, conventional theoretical calculations fail to predict the existence of such states. In this talk, I will discuss how the radiative cooling of different laser-excited small metal clusters could be measured using a time-of-flight mass spectrometer [1-5]. The size dependence (Figure 1) of the radiative rates is discussed as well as the efforts undertaken to elucidate the fundamental mechanism behind the photon emission of these systems.

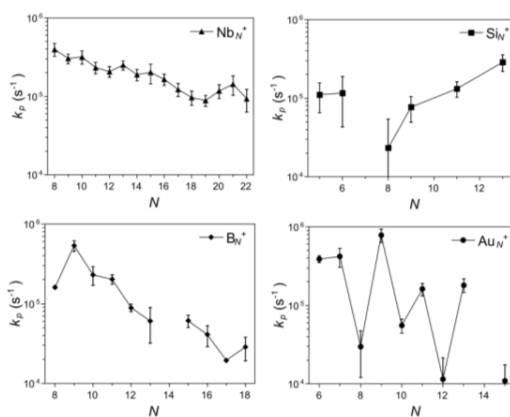


Figure 1: Rates of photon emission of Nb_N^+ , Si_N^+ , B_N^+ and Au_N^+ clusters, measured in a reflectron time-of-flight mass spectrometer.

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THE STABILITY OF THE SMALLEST CARBON CLUSTER DIANION: C_7^{2-}

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Small carbon cluster dianions, C_n^{2-} ($n > 6$) have been demonstrated to survive on microsecond timescales in pioneering mass spectrometry experiments [1-4]. The extreme high vacuum (10^{-14} mbar) and cryogenic conditions (13 K) of the cryogenic electrostatic ion storage ring, DESIREE, enable us to study the stabilities of these systems on much longer time scales [5]. Here, we store 20 keV $^{13}C_7^{2-}$ ions in one of the DESIREE storage rings and monitor their decay by dumping them onto a detector after certain storage time. In Fig. 1 we show the average number of ions (per injection) remaining in the ring as a function of time. At early times (up to ~ 10 ms) the signal follows a power-law dependence due to spontaneous electron emission from hot dianions. On longer timescales, the signal is slowly decreasing with a characteristic decay time exceeding 100 s. This is consistent with the storage lifetime for a stable ion beam decaying due to background collisions. We thus find that C_7^{2-} has a lifetime on the order of minutes or longer, i.e. about eight orders of magnitudes longer than previously reported.

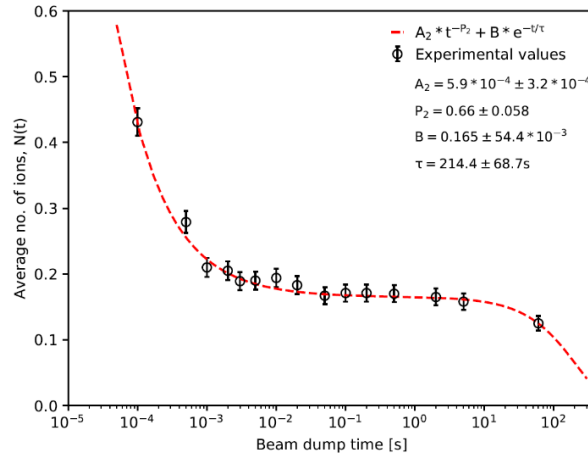


Figure 1: The average number of C_7^{2-} ions circulating in the ring as a function of storage time.

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ION-COLLISION INDUCED REACTIVITY IN MOLECULAR CLUSTERS

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In space, the molecular matter is energetically processed by ionizing radiation and two scenarios are proposed to explain the emergence of new molecular species. On the one-hand, the *bottom-up* approach proposes the growth of larger molecules from smaller subunits. On the other hand, the *top-down* scenario considers the emission of molecular species from a large piece of matter. Here we will consider an intermediate approach, the energetic processing of molecular clusters.

Molecular clusters are weakly bonded assembly of molecules. Thus it is a reservoir of molecular matter for the growth of new species. Moreover it can be also consider as a buffer, its dissociation allowing to dissipate an excess of energy. In the last years, we have shown that a wealth of new species may be formed inside of a molecular cluster after interaction with keV ions.

The reactivity induced by ion-collision will be discussed considering the charge and energy transfers associated with the ion-cluster interaction.

Acknowledgement: this work has been performed in collaboration with colleagues at Stockholm University, Universidad Autonoma de Madrid, and in the J. Heyrovsky Institute of Physical Chemistry in Prague. We acknowledge the financial support from the CNRS through the international associated laboratory DYNAMO (CIMAP/Stockholm University/ Universidad Autonoma de Madrid) and from the bilateral Barrande program (CIMAP/J. Heyrovsky Institute).

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GAS-PHASE MOLECULES THROUGH THE LENS OF (TIME-RESOLVED) PHOTOELECTRON SPECTROSCOPY

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This talk will focus on the dynamics of photoemission processes for molecules in the gas phase. It will be structured according to three main research directions: (i) the investigation of highly correlated systems through photoelectron spectroscopy (PES); (ii) the extension of the theoretical model and the computational tools used for PES to the time-domain; (iii) the exploration of chirality by PES.

PES applied to molecules in gas phase is a powerful tool to significantly enhance our understanding of electronic structure, chemical bonding and mechanisms of chemical reactions. Fundamental issues concerning multiple electron ejections, satellite transitions and ionization of excited states are still open and controversial. Therefore, it is of pivotal importance to shed light on the photoionization process in highly correlated gas-phase samples. Furthermore, the study of chirality in relation to PES will be discussed. In particular, a chiroptical effect, known as photoelectron circular dichroism (PECD), will be considered. PECD experiments provide a more sensitive probe of the photoelectron dynamics and of the molecular and conformational structure than traditional photoionization experiments.

Some significant results will be presented together with current new computational developments and open issues related to the limitations in the theoretical approaches.

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INTERACTION OF LOW ENERGY ELECTRONS WITH BIOMOLECULES AND CLUSTERS OF BIOMOLECULES

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The talk overviews our recent experiments with biomolecules and their clusters. Clusters are unique model species enabling studies of bulk and surface processes by vacuum restricted methods. This is of particular importance for the reactions of low energy electrons, which have extremely short penetration depth in such environments.

Presently studied systems are substituted pyrimidines as models of radiosensitizers and small amides as models of peptide bonding.

In pyrimidines, attachment of low energy electron results in hydrogen loss forming typical (M-H)⁻ base radical anions. In our study [1], we demonstrated closing of this dissociation channel by the water environment. Such closing is caused by caging of the dissociation products and intermolecular energy transfer. [2] Estimations of absolute values of the energy transferred to solvent in these studies is complicated due to unknown internal energy of molecules in the molecular beam. Here, we will show that electron attachment spectroscopy can be used to estimate the vibrational temperature.

For the dissociation of DNA bases are important nuclear excited (vibrational) Feshbach resonances at low electron energies. On the other hand, dissociation of amides primary occurs at high energies via core-excited (electronic) Feshbach resonances. These resonances were proposed as an important peptide bond dissociation mechanism by low energy electrons. [3] Here, we will demonstrate that in contrast to nuclear excited Feshbach resonances, core-excited Feshbach resonances remain open even in complex environment modelled by homogeneous and heterogeneous clusters.

We acknowledge the support by Czech Science Foundation grant no 19-01159S and Czech Ministry of Education Youth and Sports via OP RDE Grant no. CZ.02.2.69/0.0/16_027/0008355.

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HIGHLY CHARGED HELIUM DROPLETS

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Helium nanodroplets have been the focus of much interest over the past several decades [1]. This has revealed a number of interesting properties resulting from the superfluid nature of these nanoscale cryo-vessels with their equilibrium temperatures of 0.37 K [1]. He nanodroplets have also found use in the study of molecules, ions, and clusters, that be collected and grown as dopants in this cold environment and studied using spectroscopic and mass spectrometric techniques [1]. However, until recently there had been no reported studies on He droplets containing more than two net charges and there was some debate as to whether multiply charged droplets were even stable at all.

In a new set of experiments, we have produced and studied beams of highly charged cationic He nanodroplets containing anywhere from thousands of atoms to billions [2]. Using a pair of electron impact ionization sources and electrostatic analyzers operated in tandem, we are able to resolve charge states of up to 55 net positive charges and determine the minimum appearance sizes of these droplets [2]. Using the techniques learned from this study we have also developed methods for producing intense beams of size- and charge-selected He droplets that have potential applications in the growing of nanoparticles.

In my talk I will present this work and recent developments, including measurements of negatively charged droplets.

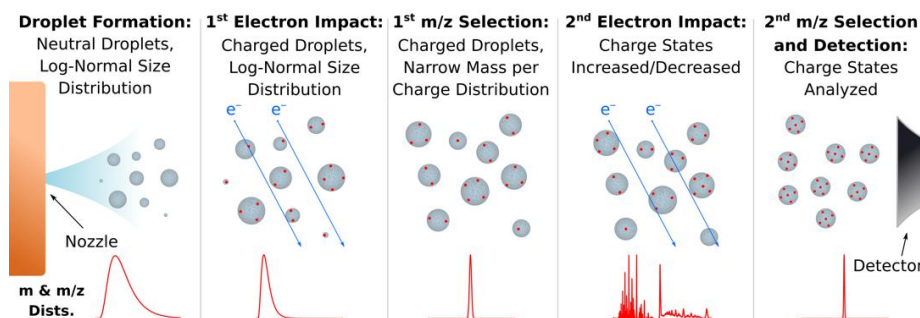


Figure 1: Schematic representation of the experimental steps involved in our measurements.

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CREATION AND DESTRUCTION OF CHEMICAL SPECIES IN LIQUIDS TREATED BY ATMOSPHERIC PRESSURE PLASMAS - FROM GAS PHASE CHEMISTRY TO BULK LIQUID

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Large number of recent studies are investigating operation of cold atmospheric pressure (CAP) plasmas in contact with liquids. This is a continuation of the research related to biomedical applications where CAP has proved its excellent potential for sterilization and cleaning of both living tissues and inorganic materials from pathogenic microorganisms [1]. Applications of CAP use chemically reactive gaseous environment that contain reactive oxygen and nitrogen species such as •OH, •NO, H₂O₂, NO₂-, NO₃-, HNO₃ etc. These species produced in CAP, which is in contact with the liquid, can penetrate and react with molecules in a bulk liquid modifying its physical and chemical properties [2]. This interaction goes through the interfacial region located between the gaseous plasma and a bulk liquid where many important processes involving short-lived species occur. As a result, the treated liquid is activated or, in case of polluted water, decontaminated by plasma [3]. However, in many cases specific plasma-liquid interactions behind the achieved positive results are elusive due to unknown processes in the interfacial region.

Here we will present results of laboratory-scale studies using different plasma source configurations that aim to induce decontamination of polluted water and/or activation of clean water. In all experiments we used plasma jets powered by a continuous kHz signals with the liquid samples placed below the jets. We will show results of detailed plasma diagnostics as well as measurements of basic physico-chemical properties of treated samples in order to reveal the influence of the plasma treatment. Special attention will be devoted to the possibility of assessing reactions in the interfacial region in order to clarify important reactions which exist in the particular treatments.

Acknowledgement: This work is supported by projects ON171037 and III41011 of the MESTD, Republic of Serbia.

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RESONANT INELASTIC X-RAY SCATTERING ON CHLOROMETHANES

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Resonant inelastic x-ray scattering (RIXS) in the vicinity of a deep ionization edge offers important information about unoccupied states in matter, allowing, in principle, to reconstruct XANES spectra with a ‘‘subnatural’’ energy resolution (HERFD) [1]. It also allows to separate contributions of doubly excited and shake-up/off states from the predominant ionization continuum which cannot be done reliably by using a normal photoabsorption spectrum [2]. A variant of the RIXS method (HEROS) offers an opportunity to obtain a full photoabsorption spectrum by using the monochromatic photon beam [3]. This is welcomed possibility for intense light sources where the target is destroyed in a single pulse of light. Another advantage of RIXS method is its sensitivity to the dynamics via the inherent timing powered by the core hole decay. In this case, a delay knob is turned by detuning photon impact energy from the resonance, having an effect of reducing the time between the absorption and emission event. The ‘‘core-hole-clock’’ method works fine in the fs time range, limited by the lifetime of the selected core hole and is often used to study molecular dissociation and fast charge transfer at the solid state interfaces [4].

We will illustrate the above properties of RIXS for the case of Xe L₃ electron photoexcitation by looking at the L α ₁ emission spectrum. The ‘‘core-hole-clock’’ method will be presented for chloromethanes where the molecular dissociation triggered by the σ^* excitation competes with the fluorescence decay of the Cl K-hole.

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ELASTIC ELECTRON SCATTERING ON MOLECULES IN THE GAS PHASE AT MEDIUM ENERGY RANGE

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We have investigated elastic electron scattering in the medium energy range from molecules in the gas phase. The measurements of the elastic differential cross sections (DCS) are performed with a cross electron-target beam apparatus UGRA [1], settled in the Institute of physics in Belgrade. Relative DCSs were normalized to the absolute scale according to points obtained using a relative flow technique. For this procedure Ar was used as a reference gas [2]. We have performed measurements for elastic electron scattering on different molecules, including anaesthetics [3], and absolute DCS for elastic electron scattering on sevoflurane at 300 eV is presented in Figure 1.

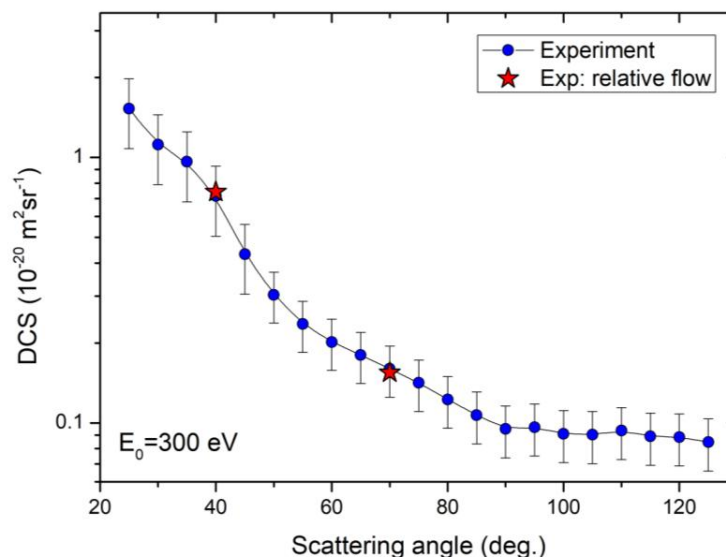


Figure 1: Angular dependence of the DCSs for elastic electron scattering from sevoflurane at 300 eV. Circles represent absolute experimental differential cross sections; stars represent absolute values obtained by relative flow method.

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EXCITED-STATE LIFETIME MEASUREMENTS OF STORED CHROMOPHORE IONS

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Molecular chromophores in photoactive proteins have attracted immense attention not only because of their crucial role for the functioning of living organisms, but also for studying elementary processes, such as photoisomerization, light-driven electron transfer and charge separation. We resolve ultrafast photo-initiated dynamics of molecular systems in the gas phase by performing femtosecond pump-probe measurements at the electrostatic ion storage ring Saphira at Aarhus University [1]. Specifically, we use the time-resolved action on the μs -ms time scale to determine the molecular response, and the well-defined femtosecond pump-probe delay to extract the short lifetimes. The method is highly advantageous for mapping the excited-state decay as well as the ground-state recovery, and is applicable for negative as well as positive ions.

In this contribution, we present how the two-pulse technique is used to study the molecular dynamics of biochromophores. We show that the fast photoisomerization of protonated Schiff-base retinal in visual rhodopsin is related to almost unhindered (low barrier) excited-state isomerization [2]. In green fluorescent proteins, on the other hand, isomerization is prevented in the excited state by the rigid protein environment. In the gas phase, the excited-state lifetime is found to be temperature dependent due to the presence of excited-state energy barriers and varies from ps to ns [3].

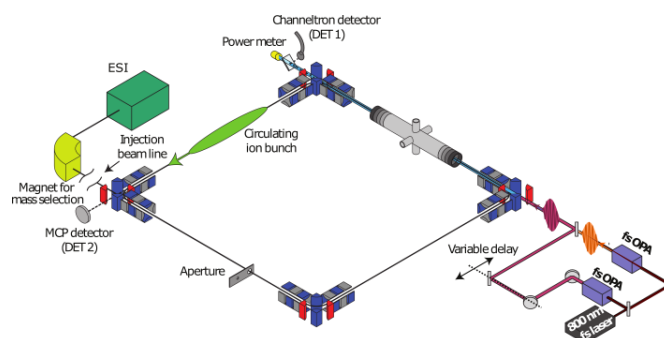


Figure 1: Schematic of the electrostatic ion storage ring Saphira at Aarhus University.

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Automated discovery of chemical reaction mechanisms

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A computational method is proposed in this talk for use in discovering reaction mechanisms and solving the kinetics in reactive systems. The method does not rely on either chemical intuition or assumed a priori mechanisms, and it works in a fully automated fashion. It has two components: accelerated MD simulations and a post-processing algorithm based on Graph Theory, that selects suitable transition state (TS) guess structures.

The method has been successfully employed to study the photolysis of small organic molecules, simulation of mass spectrometry experiments, the ozonolysis of α -pinene, van der Waals structures, and even in the study the cobalt-catalyzed hydroformylation of ethylene.

LASER INDUCED FABRICATION OF 3D NANOPARTICLE STRUCTURES BY FEMTOSECOND LASER RADIATION

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Glasses composed by noble metal nanoparticles attract significant attention due to the unique optical properties that they express in the near UV and visible spectral range. These are related to the high values of the extinction cross section and nonlinear optical characteristics.

In this work, we present results on the response of noble metal-doped borosilicate glass to laser radiation with femtosecond pulse duration. Furthermore, the ability of laser irradiation to induce modification of the optical properties of borosilicate glasses doped with gold and silver ions is used. The samples are obtained by conventional melt quenching method and noble metal concentration up to 10 wt%. Morphology and optical changes of the glass samples induced by femtosecond laser pulses within a wide range of parameters are investigated. The femtosecond processing is done by regenerative Ti:Sapphire amplified laser system that generates laser pulses with 35 fs duration, at repetition rate of 1 kHz.

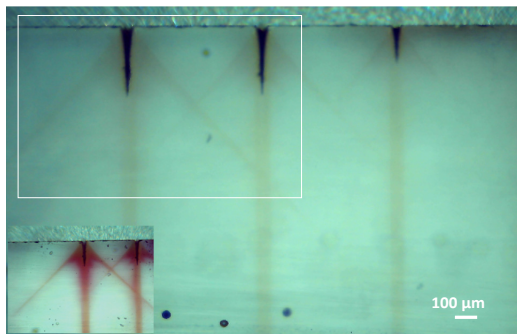


Figure 1. Cross section of ablation lines fabricated in glass with 1 wt % Au

of noble metal in the glass at concentrations up to 10 wt% (the maximal used) does not influence the ablation rate.

Two regimes of laser-matter interactions are considered: i) at laser fluences below the ablation threshold, and ii) above the ablation threshold. Defects associated with formation of color centers in the material, below the permanent modification threshold, are observed (Figure 1). Their properties as a function of the processing conditions are discussed. When permanent morphology modifications are induced, different micro- and nanostructures are observed depending on the laser parameters. The morphology of the ablated area is studied as function of the laser fluence and number of the applied pulses. It is found that the presence

Novel effects related to laser irradiation refraction by the formed ablated grooves are demonstrated. A special attention is dedicated to estimation of the main ablation parameters, the structure and composition modifications in the laser effected zones.

ULTRAFAST LASER FABRICATION OF ION MICROTRAPS VIA MULTIPHOTON PROCESSING TECHNOLOGIES

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Recent advances in high resolution laser processing technologies offer cheap and reliable tools for experimental activities. Some prominent emerging technologies are represented by multiphoton laser 3D printing. Among these, laser direct writing via two-photon polymerization, also known as 3D lithography (3DL) has a rapidly growing presence in the scientific community. The main features of this technology are reduced costs, ease of use and resolution significantly below the diffraction limit.

In our work, we have developed and characterized a series of microstructures fabricated via 3DL for various applications: diffractive optical elements for beam modulation, micro-optics and phase masks such as Fresnel lenses and spiral phase plates, integrated optical components such as waveguides, Bragg couplers, splitters, etc, scaffolds for bone tissue engineering, micro-targets for laser driven particle acceleration and others.

We have approached our activity from two different angles: design and material. From the design point of view, we developed specific laser paths to improve both the geometrical features of microstructures, and fabrication time efficiency. This path takes into account laser spiking, volume pixel overlap, energy dose deposited in the photoresist, etc. From the material point of view, we have developed composite materials in order to improve microstructure functionality. More precisely, we have deposited various thin films on microstructures without affecting the geometry, and successfully dispersed superparamagnetic nanoparticles inside the photoresist.

Applications of 3D printed microstructures can be expanded to new domains such as micro-electromechanical systems, dielectric laser acceleration, compliant micromechanisms, ion microtraps and others. Multiphoton 3D printing techniques, combined with the development of high resolution photoresists that are responsive to external electric and magnetic fields, show great potential for designing microstructures for laser cooling and optical ion trapping.

ENERGETIC PROCESSING OF BIOMOLECULAR SYSTEMS

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Hypoxanthine is a purine derivate, similarly to adenine and guanine. It can be found in both DNA and RNA, because of adenine deamination, where it can have either a detrimental or an advantageous effect. Moreover, in its nucleoside form, named inosine, hypoxanthine plays some interesting roles in the central neural system and it has regulatory roles in hypertension and obesity. Because of its role intrinsically connected to multiple biological pathways, getting a better insight on this molecules behaviour upon irradiation is mandatory.

We have performed mass spectrometry studies using ion collisions in the gas phase on the isolated molecule, pure hypoxanthine clusters, and hydrated clusters. Especially, the clusters can mimic a simple environment, going more and more “complex and realistic” with the hydrated ones. After the collisions, the molecule is typically ionised, excited, and undergoes fragmentation, resembling what actually could happen in a biological environment undergoing a radiation damage. The fragmentation dynamics of the hypoxanthine was studied as a function of the chemical environment comparing the branching ratios of the fragmentation channels and looking for appearance of new pathways. In the case of the isolated molecule, we also performed multi-coincidental mass spectrometry. The obtained coincidence map (see Fig.1) was compared to the one obtained for adenine fragmentation [1-2]. The comparison aims to evaluate the degree of similarity among those purine derivatives, reinforcing hypoxanthine importance when considering radiation damage studies on DNA and RNA.

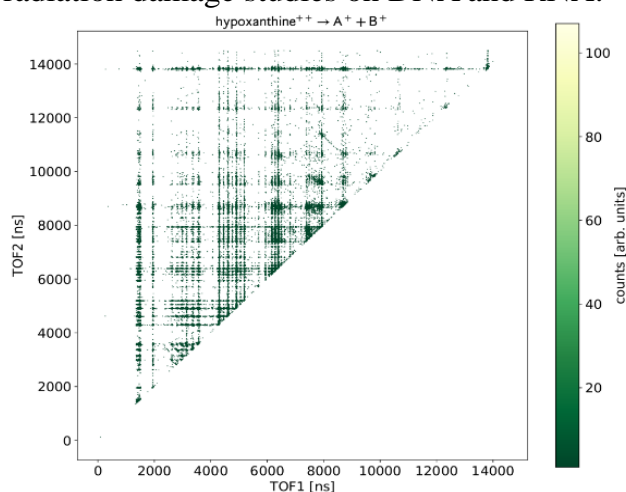


Figure 1: Ion-ion coincidence map for the fragmentation of hypoxanthine dication produced after the interaction with 90 keV O⁶⁺ ions.

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STABILITY AND IR SIGNATURES OF CARBONACEOUS MOLECULES

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Polycyclic Aromatic Hydrocarbons (PAHs) are a family of carbonaceous molecules formed by multiple fused aromatic rings. These molecules are essential to understand the global evolution of carbon and the energetic processes and reactions that occur in space.[1] Among them, the hydrogenation/dehydrogenation processes might lead to hydrogenated PAHs where an excess of hydrogen atoms is found.

The study of these hydrogenated PAHs is not trivial since there can exist billions of possible structures. In this sense, theoretical simple models that allow us to obtain the most stable structures without the need of performing costly calculations are very helpful especially when molecular dynamics approaches fail to overcome high-energy barriers.

We have extended our simple models developed for fullerenes[2-4] to study hydrogenated PAHs. The most stable structures have been obtained showing that the stability depends on the aromaticity of the substructure that remains after hydrogenation.[5] In addition, the computation of the theoretical IR spectra of selected isomers of hydrogenated PAHs has explained the different features observed in the 3 μ m region of different astronomical objects.[6]

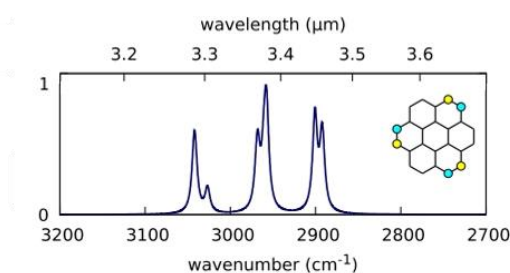


Figure 1: IR spectra of the most stable isomer of $C_{24}H_{12}X_6$ being X_n the number of additional H atoms

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MD STUDY ON REVERSIBLE FOLDING OF TETRAKISTRIAZOLE CATALYSTS AND THEIR BINDING WITH ANIONIC SUBSTRATES

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Asymmetric catalysis^[1] plays an essential role for the synthesis of enantiomerically pure compounds, which are key in the development of drugs, agricultural chemicals, flavours and fragrances, as well as certain advanced materials. Of especial interest is the eco-friendly metal-free approach, in particular anion-binding (AB) organocatalysis.^[2]

In this regard, the recently developed chiral AB organoreceptor **1a** offers a high flexibility and tunability to control the enantiomeric excess for challenging reactions upon binding via weak interactions with anion and cationic counterparts through eight hydrogen bonds (see Fig.1).^[3] However, to understand and optimize this process in the laboratory, theoretical approaches are necessary. In particular, molecular dynamics (MD) calculations and wave function analysis methods were applied to study these weakly interacting complex systems. The calculations confirm the helical structure of the tetrakistriazole catalyst and via correlation with the NMR experiments, allows us to quantify the binding strength and folding mechanism of the catalyst in the presence of the guest molecule.^[4]

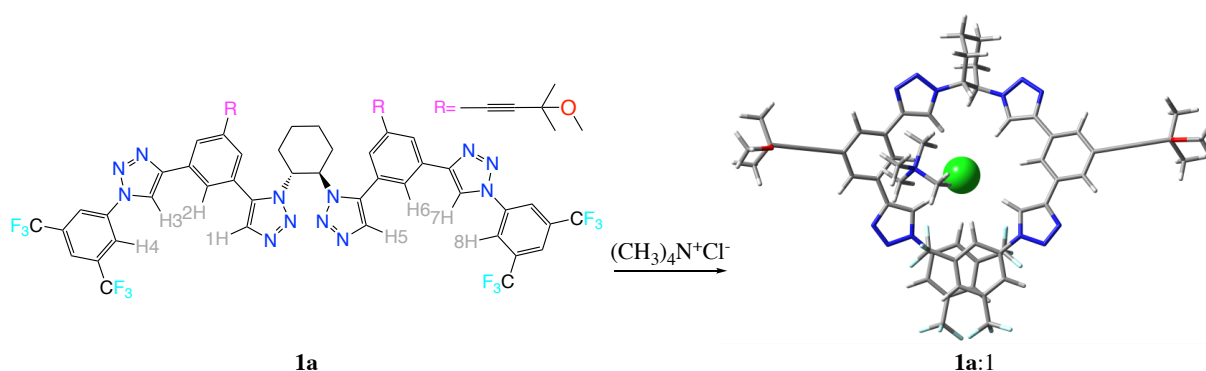


Figure 1: Tetrakistriazole catalyst **1a** and its **1a:1** complex with $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ guest.

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- [4] D. G. Piekarski, P. Steinforth, J. Bamberger, M. Gómez-Martínez, O. García Mancheño, *to be submitted*.

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Abstracts of posters

PHOTODISSOCIATION OF SOME MOLECULAR IONS OF ASTROPHYSICAL INTEREST

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Opacities of stellar atmospheres are caused by a huge number of radiative processes. As part of the development of more sophisticated stellar atmosphere models, we can further explore known processes and include all processes not previously discussed [1]. The average cross-section for the photodissociation and the corresponding spectral absorption coefficients of the molecular ions Li_2^+ , Na_2^+ , LiNa^+ , H_2^+ and HeH^+ are calculated for the wide region of temperatures and wavelengths ready for further use with a particular accent to the applications for astro plasma research and low temperature laboratory plasma research. The results for the average photodissociation cross-section on the example of the Na_2^+ molecular ion is illustrated by Fig. 1. The curves in this figure show the behavior of destruction cross-section as a function of wavelengths, for a wide range of temperatures T , which are relevant for modeling astrophysical plasmas [2] and low temperature laboratory plasma research created in gas discharges, where plasma conditions may be favorable for processes investigated here [3].

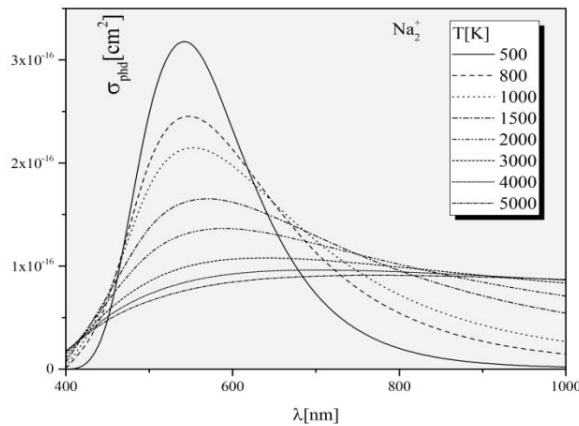


Figure 1: The averaged photodissociation cross-section of Na_2^+ molecular ion, as a function of λ and T .

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REACTIVE COLLISIONS OF ELECTRONS WITH MOLECULAR CATIONS: EFFECTS AND APPLICATION TO H_2^+ , BeH^+ AND THEIR ISOTOPOMERS

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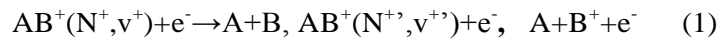
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Dominant elementary processes in numerous cold ionized gases are dissociative recombination (DR), elastic collisions (EC), vibrational excitation (VE) (inelastic collisions), vibrational de-excitation (VdE) (superelastic collisions), and dissociative excitation [1, 2]:



where N^+ / v^+ stand for the rotational/vibrational quantum numbers of the cation.

In this work, using a stepwise method based on Multichannel Quantum Defect Theory (MQDT), cross sections and rate coefficients have been obtained for reactions induced on H_2^+ [3] and BeH^+ [4] and their isotopomers.

The different mechanisms taken into account for H_2^+ and HD^+ , i.e. direct vs indirect and rotational vs non-rotational processes are presented in this work.

A set of vibrational cross sections and rate coefficients for BeD^+ [5] and BeT^+ [6] cations reactive collisions with electrons below to the ion dissociation threshold is provided.

The incident electron energy range is 10^{-3} - 2.7 eV and the electron temperature range is 100 - 5000 K. The study of the isotopomers of BeH^+ at low energy collisions shows that the Maxwell rate coefficients of these excited ions significantly depend on the initial vibrational level of the molecular ion.

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ORIGIN OF THE STRANGE ARRHENIUS BEHAVIOR OF COMPLEX-FORMING BIMOLECULAR REACTIONS

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There are a number of bimolecular reactions that possess U-shaped Arrhenius plot, where the activation energy changes from positive to negative. These fall into the general category of reactions that proceed over a van der Waals complex with a submerged ('negative energy') barrier. Most of the studied reactions were of the type $R + HX \rightarrow RH + X$, where $X = \text{Br, I, OH, CN}$ and R could be an alkyl radical. $\text{HBr} + \text{CH}_3 \rightarrow \text{Br} + \text{CH}_4$ is the prototype of this class of reactions.

In this work we report on quasiclassical trajectory calculations (QCT) performed to explore the detailed dynamics and kinetics of the reaction of $\text{HBr} + \text{CH}_3 \rightarrow \text{Br} + \text{CH}_4$ and to find the origin of the strongly nonlinear Arrhenius curve. In our calculations we used the global ab initio potential energy surface developed by Czakó [1]. The rate coefficients obtained with the QCT method match excellently those measured by Seakins et al. [2] by Nicovich et al. [3] and Seetula [2] (Fig 1). The role of the BrH-CH_3 van der Waals complex and the effect of the rotationally and vibrationally excitation of reactants will be discussed in the presentation.

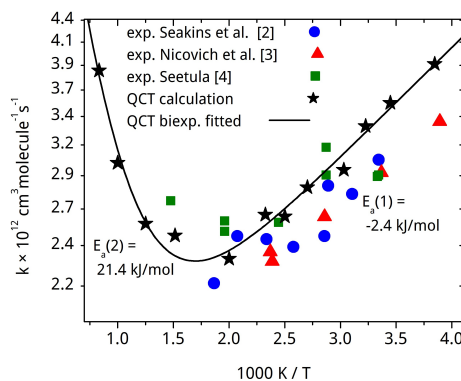


Figure 1: Calculated and experimental Arrhenius plots of the $\text{HBr} + \text{CH}_3 \rightarrow \text{Br} + \text{CH}_4$ reaction

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THE STABILITY OF DAMAGED CORONENE

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A collision of an atom or ion, at energies below about 1 keV, with a polycyclic aromatic hydrocarbon (PAH) molecule may lead to the direct loss of a single C atom from the molecular lattice. The fragments formed due to single-carbon knockout are highly reactive and were suggested as possible precursors for formation of larger molecules in space [1,2]. Yet, it is unclear whether PAH fragments formed after the knockout of a C atom can survive for beyond microseconds timescales, which is required for them to play a role in the chemistry of the interstellar medium. Hence, we have measured the spontaneous decay of hot PAH cations and their fragments at the DESIREE facility [3]. Namely, intact coronene Cor^+ ($\text{C}_{24}\text{H}_{12}^+$), as well as fragments formed by single C–, $(\text{Cor-CH}_x)^+$, and double C–loss, $(\text{Cor-C}_2\text{H}_x)^+$, possibly alongside one or several hydrogen atoms, formed by the collision with helium at a center-of-mass energy of about 100 eV. The spontaneous decay follows a t^p behavior, as depicted in figure 1, as the ions cool during the first few milliseconds of storage time. At later times, the ions are too cold to spontaneously fragment, but remain in the ring and can be monitored by dumping the ion beam onto one of the detectors for neutral fragments after a certain storage time. These measurements show that the fragments are indeed stable on long timescales (up to minutes).

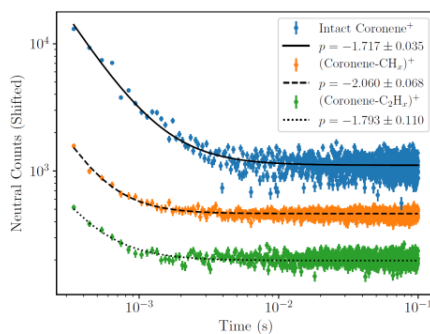


Figure 1: Neutral yield produced by intact coronene, Cor^+ (in blue), $(\text{Cor-CH}_x)^+$ (in orange) and $(\text{Cor-2CH}_x)^+$ (in green), as function of the storage time. The dashed lines are a fitting of the experimental data with a power-law function, t^p .

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MODELING ALKALI-CATION DIMERS IN HELIUM CLUSTERS

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Doped He droplets constitute an important environment as ultracold homogeneous matrices for spectroscopic studies. Alkali metal dopants have a series of interesting properties, *e.g.* neutral atoms attached to the surface of the droplet, forming eventually cold molecules, while charged dopants form solvation shells, related with the low mobility of the ions observed in experiments. So, investigations on the underlying intermolecular forces, and on the microscopic structures of alkali-cation-He complexes is essential.

A detailed theoretical investigation on intermolecular interactions of cationic alkali-dimers solvated in small He clusters will be presented [1,2]. In particular, interaction energies are obtained from CCSD(T)/CBS and MRCI+Q calculations, depending on the single- or multi-reference character of the systems under study, while the potential energy surfaces are constructed employing an interpolation technique within the Reproducing Kernel Hilbert Space (RKHS) method, and were used to evaluate the trimers' nuclear quantum effects. By analyzing the potential anisotropy and the spatial arrangement of the ground and excited vibrational states, we found that energetically the most stable conformer corresponds to linear arrangements for all complexes studied.

Further, we have looked into the behavior of higher-order species with more He atoms surrounding the cationic dopant. A simplified sum of the three-body *ab initio*-based potential approach is employed to describe the microsolvation of ground A_2^+ molecular ions (A=Li, Na, K, Cs, and Rb) in He clusters by analyzing the structural stability of clusters with up to six He atoms in comparison with interactions energies obtained from quantum chemistry methods. The optimized structures are analyzed in terms of their geometric features, confirming the dominance of ionic forces in driving the shape of the cluster, and their crucial role by changing the competitive strength of the cation-He interaction with respect to the He-He (pure solvent) network of interactions. Such interplay creates collocations, like the equilateral He₃ motifs at the two ends of each ionic dimer, that provides some initial information on solvation process at microscopic level.

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MD STUDY ON REVERSIBLE FOLDING OF TETRAKISTRIAZOLE CATALYSTS AND THEIR BINDING WITH ANIONIC SUBSTRATES

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Asymmetric catalysis^[1] plays an essential role for the synthesis of enantiomerically pure compounds, which are key in the development of drugs, agricultural chemicals, flavours and fragrances, as well as certain advanced materials. Of especial interest is the eco-friendly metal-free approach, in particular anion-binding (AB) organocatalysis.^[2]

In this regard, the recently developed chiral AB organoreceptor **1a** offers a high flexibility and tunability to control the enantiomeric excess for challenging reactions upon binding via weak interactions with anion and cationic counterparts through eight hydrogen bonds (see Fig.1).^[3] However, to understand and optimize this process in the laboratory, theoretical approaches are necessary. In particular, molecular dynamics (MD) calculations and wave function analysis methods were applied to study these weakly interacting complex systems. The calculations confirm the helical structure of the tetrakistriazole catalyst and via correlation with the NMR experiments, allows us to quantify the binding strength and folding mechanism of the catalyst in the presence of the guest molecule.^[4]

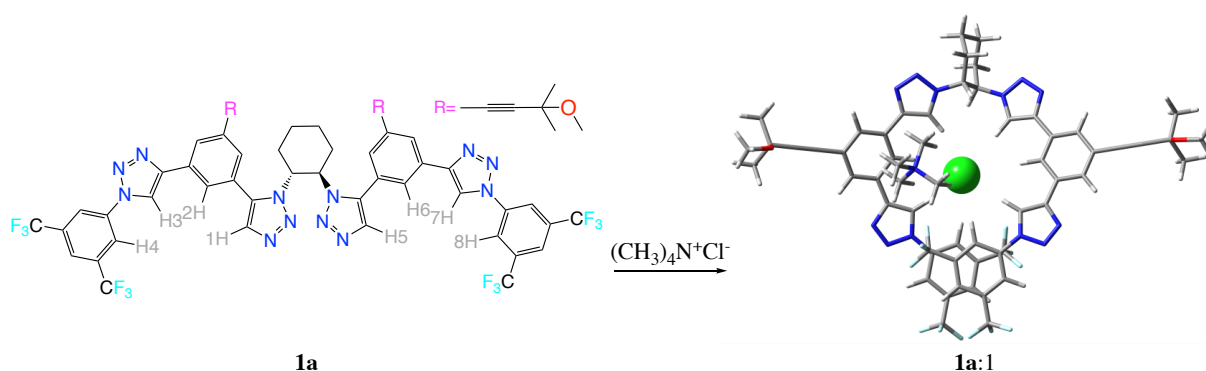


Figure 1: Tetrakistriazole catalyst **1a** and its **1a**:1 complex with $(\text{CH}_3)_4\text{N}^+\text{Cl}^-$ guest.

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Effects of ionizing radiations on the reactivity inside clusters of linear hydrocarbons: polymerization vs. cyclization

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Recently, 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 particle scale. Polycyclic Aromatic Hydrocarbons (PAHs) have been identified by Cassini's spectrometers. PAH and their clusters are important components in terrestrial soot formation and their presence in Titan's atmosphere can be considered as a nucleation agent, which triggers aerosol formation in the 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].

In order to understand the formation process of larger particles, we have studied collisions of low energy ions with loosely bound clusters of molecules. We aim to analyze either the fragmentation processes - which occur due to the transfer of energy and charge - and on the other hand, the complementary processes which lead to molecular growth and the formation of new, larger, covalently bound molecules. These processes are based on the energy transfer into the heavy particle system (nuclei). In the case of ion collisions, this can take place either by electronic excitation or by the direct knockout of an atom from the molecule. In the first case, the process ends up in longer time scale via coupling into vibrational motion degrees of freedom, while in the latter we obtain a prompt (fs) removal of atoms during the ion-molecule collision. By the knockout of an atom, highly reactive radicals and molecular species are formed which on very short time scales (\leq ps) react with their neighbor molecules in the cluster. When several atoms are kicked out along the ion trajectory in the cluster, large covalently bound systems can be formed.

We present results on cluster systems containing linear chain molecules like butane and butadiene. We will discuss the formation of ring structures and the path to aromatic molecules. The irradiation of hydrocarbons clusters using different radiation sources (electrons, ions and UV photons) allows to determine 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].

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SPECTROSCOPY AND DYNAMICS OF FLAVIN IONS IN THE GAS PHASE

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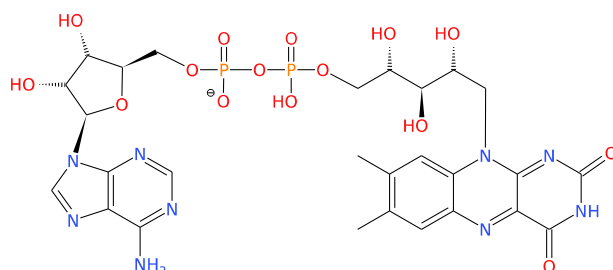


Figure 1: Structure of Flavin Adenine Dinucleotide mono-anion [FAD-H]⁻

The flavin family of biomolecules is built upon the tricyclic iso-alloxazine moiety. These ubiquitous chromophores perform a wide range of light-dependent reactions in proteins, where micro-environmental interactions may perturb their optical spectra. Flavins are also present in many foods and beverages, which has led to extensive research on the photochemical degradation of flavins in solution. Here there is a history of debate regarding which photoproducts are the result of purely intramolecular processes and which are solvent-assisted or more complex reactions photosensitized by flavins.

We are investigating the intrinsic photochemistry of flavin ions in the gas phase using multiple types of action spectroscopy. This work is elucidating the photoprocessing of flavins and is also revealing how the optical spectra of flavins in various charge and redox states are affected by micro-environmental perturbations. One emerging theme is that photo-induced intramolecular proton transfers between the iso-alloxazine moiety and the phosphoribityl sidechain are dominant processes in the gas phase [1,2]. The spectroscopy of fully oxidized flavins (structure shown in Figure 1) in the gas phase is found to closely resemble that in solution [1-3]. Other forms, such as where the iso-alloxazine is deprotonated, exhibit strong charge transfer character and sensitivity to micro-environmental perturbations [2].

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Gas-phase linear and cyclic dipeptides: a study of peptide bond formation and decomposition

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Synopsis: The peptide bond formation and decomposition is studied by photoelectron spectroscopy, time-of-flight mass spectrometry and photoelectron-photoion coincidence (PEPICO) spectroscopy in a series of isolated linear and cyclic-dipeptides. Interesting cyclization mechanisms are observed.

We have undertaken a study of the peptide bond formation and degradation on the simplest peptides, the cyclic (*c*) and linear (*l*) dipeptides in the gas phase, by photoionisation and ion collision experiments. In the poster, preliminary results on the study of *c*- and *l*- GlyGly, AlaAla, GlyPhe, GlyAla and of *l*-PheAla by mass spectrometry and PEPICO experiments are presented. These measurements show that the most important fragmentation channel is the loss of the OCHN (43 amu) moiety, with the resulting charge fragments at *m/z* 99 and 85 in *c*-AlaAla and *c*-GlyAla, respectively. The lighter fragments at *m/z* 44 (*c*-AlaAla) and 30 (*c*-GlyAla) become important for binding energies >12 eV and are likely related to sequential rearrangement and secondary fragmentation of larger fragments.

The mass spectra of the *l*- species show a common pattern of fragmentation, dominated by *m/z* peaks attributable to the cyclic structure. The parent ion and fragments attributable to the *l*- species, if present at all, diminishing with time.

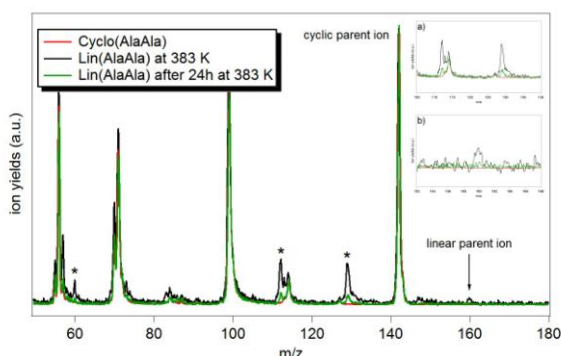


Figure 1. The mass spectra of *l*- (black curve) and *c*- (red curve) AlaAla at photon energy 21.22 eV. The *l*-AlaAla spectrum (green curve) after 24h at the same sublimation temperature clearly shows the disappearance of the parent ion and associated fragments (indicated by the *). Insets a) and b) show the *m/z* ranges 105-140 and 152-168, respectively.

These observations may suggest that cyclisation occurs at some stage of the experimental procedure [1,2,3], driven either by the temperature in the condensed phase or the ‘electrostatic forces’ in the

unstable zwitterion produced in the sublimation or the fast rearrangement of the highly reactive cation following ionisation. In the *l*-AlaAla molecule, for example, a careful characterisation of the mass spectrum as a function of the temperature (Figure 1) suggests a temperature induced cyclisation in the condensed phase, prior to sublimation. This hypothesis, in the case of *l*-PheAla molecule has been confirmed by IR measurements of the sample before and after sublimation (Figure 2).

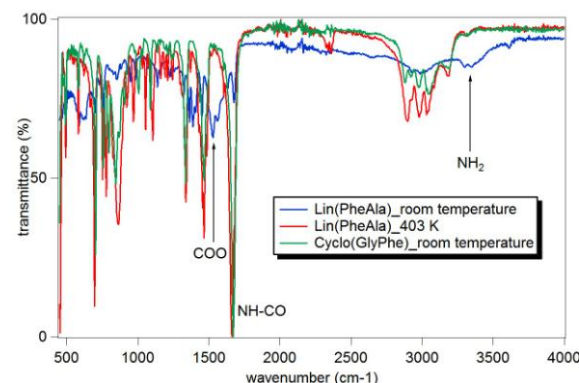


Figure 2. Comparison of the *l*-PheAla and *c*-GlyPhe IR spectra. The IR spectrum of *l*-PheAla at 403 K shows evidences of cyclisation: the high intensity of the NH-CO signal and the disappearance of the NH2 and COO signals.

Different samples, however, have shown different behaviours, suggesting that a complex and not easily predictable chemistry occurs. This sets a limit of feasibility for the study in the gas phase of polypeptides by thermal evaporation.

Acknowledgment: MAECI Italia-Svezia and Progetto Gruppi di Ricerca Regione Lazio, DESIR.

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DISSOCIATION DYNAMICS OF THE DIAMONDOID ADAMANTANE UPON PHOTOIONIZATION BY XUV FEMTOSECOND 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 C₁₀H₁₆. 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].

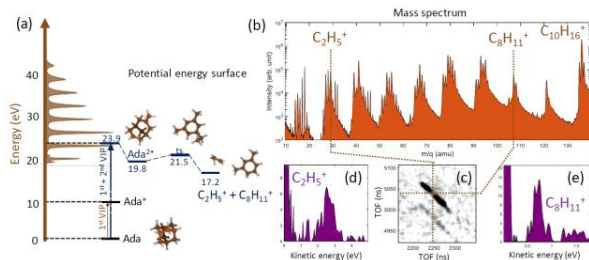


Figure 1. Example of experimental and theoretical

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 dissociation, 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, C₁₀H₁₆²⁺ → C₂H₅⁺ + C₈H₁₁⁺, is highlighted as an example.

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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 [4]. The photoions were detected by a velocity map imaging spectrometer [5] recording the mass spectrum and the ion momentum distribution on a single shot basis, allowing for the use of covariance analysis to

AB INITIO-BASED INTERACTIONS AND SPECTROSCOPIC CHARACTERIZATION OF AR CONTAINING CATIONIC SPECIES

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Theoretical-computational studies together with recent astronomical observations have shown that under extreme conditions in the interstellar medium (ISM), complexes of noble gases may be formed. Thus, as a first step, we present results from high level ab initio calculations to determine the intermolecular interactions in small Ar-containing cationic complexes, such as ArH^+ , ArHAr^+ and ArCN^+ , considering bent configurations. In particular, we carried out electronic structure calculations at MP2, CCSD(T), CCSD(T)-F12 and MRCI+Q levels of theory with large basis sets and extrapolating energies at their complete basis limit. Our results on the potential interactions are analysed and their comparison with previous data available in the literature are discussed. We found that for ArH^+ the MRCI+Q energies are in very good agreement with recently reported potential curves, for the ArHAr^+ the available data in the literature are limited only at linear geometries of the system, and for the ArCN^+ complex only equilibrium geometry and frequencies from quadratic force field potentials have been reported. In turn, we performed reduced bound states calculations in order to characterize spectroscopic properties, such as binding energies and vibrational constants. Our findings suggest the need of further calculations, involving full dimensional and/or multireference treatments, in order to provide information that may serve to indicate their possible detection under specific thermodynamic conditions.

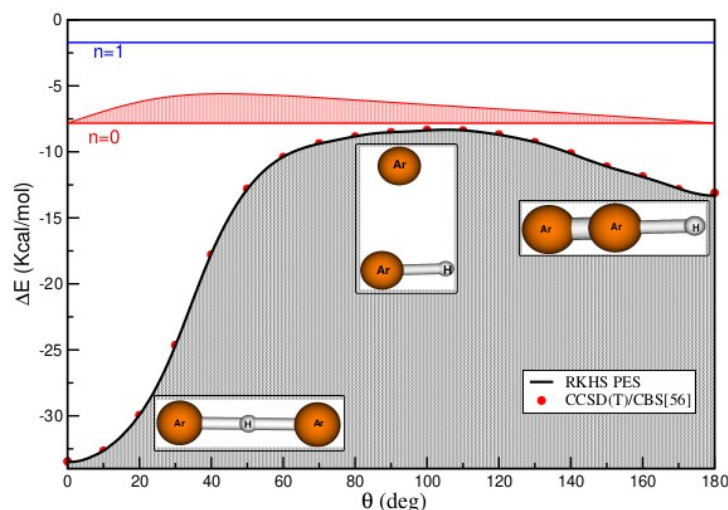


Figure 1: Angular distributions of calculated bound states of Ar_2H^+ using the 2D RKHS PES.

References

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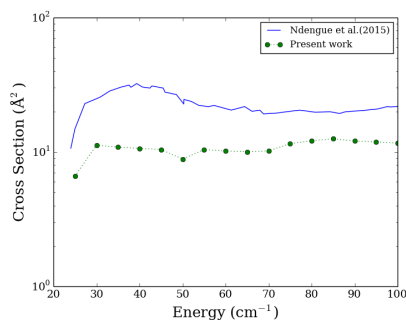
COLLISIONAL EXCITATION IN CO-CO AND H₂O+H₂ SYSTEMS.

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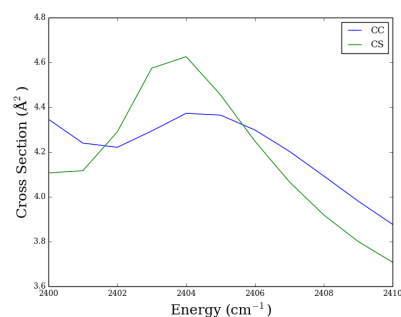
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Accurate determination of the physical conditions in comets and protoplanetary environments can be inferred from the modeling of molecular spectra. However, the full exploitation of molecular spectra requires to go beyond the local thermodynamic equilibrium (LTE) approach and hence requires radiative and collisional properties of the molecular species. Here, we present new scattering calculations for the rotational excitation in CO-CO and H₂O+H₂ collisional system using a non-reactive quantum scattering code MOLSCAT [1].

CO-CO calculation were performed using coupled-channel methods within the coupled states approximation, using the four-dimensional potential energy surface calculated of Vissers et al. [2]. Collisional rate coefficients are provided for rotational levels up to $j = 10$ and for temperatures up to 150K. The new results are compared to the partially converged results of Ndengué et. al. [3] and significant differences are found, especially for the dominant transitions. For the H₂O+H₂ system calculation were also performed using coupled-channel methods within the coupled states approximation, using the adiabatically reduced dimensional potential of Scribano et. al. [4]. Calculations with this potential shows good agreement with converged full 5D results, with a considerable gain in CPU time. Using this potential, we extend collisional data calculated by Daniel et. al. [5] to rotational states with j up to 17 and to temperatures up to 2000K.



Comparison of cross-section for transition of CO from level 00 to level 22



Comparison of cross-section for Close-Coupling and Coupled-state method for H₂O transition from level 15₀₁₅ to level 14₁₁₄

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A NEW 5D POTENTIAL ENERGY SURFACE FOR THE $\text{H}_3\text{O}^+ - \text{H}_2$ COLLISIONAL SYSTEM

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Hydronium cations (H_3O^+) have been detected in dense and diffuse interstellar medium (ISM), in both ortho- and para-state [1]. It was also shown that the H_3O^+ cation is one of the backbones of oxygen and water chemistry in the ISM. While the spectroscopy of the hydronium cation was intensively investigated in last decades [2], the processes of its collision with interstellar atoms and molecules are poorly studied [3].

The aim of our work is to study the collisional excitation and de-excitation of H_3O^+ in collisions with H_2 molecules, the dominant collisional partner in the interstellar medium. In order to model the collision dynamics and calculate the corresponding cross sections and rate coefficients, it is first necessary to determine the interaction potential (the so-called potential energy surface, PES) of the $\text{H}_3\text{O}^+ - \text{H}_2$ complex (see Fig.1). The PES calculations were performed using the explicitly correlated CCSD(T)-F12 method along with the AVTZ basis set. There were calculated 3000 random angular orientations totally at $R = 4-30$ a.u. radial distances. The *ab initio* potential was fitted by analytical functions. The RMS of the fit is always below 1% of the isotropic potential and equals 0.2 cm^{-1} at 5.5 a.u. radial distance, where the isotropic potential is the most attractive (608 cm^{-1}), while at 5 a.u. (see the right plot of Fig. 1) it equals 0.7 cm^{-1} .

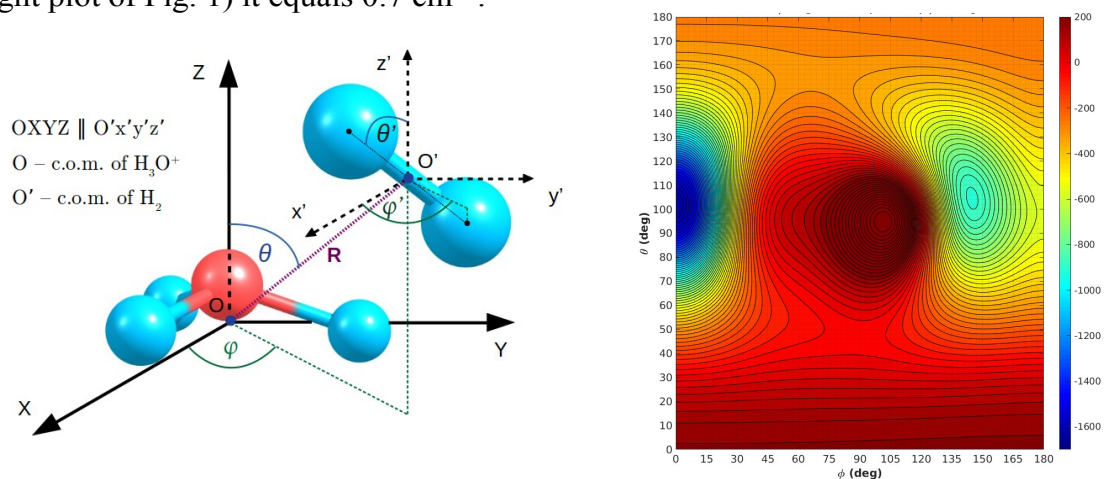


Figure 1: The $\text{H}_3\text{O}^+ - \text{H}_2$ coordinate system (left) and the θ vs. ϕ contour plot of the PES (right).

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INTERMOLECULAR POTENTIAL ENERGY SURFACES FOR DIPHENYLCHLOROARSINE AND WATER

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The description of intermolecular interactions between chemical warfare agents (CWAs) and water will lead to understanding of the neutralization process of chemical warfare agents dumped into the Baltic Sea after the World War II. One of the possible ways of neutralization process is a hydrolysis and therefore understanding of specific intermolecular interactions between CWAs and water is crucial for getting the deeper insight into the reactivity of this compound.

We present results of our work on the diphenylchloroarsine (DA)-water interactions. In particular, the fitted analytical form of intermolecular Potential Energy Surface for DA and water obtained from symmetry-adapted perturbation theory including dispersion energies from time-dependent density functional calculations SAPT(DFT)[1] calculations supported by AutoPES[2] package is presented. Additionally, the full conformational analysis for DA is performed in order to include the influence of all the conformational diversity on the mutual water-DA interactions and therefore for its possible neutralization mechanism.

This work was supported by National Science Centre, Poland, under research project no. 2017/25/B/ST4/02662

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REACTIVITY OF STATE-SELECTED IONS PROBED WITH SYNCHROTRON RADIATION

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Reactivity of ions plays an important role in various environments in the production, growth and destruction of ions. Depending on the processes leading to the creation and transformation of ions (electron impact, photoionization, reaction, dissociation of multiply-charged ions with large recoil energy, turbulence, shocks, ...) and the location where it occurs (planetary ionosphere, interstellar medium, ...), ions are produced in ground- and excited states and with variable kinetic energy.

This is why our team has been developing and operating for years an experimental setup called CERISES designed for the measurement of the reactivity (absolute reaction cross sections) of both cations [1-4] and anions [5], with a specific focus on effects on reaction dynamics of both the ion excitation and/or kinetic energy, which makes this setup an unique instrument. Photoionisation with VUV radiation (6-40 eV) from the DESIRS beamline at SOLEIL associated with the TPEPICO technique is used for the production of the state-selected cations.

The ions studied are simple cations such as CO₂⁺ [1], O₂⁺ or O⁺ [3] produced by ionization or dissociative ionization of stable molecules (CO₂, O₂). The recent development of a molecular beam has enabled the energy dependent production of ionized radicals, such as CH₃⁺ [2], C₂H₅⁺, or ionic clusters A_n⁺ produced by the photoionization of neutral radicals (CH₃[•], C₂H₅[•]) or clusters (A_n) respectively. Interestingly for the future, the combination of these methods enables the production of isomeric ions whose reactivity can be compared, such as in the recent study of the reactions of CH₃CN⁺ and CH₂CNH⁺ with C₂H₄ by Poláček *et al* [4]. Finally, dissociative electron attachment on BrCN and BrC₃N is used to prepare anions such as CN⁻ or C₃N⁻ [5] belonging to the series of cyano-polyne anions whose growth by reaction has been discussed [6] in the context of the surprisingly large amounts of anions observed in the Titan ionosphere.

CERISES is installed either at the Institut de Chimie Physique or at SOLEIL, the french synchrotron, and is open to external users through an association with SOLEIL. Hence, several groups in Europe have taken the opportunity to study ion reactivity in collaboration with our team, among which, recently, M. Poláček & J. Žabka (J. Heyrovsky Inst., Prague), D. Ascenzi *et al* (Univ. of Trento), W. Geppert *et al* (Univ. of Stockholm), E.-L. Zins *et al* & M. Bertin (Sorbonne Univ., Paris), J. Lemaire *et al* (ICP, Univ. Paris-Saclay). Results of ion reactivity obtained with CERISES complement experiments or calculations realized in their laboratories.

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QUANTUM CONTROL OF THE SPIN-ORBIT INTERACTION USING THE AUTLER-TOWNES EFFECT

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The spin-orbit interaction (between electronic spin and orbital angular momenta) in an atom or molecule can cause mixing of electronic states of different spin multiplicity, where the degree of mixing depends on the strength of SO interaction, as well as the energy separation between the interacting states. On the other hand, strong electromagnetic fields lead to shifts in the atomic/molecular energy levels due to the Autler-Townes (AT) effect [1]. Thus, as shown theoretically [2], control of SO interaction can be realized by using resonant or non-resonant laser fields.

In this work [3] we demonstrate quantum control of the SO interaction via the AT effect in a molecular system using cw optical fields. We show that the enhancement of the SO interaction between a pair of weakly interacting singlet-triplet rovibrational levels in Li_2 , e. g. $G^1\Pi_g(v=12, J=21, f) - 1^3\Sigma_g^-(v=1, N=21, f)$, initially separated by 750 MHz, depends on the Rabi frequency (laser power) of the control field. This increase is observed experimentally as a change in the spin character of the individual components of the perturbed pair.

To model theoretically the experimental results we follow the theoretical framework introduced in [2] using the standard density matrix formalism [4]. We obtain an excellent agreement between numerical calculations and experimental data and show that we were able to enhance the singlet character of the predominantly triplet state from 13% to 28%.

Our proof-of-concept demonstration can be extended to experiments with stronger control fields, especially since the control laser does not need to be resonant with a populated ground state level. This control scheme can also be used for controlling photochemical reactions and intersystem crossings by means of optical fields, to investigate the role of electron spin in excited state reactive collisions, as well as in the preparation of optical spin switches.

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NEGATIVE ION CREATION IN GAS-PHASE ION-MOLECULE COLLISIONS IN THE SOLAR WIND ENERGY REGION

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Collisions between positive ions and molecular targets is an essential process in several areas of physics, biology, and chemistry. Negative-ion formation in such collisions is scarcely studied. However, we found recently that this process is a general process in ion-molecule collisions at impact energies of a few keV [1-4]. This impact energy range is typical for solar wind ions, which implies that anions can be formed in cometary and planetary atmospheres. Water molecules are the main constituent of biological tissues and are prominently present in the atmosphere of comets, moons and planets. Recently, anion and cation emission following water dissociation was studied for 6.6-keV $^{16}\text{O}^+ + \text{H}_2\text{O}$ collisions [3-4]. Absolute cross sections for the emission of all positively and negatively charged fragments, differential in both energy and observation angle, were measured. A striking feature is that anions and cations are emitted with similar energy and angular distributions, with a nearly constant ratio of about 1:100 for H^- to H^+ . Model calculations were performed at different levels of complexity. Four-body scattering simulations reproduce the measured fragment distributions if adequate kinetic energy release of the target is taken into account. Providing even further insight into the underlying processes, predictions of a thermodynamic model [5] indicate that transfer ionization at small impact parameters is the dominant mechanism for H^+ creation. The present findings confirm our earlier observation that in molecular fragmentation induced by slow singly-charged ions, the charge states of the emitted hydrogen fragments follow a simple statistical distribution independent of the way they are formed. This indicates that anions are commonly created by ion impact. Anions may significantly influence the chemical composition of the surrounding media due their ability to be attached to molecules.

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HYBRID ELECTROSTATIC ION BEAM TRAP (HEIBT): DESIGN, SIMULATION AND FABRICATION FOR COLD CATION-ANION INTERACTION

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Ion reactions with neutral and other ionic species and their interaction with light are at the foundation of chemical sciences. Furthermore, cold gaseous ion chemistry plays an important role in many interstellar, planetary and other partially ionized environments.[1,2] Few experiments have been constructed using ion storage rings to understand such a cold reactions. [3,4].

The electrostatic ion beam trap (EIBT) allows trapping an ion beam between two electrostatic mirrors. Thus it has been proved to be extremely valuable research tool in many research areas including molecular dynamics, spectroscopy, mass spectrometry, lifetime measurement of metastable species and ion collective dynamics.[5] Here we present a hybrid EIBT (HEIBT) design that relies on the development of a “dichroic” electrostatic mirror—allowing for example reflecting a fast anionic beam, while transmitting a cation beam with minimal focusing.

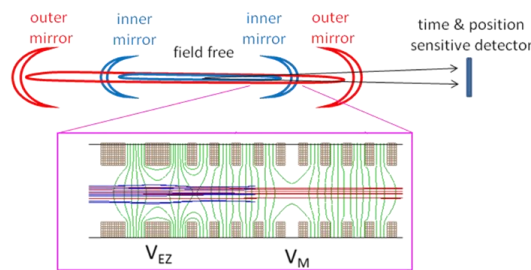


Figure 1. Schematic of the HEIBT showing simultaneous trapping of a merged cation and anion beam (top) as well as simulated cation and anion trajectories through the dichroic HEIBT mirror (bottom).

Figure 1 shows the schematic of HEIBT, consists two simultaneously trapped, which are merged in a central field free region. The inner HEIBT mirrors trap the 2.1 keV F^- beam, while transmitting the 4.2 keV F_2^+ beam, which is trapped between the outer HEIBT mirrors [6]. All the components of the experimental setup have been fabricated. Now we are assembling and testing them one by one. We anticipate first test result in few months.

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PHOTOSTABILITY OF NEW BORON-DIPYRROMETHENE DERIVATIVES

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The present study is devoted to the description of photophysical properties and photodegradation of new boron-dipyrromethene (BODIPY) derivatives obtained for the biomedical applications such as bacteria photoinactivation. In order to fully characterize the obtained molecules, the full computational chemistry study of their ground state and excited state properties has been performed. Additionally, the influence of the intermolecular interactions for their absorption and emission has been analyzed. The theoretical data fully support experimental outcomes. The exposition to the UV light has been found first to cause the decrease of the most intensive absorption band and the appearance of the hypsochromically shifted band of similar intensity. On the basis of the computational study, this effect has been assigned to the deiodization of the BODIPY dyes. After the longer exposition to the UV light, the photodegradation of the unknown mechanism has occurred leading to the disappearance of the intensive absorption bands and emerging the small intensity signals in the blue-shifted range of the spectrum. Since the most intensive bands in original dyes are ascribed to the molecular core bearing BF_2 moiety, this result can be attributed to the significant cleavage of BF_2 ring.

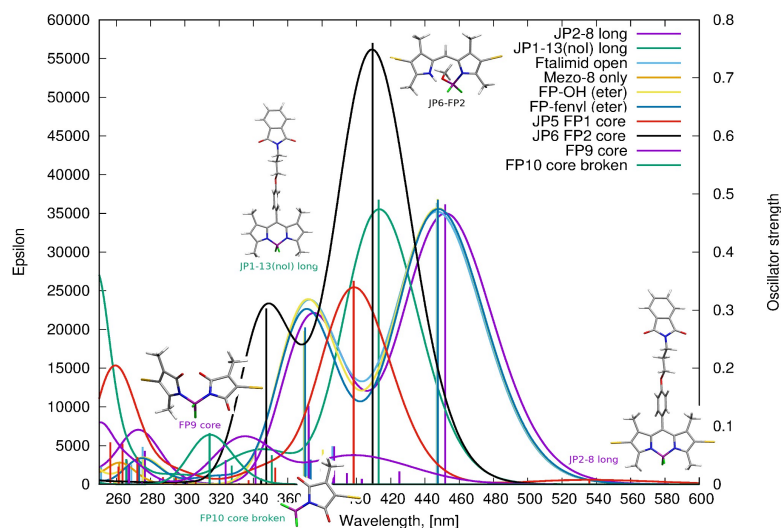


Figure 1: Photodegradation mechanism of the BODIPY dye with the N-phthalimide substituent

A LIQUID CRUCIBLE MODEL FOR AGGREGATION OF PHENYLACETYLENE IN THE GAS PHASE

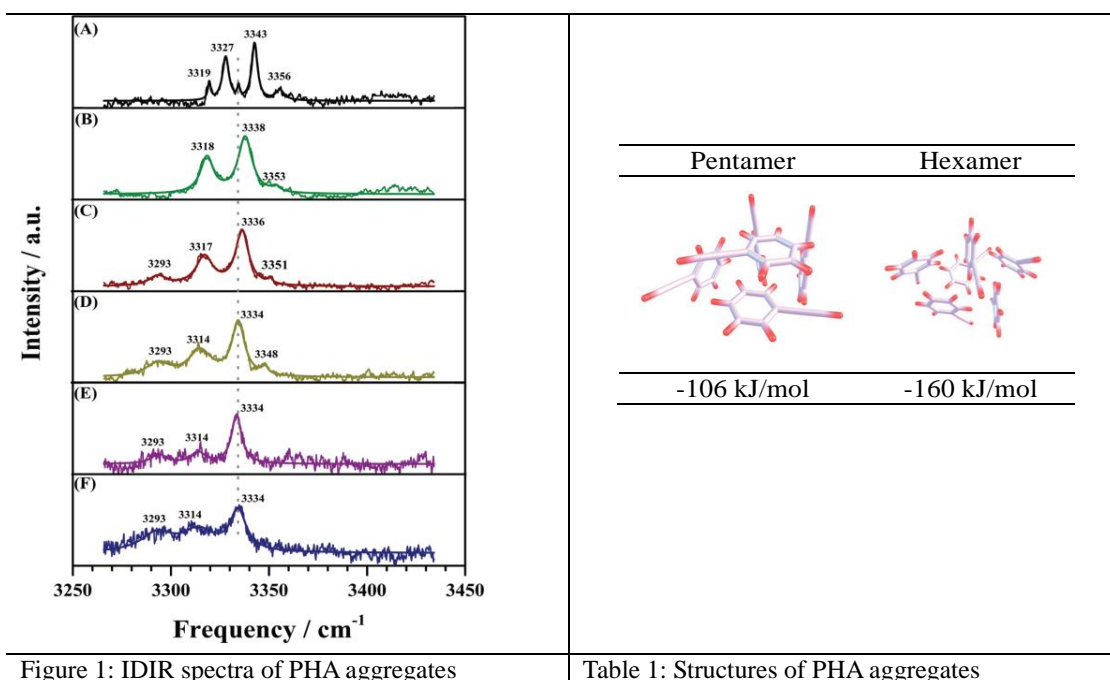
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Three polymorphic forms of phenylacetylene crystal structures have been reported using an in situ cryo-crystallographic technique.[1-3] The aggregation of phenylacetylene up to six monomer units has been studied in the gas phase.

The aggregation behaviour of phenylacetylene in the gas phase is fundamentally different from benzene, phenol and aniline vis-a-vis their crystal structures. Three known polymorphic crystals can be reconciled by the formation of supramolecular synthons with acetylenic C–H··· π , which is preferred over energetically favored aromatic C–H··· π interactions. Furthermore, by analysis of the IR spectra and computational tools, the small (phenylacetylene)_n [n = 3–6] clusters, the structures incorporating aromatic C–H··· π interactions, can be foreseen as liquid-like aggregates, which under varied conditions lead to the formation of multiple polymorphs.



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HIGH RESOLUTION SPECTROSCOPY ON ATOMS AND MOLECULES

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We report our results of the project in which the goal is to develop equipment for the laser frequency stabilisation with high accuracy. Ultraprecision optical frequency standards are required for optical fiber communications, quantum information technologies, metrology astrophysics and proofs of fundamental physical laws. We are aiming to design, and to produce frequency standards for stabilisation of blue and violet lasers based on the absorption cells filled with Te¹³⁰ isotope molecules, which have absorption spectra in a range of 300-500 nm. Since the development of Te standard is complicated, we started our investigations with well known lines of Rb atoms [1] and I₂ molecules [2]. They have absorption lines in spectral region of Ti-Sapphire laser and sufficient concentrations of atoms and molecules at room temperatures.

We have all equipment for high resolution spectroscopy measurements in our Institute. Narrow bandwidth (<100kHz) Ti Sapphire laser 750-900 nm with frequency doubling unit for 380-450 nm. Frequency Comb coupled to Rb Atomic Clock and with possibility to couple to Braunschweig frequency standard (14 digit accuracy). In our glassblower workshop we have possibility to manufacture quartz cells filled with mixtures of rare gas at different pressures and pure elements like: Rb I and Te.

The technique of saturated absorption spectroscopy is used to improve the resolution beyond the Doppler limit. [3] Firstly, we test our method on Rb cells with different buffer gas pressures. Then, Iodine cells were investigated. And now we can report on the first results from measurements on Te cells. We also present the experimental set up where the doubled frequency of Ti-Sapphire laser is used for saturation absorption measurements on Te molecular lines, while the fundamental laser beam is merged with a beam from the frequency comb. In this manner, the absolute wavelength is determined from quantum beat measurements..

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Acknowledgement

This work was supported by Effective Collaboration Grant between University of Latvia and Thorlabs Inc.

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DESIREE: THE DOUBLE ELECTROSTATIC ION-RING EXPERIMENT

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DESIREE [1] is a double electrostatic storage ring for keV beams of positive and negative atomic and molecular ions located at Stockholm University and funded as a National Infrastructure by the Swedish Research Council. The storage rings are contained in a double-walled cryogenic vacuum vessel and kept at a temperature of about 13 K. This results in a very low residual gas density of a few thousand hydrogen molecules per cm³, which in turn allows for very long storage times and thereby measurements of very long (several minutes) intrinsic lifetimes in atomic [2] and molecular [3] ions. We present the facility and recent results of metal cluster relaxation [4-6] as well as the first results of mutual neutralization between positive and negative ions stored in the two rings of DESIREE [7].

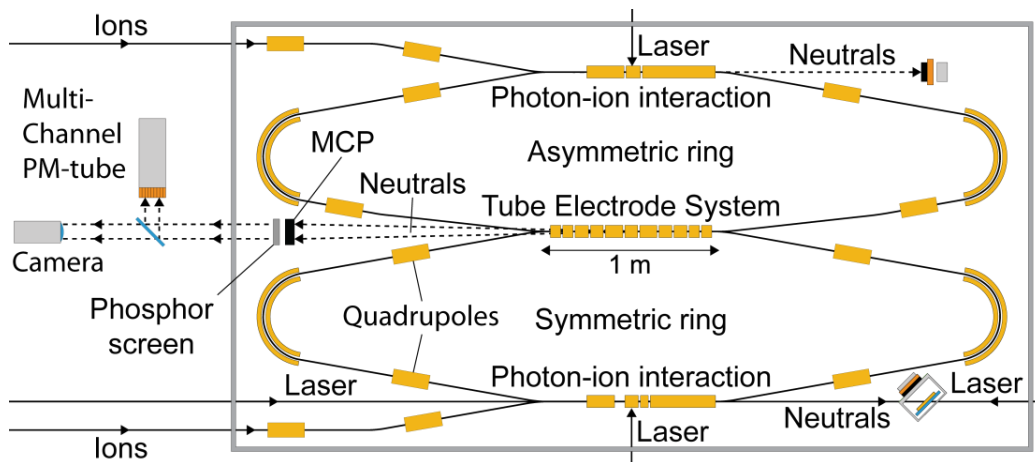


Figure 1: Schematic of the DESIREE rings.

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SPONTANEOUS DECAYS OF SMALL CARBON CLUSTER DIANIONS C_n^{2-} ($n = 7-11$)

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The existence and survival of small molecular dianions may sensitively depend on the electron tunneling probability through the so-called Repulsive Coulomb Barrier (RCB) potential [1-2]. Small carbon clusters dianions, C_n^{2-} ($n > 6$), have been demonstrated to survive on microsecond timescales in mass spectrometry experiments [3-5]. Here, we study the spontaneous decay of such ro-vibrationally hot systems in new time domains using the cryogenically cooled ion-beam storage-ring, DESIREE.

In these experiments, we monitor the production of C_n^- via vibrational autodetachment (VAD), $C_n^{2-} \rightarrow C_n^- + e^-$ as a function of storage time. We find that the decays follow power-law dependencies (see the example in Fig. 1), where the clusters containing an even number of carbon atoms decay slower compared to those with an odd number of carbon atoms. The experimental results are in good agreement with those from model calculations of VAD rates, where we use a detailed balance approach and include tunneling as a key ingredient.

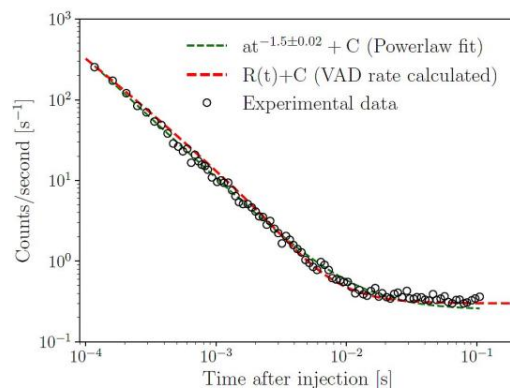


Figure 1: The cooling of C_8^{2-} via electron auto detachment ($C_8^{2-} \rightarrow C_8^- + e^-$). The red dotted line is the calculated VAD decay rate and the blue dotted line is a power-law fit to the experimental data

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PHOTOLYSIS-INDUCED SCRAMBLING LEADING TO DEUTERIUM STORAGE IN PAHS

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We investigate the possible role of UV processing of polycyclic aromatic hydrocarbons (PAHs) as mechanism towards deuterium storage in the interstellar medium [1]. We performed a spectroscopic study of various isotopologues of deuterium-enriched, protonated anthracene and phenanthrene ions to study the fragmentation behaviour following photo excitation. IR spectra and fragmentation patterns were recorded using infrared multiple photon dissociation (IRMPD) spectroscopy in a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FTICR MS) with the Free-Electron Laser for Infrared eXperiments, FELIX. The photofragmentation mass spectra reveal loss of only H atoms and no loss of any D atom from singly deuterated PAH ions, $[D\text{-PAH}]^+$. The singly hydrogenated perdeuterated counterparts $[H\text{-PAD}]^+$ exhibit a similarly strong preference for D-atom loss but with a small H-loss contribution. Upon comparison with density functional theory (DFT) calculations, the absence of deuterium loss in singly deuterated PAH ions is attributed to a scrambling mechanism following excitation, in which H and D atoms can move along the perimeter of the molecule before dissociation occurs (see example in Fig.1). The higher mobility and dissociate rate for H atoms greatly increases the chance for the H atom to end up at an aliphatic site and dissociate. The D atom in turn ends up at a strongly bound aromatic site, shielding it from dissociation.

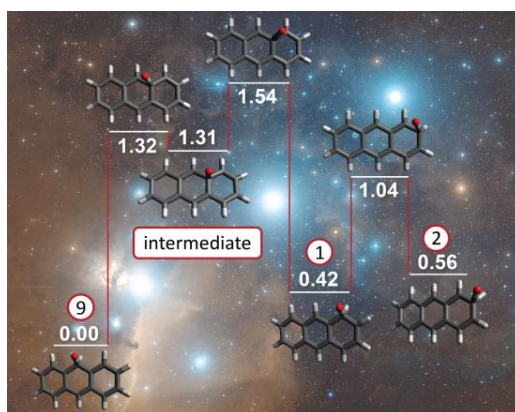


Figure 1: Energy (eV) level diagram for D migration (red) in $[H\text{-C}_{14}\text{D}_{10}]^+$

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ESTIMATION OF THE PRESSURE DEPENDENCE OF RATE CONSTANTS

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The effect of pressure on the rate constant of gas reactions is very important, specially for combustion studies. In particular, the pressure dependence of the termolecular reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ reaction is one of the main sources of error in hydrogen combustion modelling [1].

We have proposed a molecular reactor program, MReaDy (Multi-process Reaction Dynamics) [2] to model the overall hydrogen combustion process integrating the equations of motion in a global PES (gPES) surface built from PESs corresponding to each of the most important elementary reactions present in the system. We have adapted this program to study the above referred reaction.

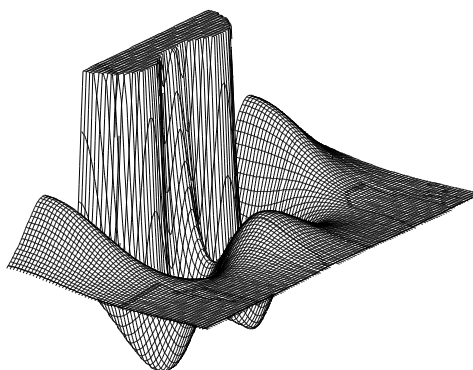


Figure 1: Three-dimensional view of a hydrogen atom around an equilibrium oxygen molecule.

We start with hydrogen atoms and oxygen molecules. By collision they form excited HO_2^* radicals whose time evolution is followed all along. When an excited HO_2^* radical is formed, the H atom stays trapped by collinear and perpendicular barriers and needs to find a way to dissociate, see Figure 1, for a view of the HO_2 potential [3]. This gives origin to long-lived species that may experiment several collisions before dissociation or stabilization.

By counting, as a function of time, the number of the excited HO_2^* radicals that are stabilised by collisions, we can calculate the formation rate of stable HO_2 radicals at different pressures and temperatures.

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REACTIVE ELECTRON/MOLECULE COLLISIONS: FROM MECHANISMS TO NEW STATE-TO-STATE CROSS SECTIONS AND RATE COEFFICIENTS

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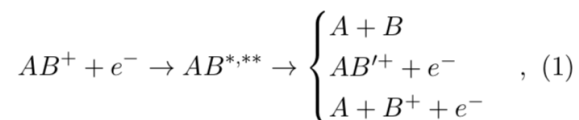
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Electron-impact dissociative recombination, ro-vibrational (de)excitation and dissociative excitation of molecular cations are at the heart of molecular reactivity in the cold ionised media [1], being major molecular ion destruction reactions, and producing often atomic species in metastable states, un-accessible through optical excitation.



These processes involve super-excited molecular states undergoing pre-dissociation and autoionization, having thus strong resonant character. We use methods based on Multichannel Quantum Defect Theory and R-Matrix Theory [2], capable to account for the strong mixing between ionization and dissociative channels, open - direct mechanism - and closed - indirect mechanism, via capture into prominent Rydberg resonances [3] correlating to the ground and excited ionic states, and for rotational effects. These features will be illustrated for several cations of high astrophysical and planetary relevance such as H_2^+ [3], CO^+ [4], SH^+ [5], CH^+ [2,6], N_2^+ [7], ArH^+ [8], $CH_2NH_2^+$ [9]. Results for reactions similar to (1) but involving the neutral target CO_2 [10] will be also displayed. Comparisons with other existing theoretical and experimental results will be given.

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HYPERFINE STRUCTURE OF ELECTRONICALLY EXCITED STATES OF BIALCALINE MOLECULES

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High efficiency production, confinement and manipulation of cold molecules need the precise knowledge of the energy structure of the molecule. In this respect a considerable amount of work has been done regarding the structure of alkali metal dimers. Due to the complexity of the problem both from theoretical and experimental point of view little is known about the hyperfine structure of molecular states, and this is particularly true for the excited states.

Our recent motivation to perform molecular hyperfine structure calculations was the possibility to shield short-range dynamics between colliding particles of an ultracold gas with an optical field which is controlled by the details of their long-range interactions. Using an asymptotic model [1], we determine the long-range interaction between an excited and a ground-state alkali-metal atom, including their hyperfine structure. Several excited electronic states, tending to the second excited dissociation limit of the KCs molecule, are found repulsive at large interatomic distances, being thus promising candidates for optical shielding [2]. The results reveal that the hyperfine coupling scheme is essentially different compared to the case of the first excited dissociation limit [1].

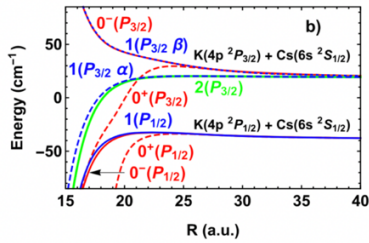


Fig. 1 Hund's case c potential energy curves (PEC) of excited molecular states of KCs molecule.

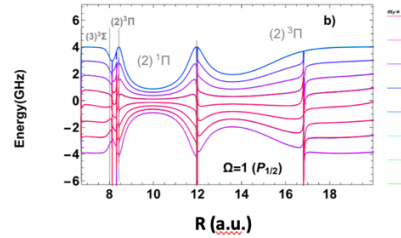


Fig. 2 ³⁹K¹³³Cs difference PECs for $\Omega = 2$ Hund's case c state. The colors correspond to different values of the molecular $|\Omega_f|$ quantum number.

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AN INVESTIGATION OF PHOTO-DOUBLE IONIZATION IN BENZENE

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Benzene is an archetypal example of an aromatic hydrocarbon, a molecule with a planar arrangement in which the π molecular orbitals overlap and the electrons are completely delocalised. Aromatic hydrocarbons have shown some interesting properties, like superconductivity at high temperatures [1] and excellent thermal properties. Hydrocarbons play a central role in biological process, astronomical process and combustion.

This experiment was conducted at the GasPhase Beamline at Elettra, using the multi-coincidence end-station, designed for angle resolved and electron-electron coincidence experiments in a versatile multichannel configuration. In this study, liquid benzene was placed in a test tube outside the vacuum chamber, freeze-pump-thawed to remove gases, and then admitted to the interaction region via a gas line. The fully linearly polarized photon beam was delivered in a spot of about 200 μm diameter to the interaction region. The 10 hemispherical electron energy analysers hosted in the multi-coincidence experimental chamber are mounted on two independent frames, holding respectively 3 and 7 analysers separated from each other by 30 degrees. In the present experiments, the two frames were placed in the plane perpendicular to the photon beam and used to detect electron coincidences from the photo-double ionization (PDI) process. A detailed description of the apparatus and the related methods of the acquisition of the triple differential cross section (TDCS) and its analysis are described in [2].

At a resonance photon energy, it has been proposed [3] that, benzene allows the formation of a two-electron pseudo-particle, which has been likened to a ‘Cooper pair’. This is only possible when the C-C distance matches the de Broglie wavelength. In this model the electron pair leaving the molecule breaks up and the electrons are emitted back-to-back. Previous results [4] have shown small enhancements in the single electron photoelectron spectra at angles of 70 and 138 degrees. However, other experiments [5] do not support this interpretation and the mechanism responsible for the enhancement is an open question. The present results, which are differential in angle and energy for each of the two electrons, provide new information on the PDI process.

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Electronic Structure Changes of Gas-Phase PAH Cations as Induced by Successive Atomic H Attachment

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Gas-phase polycyclic aromatic hydrocarbon (PAH) cations can be efficiently hydrogenated by exposing to thermal H atoms. Successive attachment of hydrogen atoms to a PAH leads to a stepwise transition from the planar aromatic molecule towards a puckered aliphatic system in geometry and reduction between HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) gap in electronic structure. The changes in HOMO-LUMO gap is clearly shown by numerical results from density functional theory(DFT). By combining synchrotron radiation and mass spectrometry, partial ion yields as a function of photon energy is recorded. The X-ray absorption spectroscopy(XAS) is confirmed by time-dependent density functional theory (TDDFT) with different functional to present the influence caused by hydrogen-attachment.

PHOTOFRAGMENTATION OF BARE AND NANO-SOLVATED LEUCINE-ENKEPHALINE-H⁺ PEPTIDE ION

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We report a computational study on the photo-induced fragmentation of protonated leucine-enkephalin (Leu-Enk-H⁺: YGGFL). Tandem mass (MS²) spectrum of nano-solvated [Leu-Enk-H·3H₂O]⁺ obtained after peptide ion exposition to vacuum UV light (VUV) shows an incredible influence of the water molecules into the backbone fragmentation pattern, while the peptide structure is not changed. This suggests that new fragmentation pathways are open up (for the same photon energy) by the presence of the water molecules.

With the aim of investigating the origin of these reactivity differences between the gas-phase ion and the nano-solvated one we have carried out a TD-DFT study (CAM-B3LYP/cc-pVDZ). In detail, we have characterized the lowest-lying (< 7.5eV) excited states nature, energies and intensities at the Frank-Condon region for both ions. Furthermore, in a subsequent step their relaxation towards the first excited state potential energy surface has been mapped. Finally, we have explored the bond cleavage mechanism for those S₁ minima most prone to yield the experimentally observed fragments.

Furthermore, we have compared the results of the excited state electronic structure calculations with molecular dynamics simulations of the unimolecular fragmentation on the ground state potential energy surface (PES) in order to determine whether fragmentation, after VUV absorption, takes place at the ground state via mobile proton model or there is a different mechanism leading to fragmentation at the excited state PES.

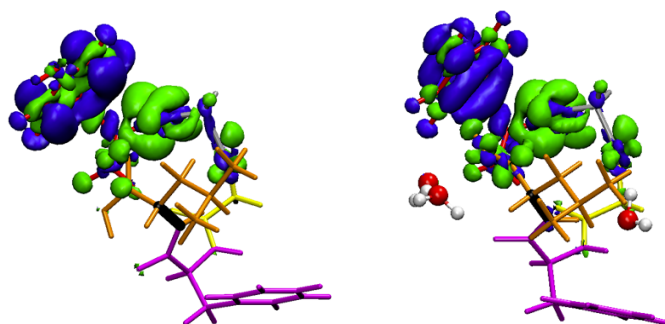


Figure 1: Excited state density differences for bare [Leu-Enk-H]⁺ and nano-solvated [Leu-Enk-H·3H₂O]⁺ computed at CAM-B3LYP/cc-pVDZ level of theory.

	Tuesday February 18	Wednesday February 19	Thursday February 20	Friday February 21
8:15-9:00	Registration			
9:00-9:30	Opening A. Domaracka & H. Zettergren	Chair: M. Łabuda Janina Kopyra	Chair: S. Indrajith Jacopo Chiarinelli 9:00 9:20	Chair: T. Kirova Elisabeth Gruber
9:30-10:00	Steen B. Nielsen	Charles Desfrancois	Ewa Erdmann 9:20 9:40	Emilio Martínez-Núñez
10:00-10:30	Xavier Urbain	Einar Uggerud	Piero Ferrari 9:40 10:00 Punnakayathil Najeeb 10:00 10:20	Ekaterina Iordanova
10:30-11:00	Coffee break	Coffee break	Coffee break	Coffee break
11:00-11:30	Chair: A. Domaracka Christine Joblin	Chair: S. Tosic Jelena Tamulienė	WG1 Kick off Meeting Manuel Alcamí	Chair: M. Castrovilli Bogdan Calin 11:00 11:20
11:30-12:00	Alessandra Candian	Béla Sulik	Patrick Rousseau	Chiara Nicolafrancesco 11:20 11:40
12:00-12:30	Elisabetta Micelotta	Sylvain Maclot	Aurora Ponzi	Paula Pla 11:40 12:00 Dariusz Piekarski 12:00 12:20
12:30-13:00	Amanda Steber	Alicia Palacios	Jaroslav Kocisek	Closing remarks
13:00-13:30	Lunch	Lunch	Lunch	Lunch
13:30-14:30				
14:30-15:00	WG2 Kick off Meeting Paola Bolognesi	WG1 Kick off Meeting Thomas Schlathöler	Chair: L. Avaldi Michael Gatchell	End of Conference
15:00-15:30	Lorenzo Avaldi	Holger Kreckel	Nikola Skoro	
15:30-16:00	Aleksandar Milosavljević	Oded Heber	Matjaz Zitnik	
16:00-16:30	Daniela Ascenzi	Eduardo Carrascosa	Jelena Maljkovic	
16:30-17:00	Coffee break	Coffee break		
17:00-17:30	POSTER SESSION	POSTER SESSION	POSTER SESSION Laboratory visit	
17:30-18:00	Cocktail	Management Committee Meeting		
18:00-18:30			19:00-21:30 Conference diner Café Mancel	