

# Book of abstracts DEEP-GAS 2022



COST Action CA18212

**MD-GAS**

Molecular Dynamics  
in the GAS phase

## About MD-GAS

The main aim of the MD-GAS COST Action (CA18212) is to develop a new physical and chemical toolbox to significantly advance the understanding of:

- Gas phase molecular dynamics induced in interactions between molecules or clusters and photons, electrons, or heavy particles.
- Its consequences for a broad range of applications in e.g. astrochemical and atmospheric sciences, and molecular radiation damage.

<https://mdgas.eu/>

[info@mdgas.eu](mailto:info@mdgas.eu)

## DEEP-GAS 2022

Among fundamental atomic and molecular physics, chemical physics, and applications in radiation therapy and -damage on the nanoscale, astrochemistry, astrobiology, atmospheric science, and climate research interests of the working groups 2 and 3, the meeting will host a session specifically focused on systems of biological interest as well as a session fully dedicated to Early Career Investigators, an essential tradition of our MD-GAS meetings!

<https://deep-gas.sciencesconf.org/>

## DEEP-GAS Committee

Sergio Díaz-Tendero (WG 3 Leader)

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Lucas Schwob (WG 2 Co-Leader)

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Ana Isabel Lozano (WG 3 Co-Leader)

Henning Zettergren (Action Chair)

Alicja Domaracka (Action Vice Chair)

# 1 Schedule

	<b>Tuesday 4th</b>	<b>Wednesday 5th</b>	<b>Thursday 6th</b>	<b>Friday 7th</b>
<b>09:00</b>	Registration			
<b>09:45</b>	Welcome			
<b>10:00</b>	Raimund Feifel (Chair: Paola Bolognesi)	Rebecca Boll (Chair: Sylvain Maclot)	Lorenzo Avaldi (Chair: Henning Zettergren)	Patrick Španěl (Chair: Rita Prosmitti)
<b>10:45</b>	Coffee break	Coffee break	Coffee break	Coffee break
<b>11:15</b>	Chair: Cristina Sanz-Sanz	Chair: Alicia Palacios	Chair: Lucas Schwob	Chair: Sergio Díaz-Tendero
	Vincent Wanie	Laura Rego	Marc Simon	Mathieu Gisselbrecht
<b>11:45</b>	Janina Kopyra	Eva Muchova	Teodora Kirova	Yoni Toker
<b>12:15</b>	João Ameixa	Rocío Borrego	Aleksandar Milosavljević	Károly Tőkési
<b>12:45</b>	Francisco Fernández-Villora	Eva Vos	Juliette Leroux	Nicolina Pop
<b>13:05</b>	<b>LUNCH</b>	<b>LUNCH</b>	<b>LUNCH</b>	<b>LUNCH</b>
<b>14:30</b>	Chair: Ana Lozano	Chair: Marta Łabuda	Chair: Wojciech Gawelda	
	Mathias Poline	Felix Jacob	Ori Licht	
<b>14:50</b>	Carlos Guerra	Demeter Tzeli	Branislav Milovanović	
<b>15:10</b>	Bart Oostenrijk	Vincenzo Laporta	Dariusz Kedziera	
<b>15:30</b>	Olga Lushchikova	Oded Heber	Sándor Demes	
<b>15:50</b>	Coffee break	Poster Session + TAPAS served	Coffee break	
<b>16:00</b>	Chair: Darek Piekarski		Chair: Ewa Erdmann	
<b>16:30</b>	Patrik Hedvall		Arno Ehresmann	
<b>17:00</b>	Fábris Kossoski		Judit Montes de Oca	
<b>17:20</b>	Jacopo Chiaranelli		Jelena Maljkovic	
<b>17:40</b>	Josef Filgas			
<b>18:00</b>	Daniel González		Roof Top Evening	
<b>18:20</b>				

## 2 Abstracts - Talks

### 2.1 Tuesday 4<sup>th</sup>

09:00 - 09:45	Registration
09:45 - 10:00	Welcome (Sala de Conferencias - Módulo 00) <b>Chair: Paola Bolognesi</b>
10:00 - 10:45	Raimund Feifel, University of Gothenburg - <i>Multiple electrons on the fly</i>
10:45 - 11:15	Coffee break (Sala polivalente - faculty of science) <b>Chair: Cristina Sanz-Sanz</b>
11:15 - 11:45	Vincent Wanie, Deutsches Elektronen-Synchrotron, Hamburg - <i>Ultrafast electron and chiral dynamics in bio-relevant molecules initiated by UV and XUV light pulses</i>
11:45 - 12:15	Janina Kopyra, Faculty of Sciences, Siedlce University - <i>Electron driven fragmentation of biologically relevant molecules</i>
12:15 - 12:45	João Ameixa, University of Potsdam, University NOVA of Lisbon - <i>Gas-phase studies on electron attachment processes in model systems of mitochondrial electron carrier molecules</i>
12:45 - 13:05	Francisco Fernández, Universidad Autónoma de Madrid, IMDEA Nanociencia - <i>Time-Resolved Images of Intramolecular Charge Transfer in Organic Molecules</i>
13:05 - 14:30	Lunch break



## Multiple electrons on the fly

R. Feifel

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Multiple electrons might be emitted by an atom or molecule upon the absorption of a single or several photons of sufficiently high energy. To obtain a complete picture, multi-particle correlation spectroscopy based on a magnetic bottle [1] is now frequently used in several laboratories in combination with different light sources. I will start off with an introduction to this method, followed by highlights of what our current research activities on electron-correlation in atomic and molecular species are about. I will then present a brand-new high power laser facility called Attohallen [2] which we managed to establish at the University of Gothenburg during the pandemic and describe what we aim to achieve at this infrastructure. I will also give examples for what else might come up at this facility in the not-too-distant future, which is open for external users, in hope of inspiring and attracting many more ideas as well as stimulating mutual and fruitful collaborative efforts of experiment and theory.

### Acknowledgements

Financial support by the University of Gothenburg, the Knut and Alice Wallenberg Foundation, Sweden, the Olle Engkvist Foundation, Sweden, and the Swedish Research Council is greatly acknowledged.

### References

[1] J.H.D. Eland and R. Feifel, *Double Photoionisation Spectra of Molecules*, 1<sup>st</sup> edition, Oxford University Press 2017.

[2] <https://www.gu.se/en/news/new-laser-lab-makes-it-possible-to-capture-the-movement-of-electrons>

## Ultrafast electron and chiral dynamics in bio-relevant molecules initiated by UV and XUV light pulses

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Since the first experimental demonstration of attosecond light pulses twenty years ago, attosecond spectroscopy has opened up the possibility of observing electron dynamics in matter at their natural timescale ranging from few-femtoseconds to tens of attoseconds [1]. In bio-relevant molecules, this has notably provided a route to investigate the phenomenon of electron-driven charge migration for which, following photoexcitation, the charge density travels rapidly along the molecular structure [2]. In this contribution, I will report our most recent works devoted to the investigation of charge migration and its applications to manipulate the outcome of photochemical and photophysical processes. In a first experiment, we studied the ultrafast dynamics of the nucleobase adenine upon attosecond XUV photoionization. We identified a photoprotection scheme based on charge-directed reactivity that allowed us to produce unfragmented -doubly ionized- molecules [3]. In the second experiment, we exploited our new light source delivering few-femtosecond UV pulses [4,5] in order to photoexcite below the ionization threshold and trigger electronic dynamics in neutral methyl-lactate, a chiral derivative of lactic acid. We used time-resolved photoelectron circular dichroism (TR-PECD) [6] to image electronic coherences driving charge migration and disclose their impact on the molecular chiral response, allowing for an ultrafast chiroptical switching effect where the amplitude and direction of the photoelectron current generated by PECD can be controlled [7].

### References

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- [6] V. Blanchet *et al.*, “Ultrafast relaxation investigated by photoelectron circular dichroism: an isomeric comparison of camphor and fenchone,” *Physical Chemistry Chemical Physics* **23**, 25612 (2021)
- [7] V. Wanie *et al.*, “Ultrafast chiroptical switching in UV-excited molecules,” (Submitted, 2022).

## Electron driven fragmentation of biologically relevant molecules

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Reactions induced by electron attachment to molecules, including those which result in molecular fragmentation, play a crucial role in many fundamental areas such as technology, chemical engineering, atmosphere, radiation physics and chemistry [1].

It is by now well known that low energy electrons (LEEs), the secondary species of the interaction of ionizing radiation with matter, efficiently produce structural and chemical modifications of many complex biostructures. These secondary electrons with a kinetic energy distribution up to 20 eV [2] are created in numbers of  $5 \times 10^4$  per 1 MeV of primary energy deposited [3] that makes them the most abundant radiolytic species. Hence, reactions induced by LEEs are considered as important and decisive steps in the description of radiation damage to biological systems. Recent two decades or so have witnessed a remarkable growth in the scientific interest in studying the low energy electron attachment to biologically relevant molecules. Among them, a wealth of experimental and theoretical data have been devoted to nucleic acids and their building-blocks [4,5] 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 halo-substituted derivatives of DNA/RNA sub-units. Such chemical compounds are frequently used as biological modifiers able to alter the response to radiation. Nowadays radiation-induced responses are being increasingly used for modification of radiotherapy based on advancements in radiobiology. Therefore, it is needed to determine the behaviour of these halo-substituted sub-units under reductive conditions. In particular, during the talk emphasis will be placed on the description of the formation of the transient negative ions and the comparison of the fragmentation patterns of halogenated biologically relevant compounds.

### Acknowledgements

JK acknowledges support by the statutory activity subsidy (No 25/20/B) from the Polish Ministry of Science and Higher Education.

### References

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## Gas-phase studies on electron attachment processes in model systems of mitochondrial electron carrier molecules

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In this progress report, I will review our most recent studies on the gas-phase molecular dynamics initiated by electron attachment to model compounds for the coenzyme Q<sub>10</sub> (CoQ<sub>10</sub>, fig 1), in which we have combined experimental techniques such as mass spectrometry with quantum chemistry computational methods and elastic electron scattering calculations. In the first part, I will introduce how the mechanisms underlying the stabilization of the intact CoQ<sub>0</sub> molecular anion differ from those proposed not only for larger coenzymes Q<sub>n</sub> (n=1, 2, 4), but also for the electrophore *para*-benzoquinone (*p*-BQ, fig 1). [2] The second part will be focused on the subsequent dissociation of the temporary negative ions formed upon electron attachment to coenzyme Q<sub>0</sub> (CoQ<sub>0</sub>, fig 1) and 2,3-dimethoxy-5-methylhydroquinone (CoQ<sub>0</sub>H<sub>2</sub>, fig 1). [1]

These studies advance the knowledge on how low-energy electrons attach to building blocks of mitochondrial electron carriers. This impacts on a broad range of fields beyond chemical and molecular physics, namely biochemistry and life sciences.

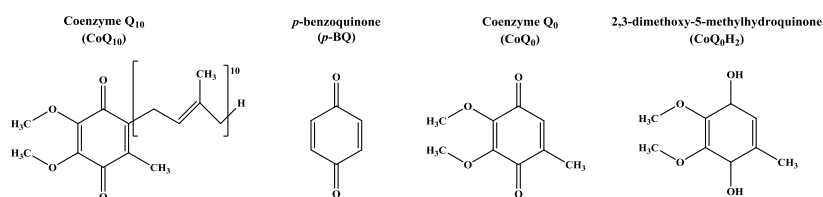


Figure 1 - Molecular structures of coenzyme Q<sub>10</sub> (CoQ<sub>10</sub>), *para*-benzoquinone (*p*-BQ), coenzyme Q<sub>0</sub> (2,3-dimethoxy-5-methyl-*p*-benzoquinone, CoQ<sub>0</sub>) and CoQ<sub>0</sub>H<sub>2</sub>.

### Acknowledgements

JA acknowledges the financial support granted by the MD-GAS COST Action CA18212 to attend the DEEP-GAS 2022 meeting.

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## Time-Resolved Images of Intramolecular Charge Transfer in Organic Molecules

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Ever since the first models of organic solar cells were proposed more than 40 years ago [1], the search for new materials with the ability to produce a charge separation, necessary for photovoltaic applications, has kept drawing the scientific community's attention. Organic photovoltaic devices usually achieve charge photogeneration by using charge transfer complexes, which act as an intermediate step between exciton dissociation and charge extraction [2].

In order to capture the real time evolution of such electronic process, which takes place in the time range between tens of attoseconds to a few femtoseconds, a sub-femtosecond time-resolution is required. Therefore, in this work we propose the use of a pump-probe scheme employing ultrafast laser sources to track the charge transfer process using as target a typical donor-acceptor molecule in the gas phase. In particular, we investigate the ultrafast dynamics following the excitation of para-nitroaniline (PNA). The molecule will be excited using a few-fs UV laser pulse. The ensuing electron-nuclear dynamics will be later probed by a time-delayed attosecond XUV pulse which will ionize the molecule. The time-varying ionization yields are expected to capture the complex dynamics triggered in the excited molecule.

As a first step to describe this process we present the simulation of the initial UV excitation and the subsequent coupled electron-nuclear dynamics. These dynamics are described by means of a surface-hopping method, i.e. within a semi-classical picture. In short, the time-dependent wave function is retrieved at each time step, computing the electronic structure on-the-fly by means of a quantum mechanical description, while the nuclear dynamics follows the classical equations of motion.

We then present an independent study of the effect of the ionization by the probing pulse, presenting both theoretical and experimental results for the different fragmentation yields induced by the photoionization process.

### Acknowledgements

Tomatto ERC Synergy Grant Project

### References

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**Chair: Ana Lozano**

- 14:30 - 14:50 | Mathias Poline, Stockholm University - *Study of mutual neutralisation reactions involving molecular ions at the double electrostatic ion storage ring DESIREE*
- 14:50 - 15:10 | Carlos Guerra, Laboratório de Colisões Atômicas e Moleculares, CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa - *Total electron detachment cross section and induced cationic fragmentation for superoxide oxygen ( $O_2^-$ ) collisions with benzene, oxygen, carbon dioxide and 1-methyl-5-nitroimidazole*
- 15:10 - 15:30 | Bart Oostenrijk, Deutsches Elektronen-Synchrotron, Hamburg - *Chemical Understanding of the Limited Site-Specificity in Molecular Inner-Shell Photofragmentation*
- 15:30 - 16:00 | Olga Lushchikova, University of Innsbruck - *The structure and reactivity of gas-phase copper clusters*
- 16:00 - 16:30 | Coffee break

**Chair: Darek Piekarski**

- 16:30 - 17:00 | Patrik Hedvall, Stockholm University - *Theoretical studies on mutual neutralization in collisions of oppositely charged atomic or molecular ions*
- 17:00 - 17:20 | Fabris Kossoski, Université Toulouse III - Paul Sabatier - *Transient negative ions of a model radiosensitizer that do not undergo dissociative electron attachment and what it means for radiosensitivity*
- 17:20 - 17:40 | Jacopo Chiarinelli, Istituto di Struttura della Materia, CNR - *Ion-Neutral coincidences: a tool to study metastable fragmentations*
- 17:40 - 18:00 | Josef Filgas, University of Chemistry and Technology - *Spin-vibronic effects in photochemical reactivity: modeling, understanding, and control*
- 18:00 - 18:20 | Daniel González, Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Ciudad Real - *The CRESU technique as a powerful tool to simulate an interstellar environment: Kinetics of the  $OH+NH_3$  reaction ( $T=11.7-177.5$  K)*

## Study of mutual neutralisation reactions involving molecular ions at the double electrostatic ion storage ring DESIREE

M. Poline<sup>1\*</sup>, M. C. Ji<sup>1</sup>, S. Rosén<sup>1</sup>, A. Simonsson<sup>1</sup>, M. Larsson<sup>1</sup>, N. S. Shuman<sup>2</sup>, S. G. Ard<sup>2</sup>,

A. A. Viggiano<sup>2</sup>, H. T. Schmidt<sup>1</sup>, H. Zettergren<sup>1</sup>, R. D. Thomas<sup>1</sup>

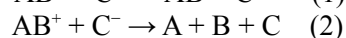
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At the double electrostatic ion storage ring DESIREE, mutual neutralisation of oppositely charged ions can be effectively studied. DESIREE is a unique facility as it is the only merged beams setup where the ions are stored prior to interaction [1]. Its cryogenic and ultra high vacuum properties mean that the ions can undergo radiative cooling via coupling to the environment, and therefore relax from their initial electronic, rotational and vibrational excited state population [2].

In recent years, study of mutual neutralisation reactions involving molecular ions have been undergoing, with focus on reactions in which a diatomic cation ( $AB^+$ ) interacts with an atomic anion ( $B^-$ ). Two outcomes are then possible:



I.e. the reaction may lead to dissociation, depending on whether the electron is captured on an attractive or repulsive potential of the formed molecular neutral. We present here some of the first merged beams results of several molecular ions, namely  $O_2^+$ ,  $NO^+$ , and  $N_2^+$  interacting with  $O^-$ . The results are interesting, as both processes (1) and (2) are observed with very different populations depending on the molecular cation, with no dependence on the bond energy. For the three-body processes (2), distinct dynamics are observed, with a clear vibrational dependence on the product yield.

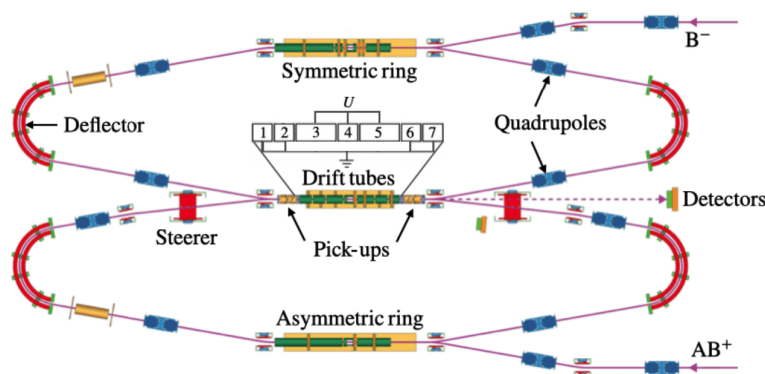


Figure 1: Schematic of the double ion storage ring DESIREE.

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[2] H. T. Schmidt *et al.*, *Phys. Rev. Lett.* **119**, 073001 (2017)

**Total electron detachment cross section and induced cationic fragmentation for superoxide oxygen (O<sub>2</sub><sup>-</sup>) collisions with benzene, oxygen, carbon dioxide and 1-methyl-5-nitroimidazole.**  
**Carlos Guerra<sup>1</sup>, Sarvesh Kumar<sup>2</sup>, Ana Lozano<sup>1</sup>, Mónica Mendes<sup>2</sup>, Paulo Limão-Vieira<sup>2</sup> and Gustavo García<sup>1,3, \*</sup>**

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### Abstract

During the last decades, studies related to collisions between anionic oxygen species and neutral molecules have taken an important relevance for different research areas as: plasma physics, astrophysics, medical physics and radiation damage [1–5].

Here we present a comprehensive investigation on collisions of superoxide oxygen anions with different neutral molecules, by using a novel transmission-beam apparatus developed, validated, and optimized by us to measure total electron detachment and ionization cross sections for these collision processes [6–8]. Novel experimental results for the absolute total electron detachment and relative partial and total ionization cross sections, by analysing the attenuation of the projectile and the positively charged species produced during the collision between the anionic oxygen beam and benzene, oxygen, carbon dioxide and 1-methyl-5-nitroimidazole (C<sub>6</sub>H<sub>6</sub>, O<sub>2</sub>, CO<sub>2</sub> and 1M5NI) molecules, for impact energies ranging from 100 to 1500 eV, are reported in this study. These experimental results have been compared, whenever possible, with previous data available in the literature. Yet, due to the scarcity or non-existence of previously published data, most of the present experimental results on C<sub>6</sub>H<sub>6</sub>, CO<sub>2</sub> and 1M5NI are completely novel and therefore may then constitute a valuable piece of information for the aforementioned scientific and technical applications.

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## Chemical Understanding of the Limited Site-Specificity in Molecular Inner-Shell Photofragmentation

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As the size of a free molecule increases, the fragmentation upon inner-shell ionization often becomes less specific with respect to the initially localized ionization site. Often this finding is interpreted in terms of an equilibration of internal energy into vibrational degrees of freedom after Auger decay. Here we investigate the X-ray photofragmentation of ethyl trifluoroacetate upon core electron ionization at environmentally distinct carbon sites [1] using photoelectron-photoion-photoion coincidence measurements (see Figure 1) and ab-initio electronic structure calculations. For all the 4 carbon ionization sites, the Auger decay weakens the same bonds and transfers the two charges to opposite ends of the molecule, which leads to a rapid dissociation into 3 fragments followed by further fragmentation steps. The limited site-specificity is attributed to the character of the dicationic electronic states after Auger decay, instead of a fast equilibration of internal energy.

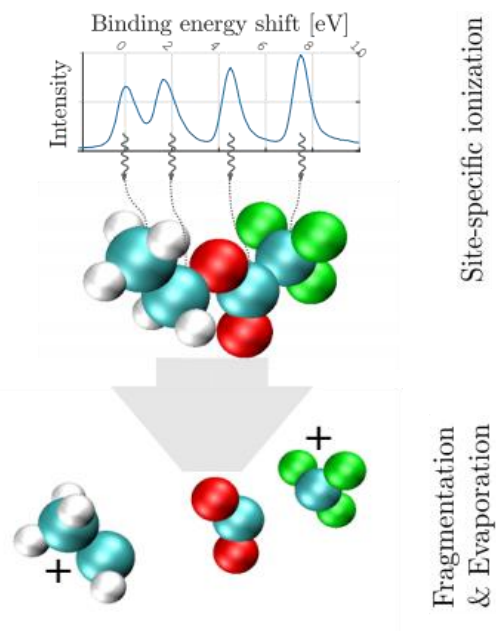


Figure 1: Visual representation of the site-specific core ionization (top) of ethyl trifluoroacetate, followed by fragmentation and subsequent evaporation (bottom). Does the memory of the core ionization site at different carbon atoms last until dissociation?

### Acknowledgements

The authors thank the Royal Physiographic Society in Lund for their financial support.

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## The structure and reactivity of gas-phase copper clusters

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Copper-based materials are among the most promising catalysts for CO<sub>2</sub> utilization. However, CO<sub>2</sub> conversion is still inefficient and requires high-energy input resulting in even more CO<sub>2</sub> emissions. Therefore, the molecular level understanding of CO<sub>2</sub> interaction with copper is crucial for the design of more efficient catalysts. In our study, we mimic the active site of the catalyst with copper clusters to study how they affect the structure of CO<sub>2</sub>.

First of all, the structure of bare Cu<sub>n</sub><sup>+</sup> is characterised.[1] The clusters are produced in a laser ablation source and are studied by IR multiple-photon dissociation spectroscopy. The experimental data is evaluated by comparison with density functional theory calculations. Further, clusters are reacted with CO<sub>2</sub> in the flow-tube reaction channel and the structure of CO<sub>2</sub> complexes formed with the bare clusters and Cu<sub>n</sub><sup>+</sup> preloaded with H<sub>2</sub> is investigated. We have observed structures with linearly bound CO<sub>2</sub> that could lead to the formation of formate intermediate on the Cu<sub>n</sub><sup>+</sup>-H<sub>2</sub> and only weak physisorption of CO<sub>2</sub> on Cu<sub>n</sub><sup>+</sup>. [2] However, when we changed polarity and studied the reaction of CO<sub>2</sub> with carbon-doped Cu<sub>n</sub><sup>-</sup>, we discovered that CO<sub>2</sub> can be activated or dissociated depending on the cluster size.[3]

As a next step, we implement He superfluid nanodroplets as ultracold (0.4 K) nano-reactors to study the reaction of CO<sub>2</sub> with both bare and metal-doped Cu-clusters. Here, we start with the verification of the cluster structure using He as a probe molecule.[4] Then, Cu<sub>n</sub><sup>+/-</sup> are reacted with CO<sub>2</sub> and fragmentation patterns and energies are investigated by means of collision-induced dissociation. As a next step, the Cu clusters will be doped with different metals, such as Ni, Au and Ag, to study the influence of the doping metal and the ratio to the CO<sub>2</sub> activation.

### Acknowledgements

This work was supported by the Dutch Research Council (NWO) and Austrian Science Fund FWF (project M 3229).

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## Theoretical studies on mutual neutralization in collisions of oppositely charged atomic or molecular ions

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In mutual neutralization oppositely charged atomic or molecular ions collide, an electron is transferred and neutral fragments are formed [1]. Due to the Coulomb attraction between the reactants and in many cases the strong non-adiabatic interactions between the ionic and covalent states at large internuclear distances, the rates for the process are often large at low energies. To perform ab initio and fully quantum studies of the mutual neutralization reactions are challenging and so far, limited to collisions of atomic ions. The main challenge is to accurately enough compute the potential energy curves and non-adiabatic interactions among all excited electronic states involved in the process [2]. A common approach is to use semi-classical models such as the Landau-Zener model with semi-empirical potentials and coupling elements to compute the cross section and to determine what fragments are formed [3]. In some cases, this method can also be applied to study the charge transfer in collisions of molecular ions.

In this talk I will illustrate the theoretical method, discuss the underlying approximations and show comparisons between theoretical results and measurements in the case of collisions of atomic ions such as  $\text{Na}^+ + \text{I}$ ,  $\text{H}^+ + \text{H}^-$  and in the case of molecular ions for  $\text{C}_{60}^+ + \text{C}_{60}^-$  and  $\text{Li}^+ + \text{CN}^-$ .

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## Transient negative ions of a model radiosensitizer that do not undergo dissociative electron attachment and what it means for radiosensitivity

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Radiosensitizers are molecules employed in chemoradiotherapy that enhance the efficacy of such treatments, while reducing the damage induced in the neighbouring healthy tissues<sup>1</sup>. While the detailed mechanisms of how radiosensitizers do their job have not yet been figured out, the production and subsequent chemistry mediated by free radicals is believed to play a key role<sup>2</sup>. In particular, low-energy electrons (LEEs) are produced during the thermalization of the primary ionising radiation and can produce free radicals through dissociative electron attachment (DEA) reactions. While LEE induced chemistry has been traditionally linked with DEA, the role of other electron-induced reactions, particularly in the context of radiosensitivity, remain much less clear.

Here, I will discuss a recent experimental-theoretical study<sup>3</sup> on the interaction of LEEs with an important model radiosensitizer, 1-methyl-5-nitroimidazole. From measurements of total electron scattering cross sections performed with a state-of-the-art setup, we found signatures of many transient negative ions (TNIs). Surprisingly, many of these TNIs have no parallel in DEA experiments<sup>4,5</sup>, which points to alternative and effective decay mechanisms for these states. While non-dissociative channels cannot be ruled out, our results support neutral dissociation through a catalytic electron<sup>6,7</sup> as a likely relaxation mechanism for these TNIs. This finding means that neutral dissociation could play an unexpected part to understanding radiosensitivity, besides the more established route through DEA. With support from electron scattering and quantum chemistry calculations, we also provide novel insights on DEA reactions occurring at the lower energies.

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## Ion-Neutral coincidences: a tool to study metastable fragmentations

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Mass spectrometry of ionized molecules in gas phase is a powerful technique to shed light on the molecular composition and the chemical-physics processes taking place in several environments from the deep space to the human body. The aim of the technique is to reach the most complete as possible description of the fragmentation paths resulting from the ionization of the target molecule. However, the full definition of the path is not a simple task because of the numerous undetected neutral moieties involved.

A ion-neutral coincidence experiment, performed by using time of flight mass spectroscopy (TOF-MS), is a powerful tool to provide information on all the *actors* of a metastable fragmentation, even when subsequent processes take place [1]. As an example, the ion-neutral coincidence map of the cyclo-alanine alanine (cAA) [2] molecule produced in the interaction with the VUV radiation of a discharge lamp (21.22 eV) in the TOF-MS of our lab in Rome [2] is shown in Fig. 1. The sequence of successive fragmentations starting from the parent ion as well the existence of competing channels (for example  $99^+ \rightarrow 71^+, 58^+$  and  $44^+$ ) are clearly identified in the map.

A part from providing information on the produced fragments, the technique enables to access the time domain discriminating among prompt (ps) and metastable (ns/ms) processes and, for the latter, provides information on the decay rate and the kinetic energy release in the process [3].

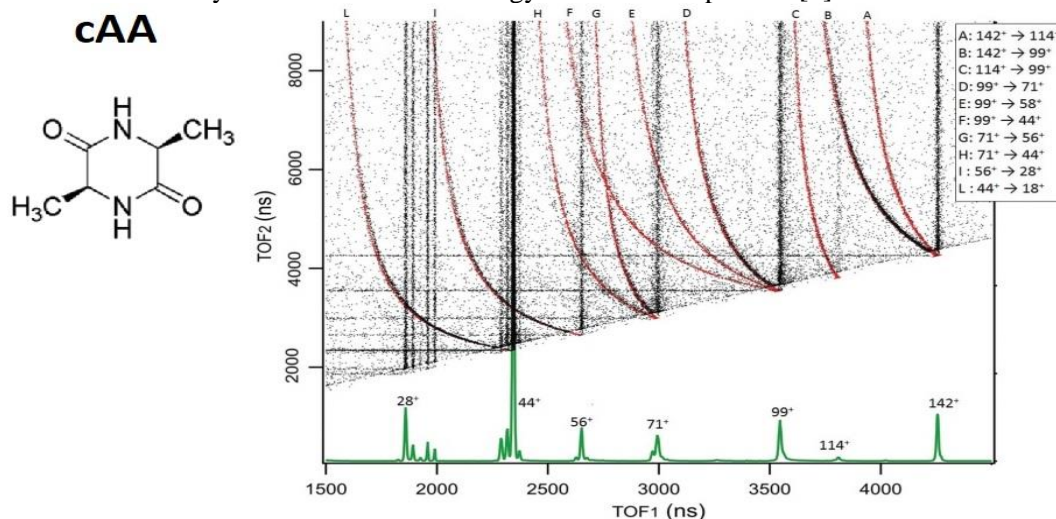


Figure 1: The mass spectrum (green) and 2D coincidence map obtained of the VUV photo-fragmentation of cAA molecule. The traces due to ion-neutral coincidences of metastable fragmentations are highlighted in red while the involved ionic moieties are reported in the inset.

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## Spin-vibronic effects in photochemical reactivity: modeling, understanding, and control

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The spin-vibronic coupling, i.e. the coupling between the vibrational motion and strength of the spin-orbit coupling, is increasingly recognized to play an important role in light-induced transformations. Here, we focus on the explanation of the structural dependence of the quantum yield of the intersystem crossing for nine iodinated BODIPY (boron-dipyromethene) derivatives (see Figure 1), using the methods of the quantum theory of molecules. Compounds with iodine atoms in the central part (structures 3–6 and 9 in Figure 1) exhibit enhanced intersystem crossing rates, while the periphery iodine atoms (present in structures 2, 4, 6, and 7 in Figure 1) do not affect this process. This observation has relevance, for example, to the development of photochemical leaving groups in the visible range of the spectrum.

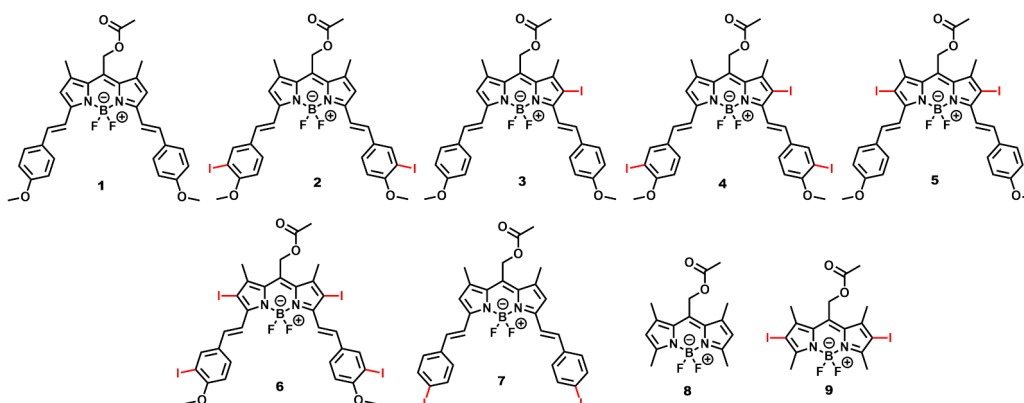


Figure 1: The studied BODIPY derivatives.

We demonstrate that multireference approaches involving the dynamical correlation are necessary to describe the molecules in question. The calculations also required the use of a relativistic description beyond the electron pseudopotentials. In this work, it is achieved by the Douglas–Kroll–Hess Hamiltonian. The calculations in the optimal geometries failed to explain the experimental observations. It was necessary to include the coupling between the vibrational motion and the spin-orbit coupling.

The minimal-energy structures of this crossing exhibit a specific geometric deformation. In these geometries, the values of the spin-orbit coupling correspond to the experimentally observed trend of the quantum yields of the intersystem crossing. Löwdin population analysis followed by the analysis of the spin-orbit coupling matrix elements explained this trend. The geometric deformation mentioned above causes a change in the character of the molecular orbitals involved in the transition. This change occurs only on the central iodine atoms and allows an increase in the magnitude of the spin-orbit coupling.

### Acknowledgments

The work was supported by the Czech Science Foundation projects No. 20-15825S and 21-26601X.

## The CRESU technique as a powerful tool to simulate an interstellar environment: Kinetics of the OH+NH<sub>3</sub> reaction (T=11.7-177.5 K)

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Astrochemistry is a field that has experienced an enormous increase in the last decades due to the development of the radioastronomy, making possible the detection of more than 270 molecules in the interstellar medium (ISM) or circumstellar shells [1]. The discovery of this chemical richness has strengthened the exogenous hypothesis, in which the prebiotic molecules were synthesized in space and then delivered to the Earth by meteorites, comets or asteroids [2]. For example, the chemistry of N-bearing species in the coldest regions (~10-100 K) of the ISM is thought to be closely linked to the formation of amino acids in the ISM. Astrochemical networks model the abundances of the IS species using hundreds of reactions. Thus, they are constantly being improved with the inclusion of the rate coefficients ( $k$ ) for the different processes, such as radical-molecule reactions in the gas-phase. However,  $k$  must be characterized under the appropriate temperature range in laboratory experiments. For this purpose, the CRESU (French acronym for *Reaction kinetics in a Uniform Supersonic Flow*) technique has been the most suitable and powerful tool to, firstly, study ion-neutral reactions [3] and later, adopted for the neutral-neutral ones [4]. This method is based on Laval nozzle gas expansions from a high-pressure reservoir to a low-pressure chamber creating a uniform and supersonic cold jet. In this work, we have used a pulsed version of the CRESU technique with a rotatory disk previously described [5] to determine  $k$  between 11.7 and 177.5 K for the gas-phase reaction between hydroxyl (OH) radical and ammonia (NH<sub>3</sub>), both abundant species in the ISM. Pulsed laser photolysis and laser induced fluorescence were coupled to generate *in situ* the OH radicals and to monitor the OH temporal profile, respectively. The results have revealed an increase in  $k$  with respect to  $k(300\text{ K})$  for the title reaction as temperature is decreased, reaching a maximum at 22 K as will be discussed in the talk.

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**2.2 Wednesday 5<sup>th</sup>****Chair: Sylvain Maclot**

- |               |  |
|---------------|--|
| 10:00 - 10:45 | Rebecca Boll, European XFEL, Hamburg - <i>X-ray induced Coulomb explosion imaging of complex molecules</i> |
| 10:45 - 11:15 | Coffee break   |

**Chair: Alicia Palacios**

- |               |   |
|---------------|---|
| 11:15 - 11:45 | Laura Rego, Imperial College London, University of Salamanca - <i>Tailoring the polarization of light for chiral discrimination</i>                             |
| 11:45 - 12:15 | Eva Muchova, University of Chemistry and Technology Prague - <i>Modelling of X-ray spectroscopies of allene: Pitfalls and Solutions</i>                         |
| 12:15 - 12:45 | Rocio Borrego Varillas, CNR-IFN - <i>Ultrafast dynamics in donor-acceptor molecules investigated by attosecond spectroscopy</i>                                 |
| 12:45 - 13:05 | Eva Vos, Universidad Autonoma de Madrid - <i>Understanding the chemical evolution of DNA: A theoretical study of the photophysics of nucleobases' ancestors</i> |
| 13:05 - 14:30 | Lunch break   |



## X-ray induced Coulomb explosion imaging of complex molecules

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Recording images of individual molecules with ultrashort “exposure times” has been a long-standing dream in molecular physics, chemistry, and biology, because this would allow one to follow the motion of atoms on their inherent timescale. While X-ray and electron diffraction have been successfully used for larger molecules, both are very challenging to apply to small gas-phase molecules. Moreover, these techniques are insensitive to hydrogen atoms, which are key to many chemical reactions.

We could recently demonstrate that snapshot images of the complete structure of a molecule with eleven atoms, including all hydrogens, can be recorded by Coulomb explosion imaging (CEI) when using very intense, femtosecond soft X-ray pulses from the European XFEL [1]. While it was possible to record up to six-fold ion coincidences in the experiment, even three-fold ion coincidences can be sufficient to image the full structure of a molecule. The X-ray intensity is high enough to produce extreme charge states (e.g. up to 42+ in xenon atoms), and to Coulomb-explode molecules into individual atoms very quickly, such that the initial molecular structure is well preserved in the recorded momenta of all ions. The intriguingly clear momentum images allow us to identify each atom’s position in the molecule unambiguously.

The sensitivity of CEI to the molecular structure at the instant of ionization allows studying processes such as molecular charge-up [2], the influence of transient molecular resonances [3], intramolecular charge rearrangement [1] and fragmentation dynamics [4]. The femtosecond pulse duration opens the door to monitoring the temporal evolution of the molecular structure [5]. Furthermore, combining CEI with coincident electron detection [6, 7] provides access to molecular-frame photoelectron diffraction – a powerful tool for accessing molecular dynamics.

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## Tailoring the polarization of light for chiral discrimination

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Distinguishing between the two opposite versions (enantiomers) of a chiral molecule is vital in organic chemistry, materials science or biomedicine, but also challenging, as they behave identically unless they interact with another chiral object. Standard chiral light, i.e. circularly or elliptically polarized light, is a convenient chiro-optical tool [1], but it is highly inefficient because the enantio-sensitive response of the molecules rely on the interplay between electric-dipole and magnetic-dipole interactions.

Here we show that tight focusing can turn elliptically polarized light into an extremely efficient chiro-optical tool [2]. Upon tight focusing, a longitudinal polarization component naturally arises in the laser, so its polarization plane tilts towards the propagation direction [3] (see Fig. 1a). This tilt is opposite at opposite sides of the beam axis and is locked to the propagation direction. In an ultrashort laser pulse, the combination of the tilted electric-field vector with the propagation direction creates a chiral structure that allows us to distinguish between enantiomers via purely electric-dipole interactions.

Figs. 1b,c show that the proposed optical configuration leads to enantio-sensitive bending of the nonlinear optical response of randomly oriented chiral molecules: opposite molecular enantiomers emit harmonic light in opposite directions, and thus the enantio-sensitive direction of bending records the molecular handedness with high efficiency. Interestingly, this strongly enantio-sensitive effect is driven by purely electric-dipole interactions, even though the optical field is not locally chiral, making this optical driving field fundamentally different from previous proposals [4] and, to our knowledge, from any other optical setup for chiral recognition.

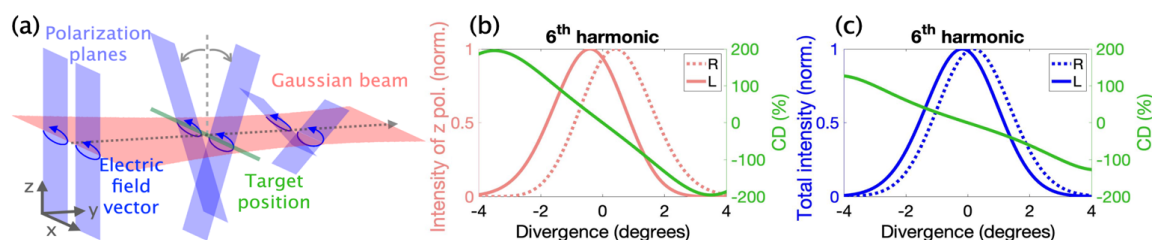


Figure 1. (a) Forward polarization tilt (blue) in an elliptically polarized gaussian beam (pink), tightly focused into a chiral medium (green). (b,c) Intensity of the z-polarized component (b) and total intensity (c) of the 6th harmonic emitted by the right- (dotted lines) and left-handed (solid lines) propylene oxide, and spatially-dependent chiral dichroism (green),  $CD=2(I_L-I_R)/(I_L+I_R)$ ; TDDFT simulations,  $I=6 \cdot 10^{13} \text{ W} \cdot \text{cm}^{-2}$ , focal diameter  $5 \mu\text{m}$ ,  $\lambda=780 \text{ nm}$ , and pulse duration 7 fs (FWHM).

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## Modelling of X-ray spectroscopies of allene: Pitfalls and Solutions

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All types of X-ray spectroscopies ranging from X-ray absorption to resonant Auger spectroscopy are used as an accurate tool for disentangling properties and dynamics of molecules because of their site and element specificity. However, the theoretical description is lagging behind because the processes are connected with difficult electronic structure and scattered electrons. In our project, we are investigating small organic molecules, namely allene, and we focus on resonant Auger spectra that include information both about the valence and unoccupied molecular orbitals. We combine nuclear ensemble approaches[1] with currently available electronic structure methods based on EOM-CCSD formalism[2] to determine not only the positions of the peaks but also their shape and intensities. We would also like to show that spectra simulations using only the minimum energy structure and Franck-Condon approximation for molecules may have some limitations.

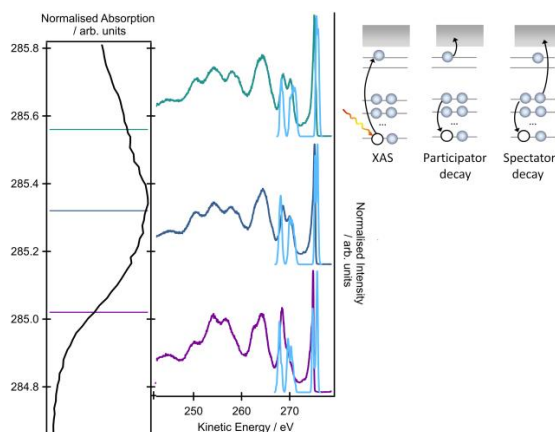


Figure 1: Experimental resonant Auger spectra of allene (left) and a sketch of possible Auger processes.

### Acknowledgements

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## Ultrafast dynamics in donor-acceptor molecules investigated by attosecond spectroscopy

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Photoinduced electron transfer (ET) and charge transfer (CT) are processes at the basis of core technologies aiming at effective conversion of solar energy into electrical energy. The full comprehension of these mechanisms requires real-time imaging of the electronic motion, which takes place on attosecond to few-femtosecond time scales [1]. By combining time-resolved photo-ion spectroscopy and synchrotron spectroscopies, we investigate the electronic structure and ultrafast dynamics initiated by XUV radiation in five nitroanilines (Figure 1), which are the simplest prototype donor and acceptor systems.

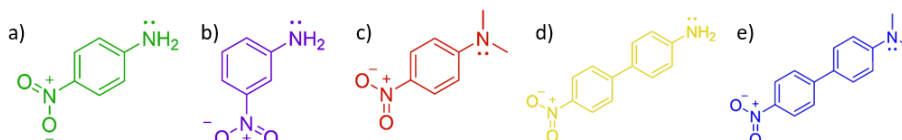


Figure 1: Chemical structure of the investigated molecules: a) *p*-nitroaniline, b) *m*-nitroaniline, c) *N,N*-dimethyl-4-nitroaniline, d) 4-amino-4'-nitrophenyl and e) 4-dimethylamino-4'-nitrobiphenyl.

Ultrafast dynamics are initiated by a short train of attosecond pulses (<2 fs) and probed with a 5-fs near-infrared (NIR) pulse. We observe two different dissociation processes. A first fragmentation channel, responsible for the central peak, involves the generation of  $\text{NO}^+$  and the radical  $\text{C}_6\text{H}_4\text{NH}_2$  [2]. The side peaks, instead, are assigned to Coulomb explosion of the NO fragment coming from a double ionization process. Photoelectron photoion coincidence experiments confirm this interpretation. Our results open the way to the investigation and control of ET and CT in push-pull molecules at the electronic time scale.

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## Understanding the chemical evolution of DNA: A theoretical study of the photophysics of nucleobases' ancestors

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Natural DNA and RNA nucleobases are characterized by their photostability upon UV light continuous exposition. The internal conversion channels, found along the main relaxation pathways of the five canonical nucleobases, ease the complete deactivation of the monomers in an ultrafast timescale, preventing the generation of photolesions in the DNA strand<sup>1</sup>.

Determining the structural and electronic factors that promote these desirable photostable properties can enormously help to understand the chemical evolution suffered by nucleobases' ancestors during the prebiotic period to lead in the current genetic alphabet. In this way, the scrutiny of the deactivation mechanism in modified nucleobases would shed light into the keys which control the interesting photophysics and photochemistry of these systems.

In this special report, we expose a complete static and dynamics analysis of oxo modified nucleobases, proposed as nucleobases' ancestors<sup>2</sup>, at one of the most sophisticated multiconfigurational methods, XMS-CASPT2<sup>3</sup>. The molecular dynamics of investigated systems have showed strong evidences of open-ring photodegradation along their decay routes, also corroborated by experimental observation<sup>4</sup>. These unexpected results shedding light on the effect of functionalization of aromatic rings and establish one of the first examples of photolabile nucleobase derivate.

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**Chair: Marta Łabuda**

- |               |  |
|---------------|--|
| 14:30 - 14:50 | Felix Iacob, West University of Timisoara - <i>Reactive collisions of electrons with <math>NS^+</math> cation in interstellar media</i>  |
| 14:50 - 15:10 | Demeter Tzeli, National and Kapodistrian University of Athens, Department of Chemistry, Laboratory of Physical Chemistry, Zografou - <i>Quadruple and sextuple bonds in diatomic molecules</i> |
| 15:10 - 15:30 | Vincenzo Laporta, Istituto per la Scienza e Tecnologia dei Plasmi, CNR, Bari - <i>Electron-molecule collisions and vibrational relaxation times for non equilibrium plasma applications</i>    |
| 15:30 - 15:50 | Oded Heber, Weizmann Institute of Science - <i>Time-dependent molecular dynamics probed by electron spectroscopy of trapped molecules</i>  |
| 15:30 - 17:30 | Poster Session + Tapas (Sala polivalente - faculty of science)   |

## Reactive collisions of electrons with $\text{NS}^+$ cation in interstellar media

F. Iacob<sup>1</sup>, N. Pop<sup>2</sup>, J. Zs Mezei<sup>3</sup>, I. F. Schneider<sup>4</sup>, T. Meltzer<sup>5</sup>, J. Tennyson<sup>6</sup>

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The recent discovery of the  $\text{NS}^+$  cation in the interstellar medium<sup>1</sup> triggered the interest in the study of its collision with electrons. In this complex process, the electron can be captured into  $\text{NS}$  Rydberg-bound states predissociated by Feshbach resonances of this latter molecule. These both types of states have been calculated within the Born-Oppenheimer approximation using a variational *ab-initio* method based on the the R-matrix theory<sup>2</sup>. The electronically-excited Rydberg states form series converging either to the ground or to the excited states of the cation. We will focus on the Rydberg series of  $^2\Sigma^+$  symmetry converging to the ground  $\text{X}^1\Sigma^+$  state of the ion, conveniently characterized by their quantum defects or effective quantum numbers – see Figure 1.

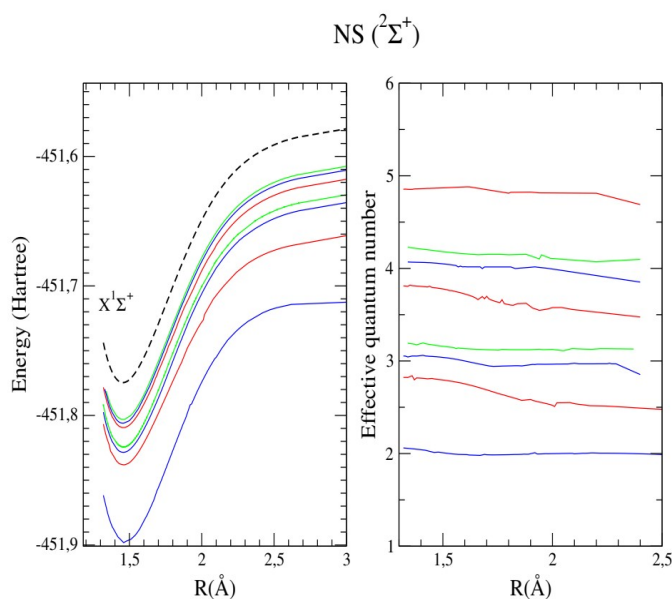


Figure 1: Rydberg series – left panel; quantum defects – right panel. Both by color shows partial wave of projectile electron for sigma symmetry

### Acknowledgements

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## Quadruple and sextuple bonds in diatomic molecules

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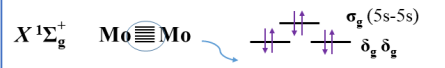





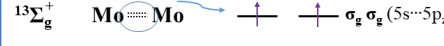
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The chemical bond is one of the most fundamental concepts in chemistry.[1] Double and triple bonds are quite common, while quadruple bonds are a true oddity, they are very rare for the main group elements and their identification is very important. Here we present high-level theoretical calculations on the isoelectronic MX molecules and MX<sup>-</sup> anions, i.e., M= Tc, Ru, Rh, and Pd and X = N, C, B, and Be, showing that such a quadruple bond with main group elements is not that uncommon for the ground and for low-lying excited states.[2-3] The requirements for the occurrence of such bonds in molecular systems are reported, while it is analyzed how the involved atomic states influence bonding, dissociation energies, bond lengths, and relative energy ordering of the states. Bond lengths, dissociation energies, dipole moments, spectroscopic parameters and relative energy ordering of the states have been calculated via multireference and coupled cluster methodology using the aug-cc-pV5ZX(-PP)<sub>M</sub> basis sets.

Nowadays, the maximum bond multiplicity is six and it has been proposed theoretically for the ground states of Cr<sub>2</sub>, Mo<sub>2</sub> and W<sub>2</sub>. [4] Here, the bonding, the dissociation energies, and the spectroscopic parameters of seven states of Mo<sub>2</sub> that correlate to the ground state products are calculated. [5] The ground state has a sextuple chemical bond and each of the calculated excited state has one less bond than the previous state. Finally, the bond breaking of Mo<sub>2</sub>, as the multiplicity of spin is increased, is analyzed in parallel with the Mo-Mo bond breaking in a series of Mo<sub>2</sub>Cl<sub>x</sub> complexes when x is increased. Physical insight into the nature of the sextuple bond and its low dissociation energy will be provided.

	Mo <sub>2</sub>		D <sub>e</sub> [D <sub>0</sub> ] (eV)
X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	Mo≡≡Mo		4.502 [4.479] Expt: [4.476]
<sup>3</sup> Σ <sub>u</sub> <sup>+</sup>	Mo≡Mo		3.33
<sup>5</sup> Σ <sub>g</sub> <sup>+</sup>	Mo≡Mo		2.23
<sup>7</sup> Σ <sub>u</sub> <sup>+</sup>	Mo≡Mo		1.25
<sup>9</sup> Σ <sub>g</sub> <sup>+</sup>	Mo=Mo		0.87
<sup>11</sup> Σ <sub>u</sub> <sup>+</sup>	Mo—Mo		0.49
<sup>13</sup> Σ <sub>g</sub> <sup>+</sup>	Mo⋯Mo		0.120 [0.117]

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## Electron-molecule collisions and vibrational relaxation times for non-equilibrium plasma applications

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In my presentation, I will illustrate my researches on non-equilibrium plasma physics and electron-molecule collisions. I will focus, in particular, on vibrational-excitation, dissociative-attachment, dissociative-recombination and dissociative-excitation processes rotationally and vibrationally resolved [1,2,3]. Concerning kinetic modelling, vibrational relaxation times in state-to-state approach [1,4], will be also presented.

The electronic structures are obtained using ab-initio quantum chemistry approaches implemented in computer codes like MOLPRO and UK-R-Matrix whereas the nuclear dynamics is studied within the theoretical models of Bardsley's local-complex-potential model, adiabatic-nuclei approximation and multichannel quantum defect theory.

These researches are performed in view of many applications: in particular in aerospace (shuttle reentry in planetary atmospheres, electric propulsion), combustion, controlled fusion reactors, astrochemistry (early Universe, interstellar medium) and chemical evolution of life.

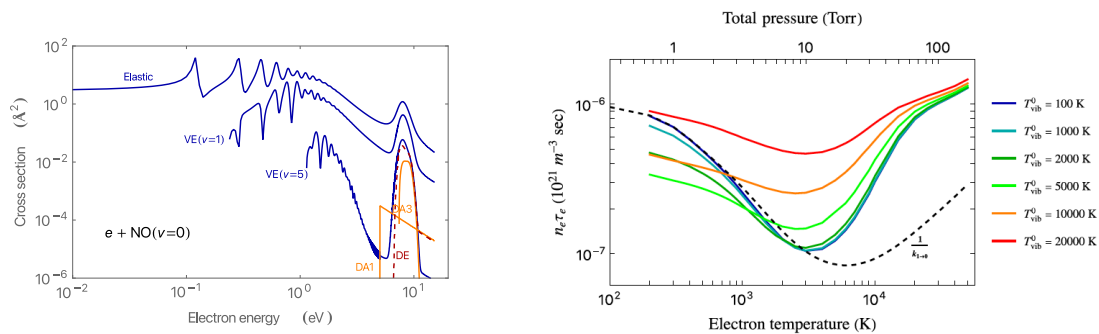


Figure 1: Vibrationally resolved cross sections for NO molecule by electron impact (plot on the left) and the corresponding relaxation times (plot on the right).

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## Time-dependent molecular dynamics probed by electron spectroscopy of trapped molecules

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An excited many-body system like a molecule can change its internal state dynamically via many processes as well as within many time scales. One of the interesting processes is the cooling of such a system on long-time scales relative to the characteristic internal motion of a molecule like rotation (picoseconds).

In this work, we present a unique probe for the time-dependent internal dynamics in molecules. This probe is the combination of an electrostatic ion beam trap (EIBT), an electron velocity map imaging (VMI) system within the trap and a laser [1]. We will show some new results on a few processes like spontaneous delayed electron emission, laser probe rotational cooling, and angular distribution for probing molecular state spectroscopy.

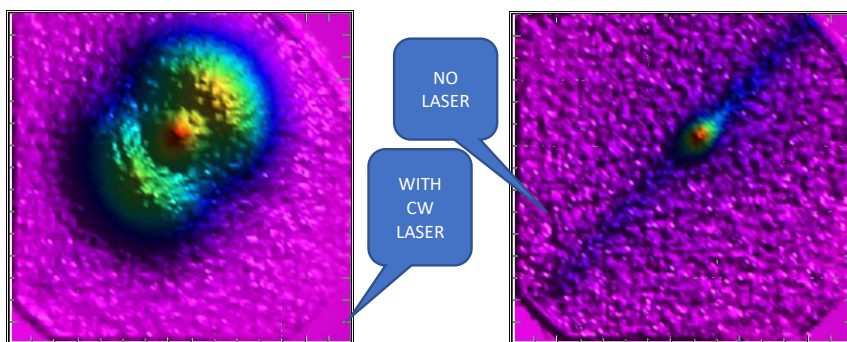


Figure 1: A VMI electron image of stored  $AlO_2^-$  molecule with and without laser. On the right side, one can see the spontaneous emission along the beam direction with close to zero energy electrons. On the left side one can see a transition between the ions to the neutral molecule with two different electronic states.

### Acknowledgements

This work was supported by the Israel Science Foundation (ISF).

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**2.3 Thursday 6<sup>th</sup>****Chair: Henning Zettergren**

- |               |   |
|---------------|---|
| 10:00 - 10:45 | Lorenzo Avaldi, CNR-Istituto di Struttura della Materia, Montelibretti<br>- <i>Photoelectron-photoion coincidence studies of molecules of biological interest</i> |
| 10:45 - 11:15 | Coffee break  |

**Chair: Lucas Schwob**

- |               |  |
|---------------|--|
| 11:15 - 11:45 | Marc Simon, Laboratoire de Chimie Physique - Matière et Rayonnement, CNRS and Sorbonne University - <i>Dynamics and structures perspectives in Atomic and Molecular Physics in the tender x-ray region (2-12 keV)</i>            |
| 11:45 - 12:15 | Teodora Kirova, Institute of Atomic Physics and Spectroscopy - <i>Numerical studies of the impact of electromagnetic field of radiation on valine</i>  |
| 12:15 - 12:45 | Aleksandar Milosavljevic, Synchrotron SOLEIL - <i>On-the-fly photoelectron spectroscopy of mas/charge selected ESI-generated ions: experimental technique and fundamental challenges</i>   |
| 12:45 - 13:05 | Juliette Leroux, Centre de recherche sur les Ions, les Matériaux et la Photonique, Caen and Deutsches Elektronen-Synchrotron, Hamburg - <i>Mapping the electronic transitions of protonation sites in peptides using NEX-AMS</i> |
| 13:05 - 14:30 | Lunch break  |

## *Photoelectron-photoion coincidence studies of molecules of biological interest*

L. Avaldi

CNR-Istituto di Struttura della Materia, Area della Ricerca di Roma 1, CP 10 00015 Monterotondo Scalo, Italy

The interaction of VUV and/or soft X-ray radiation with a molecule in the gas phase results in a single or multiple ionization event. The experiments to characterize this event therefore must involve the detection of electrons and ions. Photoelectron-photoion coincidence, PEPICO, experiments which combine photoelectron spectroscopy with mass analysis thanks to their selectivity provide valuable and unique information on dissociation dynamics. Thus PEPICO experiments with synchrotron radiation have become one of the most powerful tools to investigate dissociative photoionization. In this presentation some applications of PEPICO experiments to the study of molecular species of biological interest in the gas phase will be presented, among them the ionization via inner shell excitation and direct valence photoionization of halogenated pyrimidines to tackle site selectivity and bond breakage, the use of PEPICO data from valence photoionization to extract information on the energy distribution in collision experiments, the study of potential radiosensitizer and possible role of dipeptide in the origin of life.

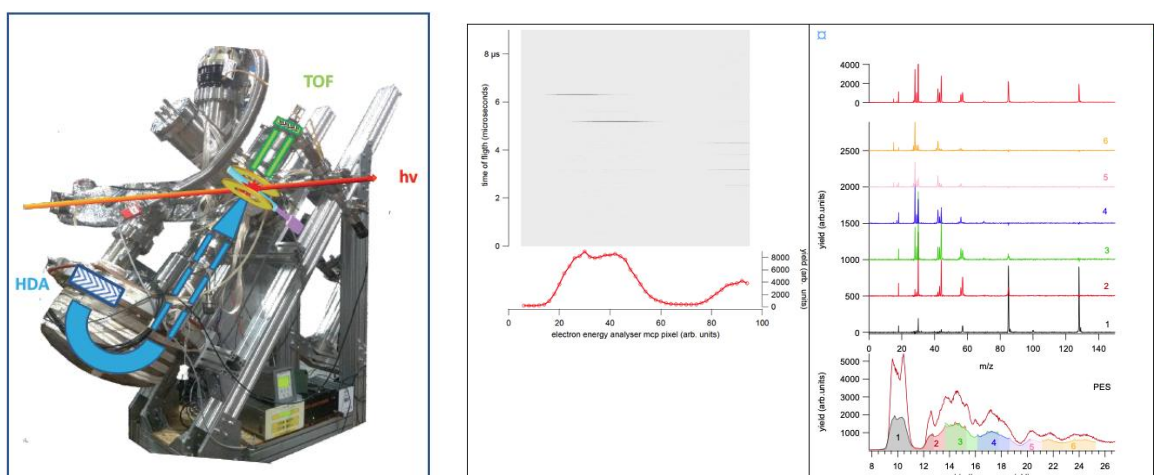


Fig. 1: Set-up for electron-ion coincidence at Elettra

Fig. 2: Left panel: example of a single PEPICO acquisition at a fixed kinetic energy corresponding to region 1 in the right panel. Right panel: the photoelectron spectrum of cyclo-GlycylAlanine acquired by the electron energy analyzer and the same spectrum 'reconstructed' by the total ion yield in the PEPICO spectra measured (shaded areas) (bottom panel). The coincidence mass spectra measured in each region are reported in the central panel. The sum of the PEPICO spectra is shown in the top panel.

## **Dynamics and structures perspectives in Atomic and Molecular Physics in the tender x-ray region (2-12 keV).**

Marc SIMON

*Laboratoire de Chimie Physique – Matière et Rayonnement, CNRS & Sorbonne University, 4 place  
Jussieu, 75005 Paris, FRANCE.*

Our research group is working on ultrafast dynamics after absorption of a tender x-ray photon (2-10 keV) by an isolated atom or molecule. Specificities of this energy domain are connected to the very short lifetime (1 fs or less), the creation of multiply charged ions by cascade Auger, emission of fast Auger or x-ray photon of high energy.

We have developed experimental setups allowing to measure x-ray emission, photoemission as well as vectorial coincidences between the momenta of electrons and ions.

I will show recent results related to the dynamics and spectroscopy of Double Core Hole states [1-3]. I will show ultrafast fragmentation examples [4-5]. High photon energy photoionization leads to strong recoil effects [6-8]. We took advantage of the fragmentation of multiply charged ions to study the localization of inner shells [8]. Two examples of attosecond electronic relaxation will be presented [9, 10].

During the talk, I will underline some perspectives of this energy domain in gas phase, with liquids and clusters, on molecules of biological interest...

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## Numerical studies of the impact of electromagnetic field of radiation on valine

T. Kirova<sup>1,\*</sup> and J. Tamulienė<sup>2</sup>

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Amino acids are the structural units of the proteins, i.e. by joining together they form peptides or polypeptides / proteins. Non-protein amino acids have important roles as metabolic intermediates, such as in biosynthesis, or are used to synthesize other molecules. Valine is an  $\alpha$ -amino acid which is used in protein biosynthesis and thus is essential in humans. In sickle-cell disease it substitutes the hydrophilic glutamic acid, and the hemoglobin becomes prone to abnormal aggregation. Shortly after the deposition of high-energy ionizing quanta into a biological medium, electrons with different energies are formed and are able to destroy biological molecules, such as DNA and proteins, and cause chromosome aberrations, leading to cancer mutations, genetic transformations etc. [1].

In this work we present the results of the numerical calculations of the effect of electromagnetic field of radiation on valine and compare with experimental results available in the literature [2]. We specifically focus on the effects of the magnetic field of radiation by introducing modified basis sets which incorporate correction coefficients to the s-, p- or only the p-orbitals, following the method of Anisotropic Gaussian Type Orbitals [3]. By comparing the bond length, angle, dihedral angles, and condense to atom all electrons, obtained without and with the inclusion of dipole electric and magnetic fields, we conclude that while the charge redistribution occurs due to electric field influence, the changes in the dipole momentum projection onto the y- and z- axis are caused by the magnetic field. At the same time the values of the dihedral angles could vary up to 4 degrees due to the magnetic field effects. We further show that taking into account of the magnetic field in the fragmentation processes provides better fitting of the experimentally obtained spectra ( e. g. the CHO<sub>2</sub> fragment is seen only when the magnetic field effects are included to the basis set of the p- orbitals). Thus, numerical calculations which include the magnetic field effects can serve as a tool for more accurate predictions, as well as analysis of the experimental outcomes.

### Acknowledgements

This article is based upon work from COST Action CA18212-Molecular Dynamics in the GAS phase (MD-GAS), supported by COST (European Cooperation in Science and Technology).

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## On-the-fly photoelectron spectroscopy of mas/charge selected ESI-generated ions: experimental technique and fundamental challenges

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There has been a long-standing need to develop a system for on-the-fly X-ray/VUV photoelectron spectroscopy of isolated mass over charge selected ions produced by an electrospray ionization (ESI) source [1]. Such system would use powerful spectroscopic techniques available at synchrotron and free electron laser facilities and allow the studying of electronic properties of a well-defined complex and fragile molecular systems, which cannot be brought to the gas-phase otherwise. It would be a complementary tool with respect to the action spectroscopy of trapped ions [2], which is now routinely performed. Nevertheless, the crossed ion/photon beams spectroscopy under high vacuum conditions is very challenging, dominantly because the target ion beam is effectively very dilute thus imposing a small signal-to-noise ratio. The present talk will describe such an experimental system (Figure 1) recently developed at PLEIADES beamline of the SOLEIL synchrotron (France). The fundamental and technical challenges will be discussed, as well as example results both for negative and positive target ions.

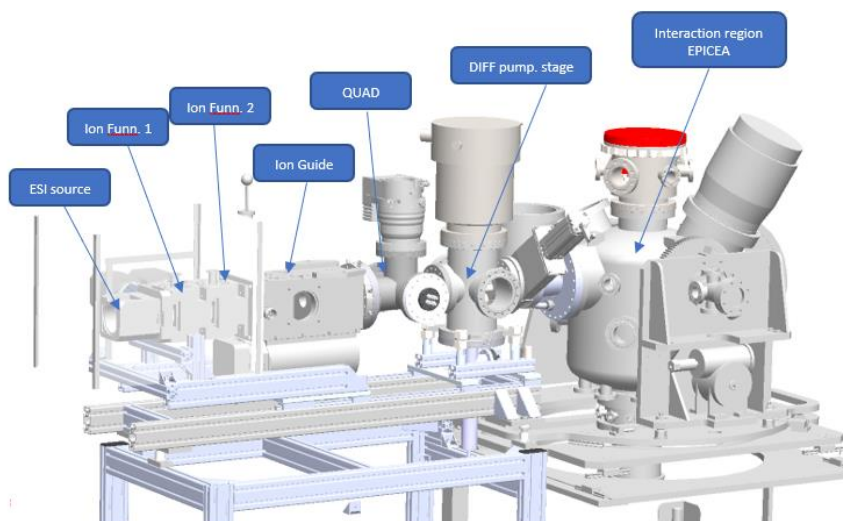


Figure 1: Schematic drawing of the ESI-EPICEA experimental setup at PLEIADES (SOLEIL).

### Acknowledgements

The author acknowledges all the colleagues from SOLEIL, ISMO, Univ. Caen, Ecole Polytechnique, DESY, Potsdam University, Lund University, Groningen and Ardara, involved in the design, development and testing of the system, as well as the first measurements.

### References

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## Mapping the electronic transitions of protonation sites in peptides using NEXAMS

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<sup>(d)</sup> *Department of Physics and Astronomy, Uppsala University, Uppsala, Sweden*

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Proton transfer is a fundamental charge transfer process in Chemistry, and it is particularly important for biological molecules, since they usually contain basic groups (DNA, peptides, proteins...). Therefore, in order to study charge dynamics in isolated biomolecules, it is crucial to determine the initial location of protons. Although it is now well established that protonation occurs primarily at nitrogens of the most basic side chains (arginine, histidine, lysine) of protonated peptides, in the absence of such group or in the case of multi-fold protonated species, the N-terminus and the peptide backbone oxygens can compete for the proton(s). This is for instance the case in protonated Ac-Ala, as IR multiphoton dissociation (IRMPD) coupled to quantum-chemical calculations has demonstrated.<sup>[1]</sup> However, the fragmentation yield falls rapidly with the number of atoms in the molecule, since IRMPD is a statistical process. Thus, there is a need for other methods able to determine the protonation sites of large systems.

In this context, near-edge X-ray absorption mass spectrometry (NEXAMS) is a promising technique as it provides a local probe into the atomic environment. NEXAMS is based on the electronic excitations of core electrons to unoccupied molecular orbitals and thus captures the electronic and geometric structure of a system under investigation. For instance, through photoabsorption around the nitrogen K-edge, it is possible to distinguish between the secondary and primary amine groups of proline and glycine, respectively.<sup>[2]</sup> In order to map the electronic transitions of the different protonation sites in peptides, we studied, experimentally and theoretically, the following tailored peptides: Gly-Gly-Gly-Gly-Xxx where Xxx is the basic residue Arginine, Histidine or Lysine (i.e. the singly-protonated peptides contain a protonated side chain and a non-protonated N-terminus), Pro-Gly-Gly-Gly-Gly and Gly-Gly-Gly-Gly-Gly (protonation on N-terminus), Ac-Gly-Gly-Gly-Gly-Gly (backbone protonation) and Gly-Gly-Gly (controversial protonation site)<sup>[3],[4]</sup>.

The NEXAMS experiments have been carried out at the P04 soft X-ray beamline of the PETRA III synchrotron (DESY, Hamburg, Germany) using our home-built tandem mass spectrometer and at the UE52\_PGM Ion trap endstation of the BESSY II synchrotron (HZB, Berlin, Germany). The analysis was supported by calculations of the electronic transitions of the most stable conformers obtained with a REMD (Replica Exchange Molecular Dynamics) method. Results obtained on the custom-made peptides at the nitrogen K-edge will be presented.

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**Chair: Wojciech Gawelda**

- 14:30 - 14:50 | Ori Licht, Department of Physics and the Institute of Nanotechnology, Bar-Ilan University - *Bond formation within amino acids clusters following irradiation by UV light*
- 14:50 - 15:10 | Branislav Milovanović, Faculty of Physical Chemistry, University of Belgrade - *Formation of Cyclobutane Dimers from the Solvated Uracil Stacks*
- 15:10 - 15:30 | Dariusz Kedziera, Faculty of Chemistry, Nicolaus Copernicus University - *Towards an effective description of hydrogen-bonded systems – modification of the hydrogen basis set*
- 15:30 - 16:00 | Sándor Demes, Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) *Recent advances in collisional excitation of interstellar polyatomic molecules*
- 16:00 - 16:30 | Coffee break

**Chair: Ewa Erdmann**

- 16:30 - 17:00 | Arno Ehresmann, Institute of Physics, University of Kassel - *Energy and charge transfer processes in clusters investigated by photon and multi-coincidence spectroscopies*
- 17:00 - 17:20 | Judit Montes de Oca, Institute of Fundamental Physics, IFF-CSIC - *New kernel-based machine-learning potential energy surfaces for spectroscopic characterization of Ng-containing molecules: the case of  $[Ar_2H]^+$*
- 17:20 - 17:40 | Jelena Maljkovic, Institute of Physics, University of Belgrade *Elastic electron scattering on the anesthetic molecules in the gas phase*
- 18:00 - 22:00 | Roof top evening

## Bond formation within amino acids clusters following irradiation by UV light

Ori Licht<sup>1\*</sup>, Dario Barreiro Lage<sup>2</sup>, Patrick Rousseau<sup>3</sup>, Alexandre Giuliani<sup>4</sup>, Aleksandar Milosavljevic<sup>4</sup>, Laurent Nahon<sup>4</sup>, Yitzhak Mastai<sup>5</sup>, Sergio Díaz -Tendero<sup>2</sup> and Yoni Toker<sup>1</sup>.

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With the goal of understanding how large and complex molecules can form abiotically, including in the interstellar medium, we have explored bond formation (PBF) within clusters. We focused on protonated serine clusters. Despite extensive works, by our group and others, peptide bond formation hasn't been observed so far in serine clusters following collision-induced dissociation (CID). We have studied photo-fragmentation of serine clusters following irradiation by UV light.

We have found that irradiation of protonated serine dimers by UV-light results in an efficient fusing of the two monomers and the creation of covalently bonded molecules, which was validated by MS<sup>3</sup> experiments. Moreover, the fragmentation channel depends strongly on photon energy. Furthermore, our results suggest that peptide bond formation is involved in the fragmentation process leading to these covalently bonded molecules.

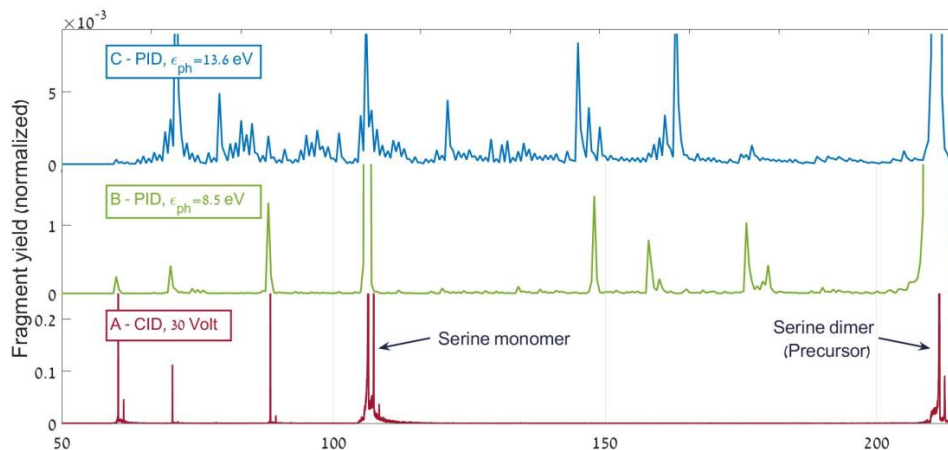


Figure 1: A comparison of CID (A) to PID (B-C) for the protonated serine dimer.

### Acknowledgements

The authors acknowledge the support from MD-GAS COST network (CA18212).

## Formation of Cyclobutane Dimers from the Solvated Uracil Stacks

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In the biological environment, RNA is prone to absorb UV light upon which the formation of intra- and inter-strand crosslinks of cyclobutane-type is possible. Mutual orientation of the nucleobases could be important since it could lead to the different photochemical products. To resolve photochemistry behind this, comparative nonadiabatic molecular dynamics study of microsolvated face-to-back (F2B) and face-to-face (F2F) stacked uracil clusters is performed using the second-order algebraic-diagrammatic-construction (ADC(2)) method. Around the half of the simulated trajectories of the microsolvated F2B stacks excited at 260 nm relaxed non-reactively to the ground state by an ethylenic twist around the one of the uracils C=C bond ( $\pi\pi^*/S_0$  CoIn) and the other half remained in the lowest  $n\pi^*$  state in which stack dissociation is observed. The dissociation of the F2B stack rule out possibility of the cyclobutane uracil dimer (CUD) formation through the triplet manifold ( $^3\pi\pi^*$  state). However, somewhat constrained translational motion of the uracils within the RNA environment could still facilitate dimerization. Photodynamics observed on this model system suggest low propensity towards CUD formation for the F2B stacks, i.e., intra-strand CUD between adjacent RNA uracils. On the other hand, analysis of the microsolvated F2F uracil stacks simulated trajectories revealed several pro-reactive trajectories in which nascent CUD product could be recognized. At the end of the simulated trajectories F2F stack reside near  $\pi\pi^*/S_0$  CoIn. These findings confirm, on the qualitative level, experimental finding that there is a greater tendency of RNA to form inter-strand cyclobutane-type crosslinks, i.e., cyclobutane-type products between the bases that are geometrically close, but distant in the primary structure. Example of such geometrical arrangement occurs in the RNA hairpin loops.

### Acknowledgements

This research has been supported by the Humboldt Foundation Linkage Programme and the Croatian Science Foundation (HRZZ) grants IP-2016-06-1142 and IP-2020-02-9932. B. M. and N. D. acknowledge the COST Action CA18212 (MD-GAS).

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## Towards an effective description of hydrogen-bonded systems : modification of the hydrogen basis set

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An adequate description of the properties of the hydrogen-bonded system, such as interaction energies or vibrational frequencies, with high accuracy, still remains challenging. We are mostly limited not by quantum chemical methods but rather by the size of the systems we deal with. Even in the case of medium-size molecules, the number of basis functions required for reproducing the properties of interest with the desired accuracy strictly limits the possibility of using advanced methods. Therefore, extended investigation of the influence of the basis set on the quality of obtained results is still of concern to society.

In order to meet this demand, the basis set effect on interaction energies, and fundamental frequencies for (HF)<sub>2</sub> and (H<sub>2</sub>O)<sub>2</sub> will be examined with the use of well-established Dunning's<sup>1</sup>, Jensen's, and Weigend's basis set families. These results will be further compared with those obtained with the recently constructed MAX (Modify Augmented X-zeta) basis set family<sup>2</sup>. Finally, promising applications of MAX basis for estimation of fundamental frequencies will be presented.

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## Recent advances in collisional excitation of interstellar polyatomic molecules

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Recent astronomical observations have been showed that the interstellar molecular clouds exhibit a very rich and complex chemistry [1]. To determine the chemical composition of these environments, a non-LTE analysis of the emission spectra is required. Such analysis however requires the prior collisional rate coefficients, since collisions, in competition with radiation, are responsible for the molecular excitation in interstellar clouds.

We report here our recent advances in rotational excitation studies of hydronium ( $\text{H}_3\text{O}^+$ ) and ammonia ( $\text{NH}_3$ ) molecular species in collision with  $\text{H}_2$  projectile. Both of these molecules are abundant in the interstellar medium (ISM), they have been detected in several interstellar molecular clouds [2,3].

State-to-state rotational de-excitation cross sections were computed using the exact close-coupling method [4]. The corresponding rate coefficients were derived up to 300 K kinetic temperatures for the  $\text{H}_3\text{O}^+$  and up to 800 K for the  $\text{NH}_3$  target species. A detailed analysis of the cross sections and rate coefficients was performed for both molecules. The use of these new molecular data in non-LTE radiative transfer models compared to the use of previously available data has a significant impact on the determination of the molecular abundance in molecular clouds.

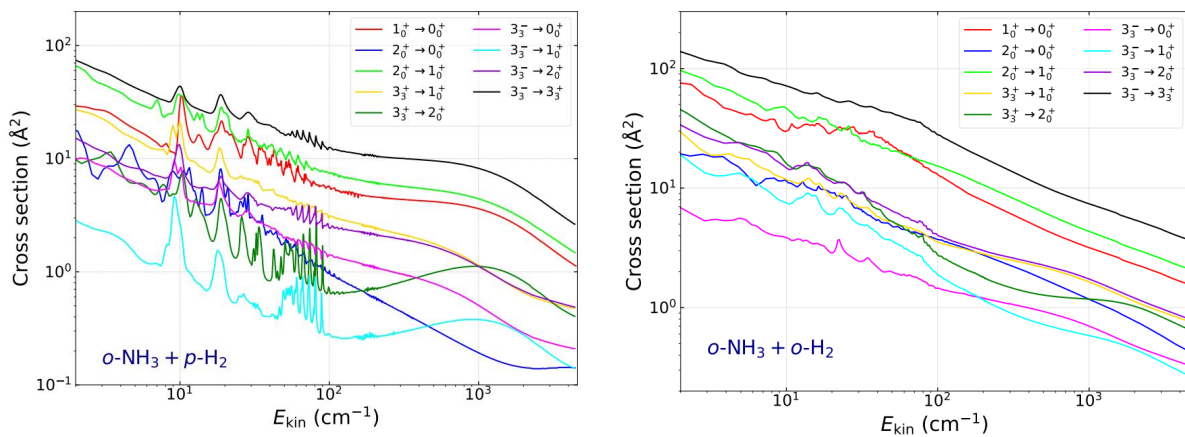


Figure 1: The variation of the state-to-state rotational de-excitation cross sections for the collision of *ortho*- $\text{NH}_3$  with *para*- $\text{H}_2$  (left) and *ortho*- $\text{H}_2$  (right) as a function of kinetic energy.

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## Energy and charge transfer processes in clusters investigated by photon and multi-coincidence spectroscopies

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The understanding of interactions between ionizing electromagnetic radiation and weakly bound dense matter is the basis for the development of measures to avoid hazardous effects in biologically relevant systems and to develop treatments for diseases occurring as consequences of such processes in living entities. Weakly bound clusters are prototypical systems to study such interactions as they can be prepared easiest as compared to real, naturally occurring, weakly bound matter. Almost 20 years ago an at that time new non-local energy transfer process (Interatomic Coulombic Decay, ICD) has been experimentally proven [1,2] based on a suggestion of previous theoretical work [3]. In the following years many other mechanisms involving non-local charge or energy transfers in clusters have been additionally identified [4]. All in all, these manifold of processes lead to a larger probability that slow electrons are created by ionizing radiation in weakly bound matter, which, in turn, are strong candidates to cause electron impact induced double strand breaks of DNA molecules, the latter being the main cause for the biotoxicity of ionizing radiation.

Although clusters are comparatively easy to prepare, the investigation and identification of individual processes in such nevertheless complex systems is not trivial. As all processes initiated by the short-wavelength photons are occurring simultaneously, one of the biggest challenges in such experiments is to disentangle these processes. Here I will show how a combination of photon and electron spectroscopies opens up routes for the determination of cross sections for cluster-specific processes and how multi-electron coincidence spectroscopies and electron-photon as well as electron-electron-photon spectroscopies are strong tools for the identification of individual processes. In particular, processes where the emission of photons are involved have rarely been investigated by coincidence techniques as photons typically are detected from a comparatively small solid angle as compared to, e.g., full solid angle electron extraction methods (like magnetic bottle setups). An appropriate reflection optic has been developed to tackle this challenge. The inclusion of photons in coincidence techniques opens new possibilities for such investigations and has already identified a process not observable by detection of charged particles alone, namely the radiative charge transfer (RCT) [5].

### Acknowledgements

Support by the great people of BESSYII, PETRAIII and SOLEIL is gratefully acknowledged

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## New kernel-based machine-learning potential energy surfaces for spectroscopic characterization of Ng-containing molecules: the case of $[\text{Ar}_2\text{H}]^+$ .

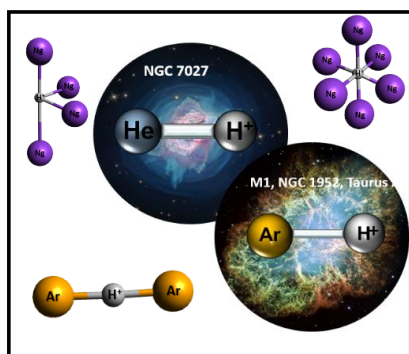
Montes de Oca Estévez M.J.<sup>1,2, a,\*</sup>, Prosmi R.<sup>1</sup>

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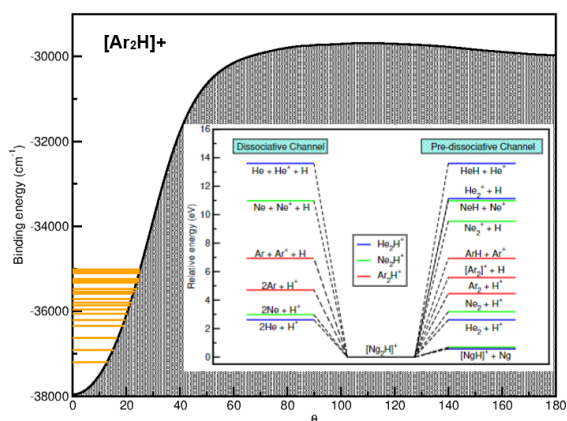
**Figure 1.** Visual description of  $\text{HeH}^+$  and  $\text{ArH}^+$  discoveries [1,2], as well as higher-order noble gas containing molecules.

Not long ago, the interstellar medium (ISM) was considered an adverse environment to molecular systems due to the extreme conditions associated with it and, for that, only a limited number of molecules could be formed. However, this viewpoint has shifted dramatically in recent decades, with over 240 compounds discovered in space. Several of the molecules formed are unusual, and quantum chemistry is an excellent tool for exploring and understanding their properties, particularly in cases where experimental methods fall short. A clear example of this is the recently recorded presence of  $\text{ArH}^+$  and  $\text{HeH}^+$  [1] in the ISM (see Fig.1) since until now they were considered little reactive species. For that, the main goal of this work is to explore trends and models for data science research, in order to propose action protocols for carrying out computational quantum chemistry investigations providing astro-chemically relevant data for identifying new noble gas containing molecules potentially detectable in the ISM.

To this end, a data-driven approach is proposed to construct a new full ML-PES based on kernel method for the computational characterization of such  $\text{Ng}_n\text{H}^+$  species in order to understand the chemical bonding and electron sharing of the simplest noble gases hydride cations cluster  $[\text{Ng}_2\text{H}]^+$ , and further to provide spectroscopic data through quantum chemical tools [3,4] (see Fig.2). Such accurate predictions on energetics and spectroscopic properties could facilitate the astrochemical detection of such noble gas compounds in some ISM regions. In the same way, the comparison with the previously reported values indicates that the present data could serve as a benchmark for future on higher-order cationic  $[\text{Ng}_n\text{H}]^+$  of astrophysical interest.

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**Figure 2.** Minimum potential energy path together with bound vibrational levels, as well as energies of dissociative and predissociative channels of  $\text{Ar}_2\text{H}^+$  using the CCSD(T)/CBS [56] RKHS PES.

## Elastic electron scattering on the aneathetic molecules in the gas phase

J. B. Maljković<sup>1\*</sup>, J. Vukalović<sup>1,2</sup>, Z. Pešić<sup>3</sup>, F. Blanco<sup>4</sup>, G. García<sup>5</sup>  
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We have investigated elastic electron scattering cross sections from anesthetics molecules in the gas phase for intermediate impact energies. Measurements of the elastic differential cross sections (DCS) have been performed with a crossed electron-target beam apparatus UGRA [1], settled at the Institute of Physics in Belgrade. Relative DCSs were put on an absolute scale by using the relative flow technique [2]. Calculations are based on Independent Atom Model (IAM) by using the screening corrected additivity rule (SCAR) technique and including interference effects. Measurements have been carried out for anesthetics molecules, such as sevoflurane [1] and halothane. Absolute DCSs for elastic electron scattering from halothane at 200, 250, and 300 eV are presented in Figure 1.

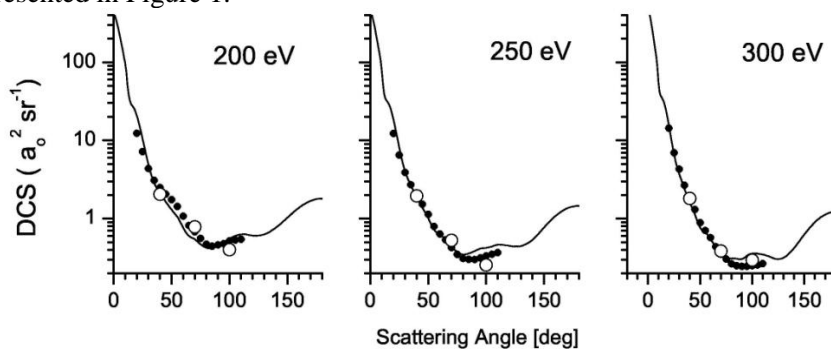


Figure 1: Angular dependence of the DCSs for elastic electron scattering from halothane at 200, 250 and 300 eV. Circles represent absolute experimental differential cross sections; open circles represent absolute values obtained by relative flow method and solid lines represent calculations.

### Acknowledgements

We acknowledge the financial support of MESTD supplied via Institute of Physics Belgrade. This collaborative work has been undertaken under COST Action CA18212 MD-GAS.

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**2.4 Friday 7<sup>th</sup>****Chair: Rita Prosmi**

- 10:00 - 10:45 | Patrik Španěl, J. Heyrovský Institute of Physical Chemistry of the ASCR  
- *Gas phase ion molecule reactions and their application to (B)VOC analyses*
- 10:45 - 11:15 | Coffee break

**Chair: Sergio Díaz-Tendero**

- 11:15 - 11:45 | Mathieu Gisselbrecht, Department of Physics, Lund University *Fragmentation of molecular clusters using synchrotron radiation*
- 11:45 - 12:15 | Yoni Toker, Institute of Nanotechnology and Advanced Materials, Bar-Ilan University - *Can Symmetric Molecules Cool Down In the Interstellar Medium?*
- 12:15 - 12:45 | Karoly Tokesi, Institute for Nuclear Research (ATOMKI), Debrecen, Hungary - *Significant improvement in the classical treatment of one-electron atomic systems with the addition of the Heisenberg correction– ionization, state selective electron capture cross sections*
- 12:45 - 13:05 | Nicolina Pop, Politehnica University of Timisoara *The electron scattering on  $H_2^+$ ,  $BeH^+$  molecular cations (and isotopologues): Dissociative recombination and vibrational transitions*
- 13:05 - 14:30 | Lunch break

## Gas phase ion-molecule reactions and their application to (B)VOC analyses

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Ion–molecule reactions (IMR) are at the very core of trace gas analyses in modern chemical ionization (CI) mass spectrometer instruments, which are increasingly being used in diverse areas of research and industry. Special attention is given to the soft chemical ionization method known as selected ion flow tube-mass spectrometry (SIFT-MS). The processes involved in the ion chemistry of the reagent cations,  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{O}_2^+$ , will be discussed in some detail. Understanding these processes is mandatory to obtain reliable analyses of humid gaseous media such as ambient air and exhaled breath. It is indicated that further research is needed to understand the consequences of replacing helium in some situations with the more readily available nitrogen as the carrier gas in SIFT-MS.

Interesting examples will include charge transfer to isoprene studied over a range of ion–molecule interaction energy,  $E_r$ , (0.05–0.8 eV) in a helium-buffered selected ion flow-drift tube, SIFDT (Figure 1). Contrary to the ion-induced dipole capture model,  $k$  for the  $\text{NO}^+$  and  $\text{O}_2^+$  charge transfer reactions almost doubled over the  $E_r$  range, while  $k$  for the  $\text{H}_3\text{O}^+$  proton transfer reaction did not significantly change with  $E_r$ , as predicted. Similar behaviour was observed for some ketones, where near-resonant product state-to-state transitions allow charge transfer to occur at a relatively long distance between the reactants.

Also interesting are ligand switching reactions of protonated acetic acid hydrates,  $(\text{CH}_3\text{COOH})\text{H}^+(\text{H}_2\text{O})_n$ , with acetone molecules,  $\text{CH}_3\text{COCH}_3$ , producing mostly  $(\text{CH}_3\text{COCH}_3)\text{H}^+(\text{CH}_3\text{COOH})$ , with minor branching into  $(\text{CH}_3\text{COCH}_3)\text{H}^+(\text{H}_2\text{O})$ .

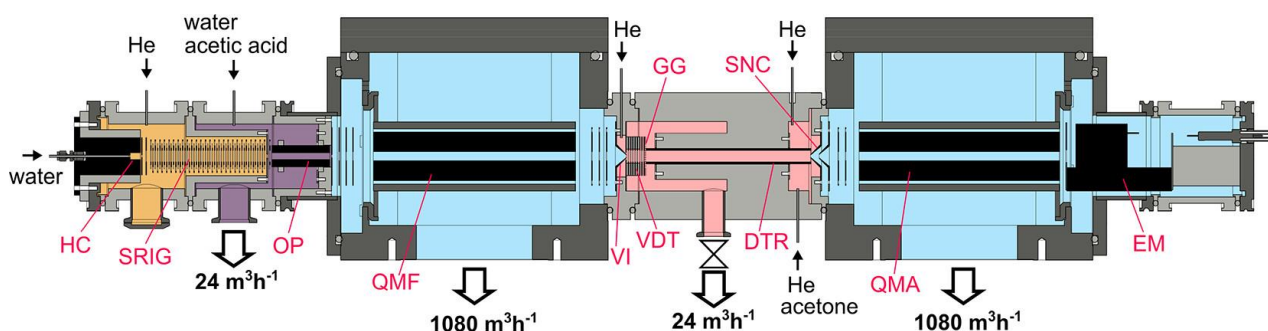


Figure 1: A SIFDT apparatus scheme.

### Acknowledgements

The author gratefully acknowledges financial support from the Czech Science Foundation (GACR; Project No. 21-25486S) and from the *Praemium Academiae* funding by the Czech Academy of Sciences..

## Fragmentation of molecular clusters using synchrotron radiation

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Molecular clusters exist in nature, particularly in the atmosphere where, for example, water clusters are intermediates in cloud formation that significantly contribute to IR absorption [1]. When other molecules, such as NH<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and organic molecules, mix with water clusters, the nucleation mechanism is altered and the resulting cluster can become an important center of condensation [2]. Similarly charged molecular clusters are expected to have a great influence on aerosol particle formation [3]. In this case, the charge transfer mechanisms are of great importance for the reactivity of the particles, in particular for the networks bound to hydrogen. However, a crucial step towards a deeper understanding of charge / proton transfer mechanisms is to study active molecules in-situ with the same level of detail as isolated molecules.

Our approach is to study using synchrotron radiation in the soft X-ray range and advanced 3D charged particle momentum imaging spectrometers, the final ionic products formed during fragmentation. In small clusters, this approach can provide detailed information on energy transfer at the atomic level during the Coulomb explosion (eg [4]). We have extended this technique to larger clusters with sizes of 1 nm containing a few tens of molecules using site selective ionization to localize the initial charges [5,6]. We will present our recent results obtained at MAX IV on several molecular clusters, with a particular emphasis on CO<sub>2</sub> clusters [6]

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## Can Symmetric Molecules Cool Down Radiatively?

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The radiative cooling of  $Al_4^-$  clusters was investigated in the cryogenic storage ring (CSR). The CSR is one of the most advanced laboratory astrophysics facilities, as it allows to store in conditions of low pressure and low temperature similar to those present in the interstellar medium, and perform a wide array of astrophysically relevant experiments. In the present work we focus on the process of radiative cooling. The ability of  $Al_4^-$  cluster to radiatively cool depends critically on the existence of intramolecular vibrational redistribution (IVR), as 3 of the molecules vibrational degrees of freedom are IR-inactive. We show that the clusters do indeed cool down, they do so on a very long time-scale, and that the cooling rate has a power-law dependence on the clusters internal energy. These results are not consistent with the commonly used rapid-exchange limit. Instead, we suggest that the results can be explained by a 'slow-exchange' model which we will introduce in the talk.

## Significant improvement in the classical treatment of one-electron atomic systems with the addition of the Heisenberg correction – ionization, state selective electron capture cross sections

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The standard three-body classical trajectory Monte Carlo (CTMC) model is a well-known classical treatment for modelling atomic collisions [1]. But due to the lack of quantum features in the standard model, the CTMC model is not able to describe accurately the cross sections mostly at lower impact energies when the quantum mechanics characteristic is dominant. Therefore, we developed a three-body quasi classical trajectory Monte Carlo (QCTMC) model taking into account quantum feature of the collision system, where the Heisenberg correction term is added to the standard classical Hamiltonian of the collision system to mimic the Heisenberg uncertainty principle [2-10].

We present ionization, total and state selective cross sections in collisions between fully stripped ions with Hydrogen atoms at the impact energies between 5-200 keV/amu by using CTMC and QCTMC models. We found that our QCTMC model remarkably improves the obtained cross sections, especially at lower projectile energies. Our results are very close and are in good agreement with the previously obtained quantum-mechanical results. Our model with simplicity can time efficiently provide accurate results where maybe the quantum mechanical ones become complicated. Therefore, our model should be an alternative way to calculate accurate cross sections providing the same results as the quantum-mechanical approaches [2-10].

### Acknowledgements

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## The electron scattering on $\text{H}_2^+$ , $\text{BeH}^+$ molecular cations (and isotopologues): Dissociative recombination and vibrational transitions

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The Multichannel Quantum Defect Theory (MQDT) has been employed in computing cross sections and Maxwell rate coefficients for electron-driven reactions of molecular cations - dissociative recombination, vibrational excitation (inelastic collisions), vibrational de-excitation (super-elastic collisions), and dissociative excitation. These data are ready to be used in the modelling of the kinetics of various cold ionized media of fundamental - early Universe, interstellar molecular space - and applied - cold plasma techniques - interest.

At very low energy, we extended our previous studies to reactive collision of  $\text{HD}^+$  [1],  $\text{H}_2^+$  [2] and  $\text{D}_2^+$  [3] with electrons in a wide range of incident collision energy and to mixed rotational and vibrational transitions. We report cross sections and Maxwellian rate coefficients of both rotational and vibrational transitions, from the lowest 30 ro-vibrational levels and outline several important features, like isotopic, rotational and resonant effects, typical for very low energies of the incident electron.

We have produced cross sections and thermal rates for  $\text{BeH}^+$  [4],  $\text{BeD}^+$  [5] and  $\text{BeT}^+$  [6] at moderately low energy, where the rotational effects are negligible. One of the important outcomes of our studies is the isotopic effect. New computations are ongoing presently, on extended energy/temperature range, up to 12 eV/30000 K, where dissociative excitation competes the other collision processes and plenty of highly-excited dissociative states contribute to the dynamics.

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### **3 Abstracts - Posters**

## **Tuning of photophysical properties of squaraines with weak intermolecular interactions**

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The growing interest in the precise manipulation of photophysical properties of dyes stimulates the development of strategies for the precise and controlled maximum absorption shift, enhancing the two-photon absorption, excited triplet state population or fluorescence quantum yields. However, most of these strategies are based on the modification of the dye structure by extending the  $\pi$ -electron scaffold and increasing the intramolecular charge transfer. Such an approach leads to the growing problems with solubility of the large aromatic molecules together with their eager aggregation via the dispersion forces. Additionally, it provides usually only the limited range of adjustments. The consequence of the self-assembly process is often the quenching of the fluorescence, what makes the dye useless. Therefore, the focus on the small dye molecules and their weak interactions can be highly beneficial from the photophysical perspective. The present study is devoted to the squaraine dyes, well-recognized for their sharp absorption band in near-IR region and intensive fluorescence. These features make squaraines a interesting object for the photovoltaic, biomedical and analytical applications among others [1,2].

The main aim of the project is to develop the supramolecular strategy of rational design of small squaraine systems for optimization of their photophysical features with respect to their applications. The strong directionality and larger diversity of halogen bonds with respect to the conventional hydrogen bonds is expected to provide numerous alternatives of a dye non-covalent binding, depending both on the bond donor character and the squaraine structure itself [3]. It can be assumed that the careful selection of the sequence of electronic, structural and environmental factors such as symmetric or asymmetric modification of the central squaric ring, the symmetric or asymmetric substitution of the dye with heteroaromatic fragments, introduction of the strong electron-donating substituents or the insertion of the bulky groups preventing stacking or the competitive interactions in solution can lead to the intentional enhancements of the photophysical properties. In order to verify the origins of these modifications and generalize the observations, the theoretical chemistry methods will be applied.

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## **Investigation of collisional processes involving molecular ions relevant for laboratory and astrochemistry: new data sets**

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Atomic and molecular data and databases have become essential for diagnostics and development of models and simulations of complex physical processes and for the interpretation of data provided by. It is crucial to emphasize how important it is to examine the optical properties in various fields, especially when modeling those systems [1]. If we have the relevant data, we could simulate spectral characteristics [2]. The collisional processes of electrons with systems involving hydrogen and alkali molecules and molecular-ions have been investigated. We obtained new datasets i.e. the cross-sections and corresponding rate coefficients. The plasma parameters i.e. conditions cover temperatures from 1,000 to 10,000 K and wavelength in EUV and UV region. The results i.e. the obtained data could be used for further applications, e.g., for some modelling or experiments like PLEIADES (SOLEIL synchrotron). Moreover, data could be useful for plasma diagnostics in astrochemistry, and also for industry.

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## Radiative and collisional processes in small molecules: A&M data

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Collisional and radiative atomic/molecular processes are of great importance for the investigation of the different environments within our universe. Especially nowadays, atomic and molecular (A&M) data and databases [1, 2] have become essential for developing models and simulations of complex physical/chemical processes and for the interpretation of results and data provided by observations and measurements, e.g., laboratory plasma, planetary atmospheres, ionosphere, etc [3, 4]. Also, these data can be used for further applications, e.g., for non-local thermal equilibrium modeling of early universe chemistry, modeling of the solar atmosphere, atmospheres of white dwarfs, etc. Therefore, there is a need for developing new methods and models and for improving the existing ones by including as many processes as possible and using more accurate data which can be properly included in modern codes. Our aim is to determine high quality data. The main objective is to obtain, cross-sections and rate coefficients for some collisional and radiative processes, for conditions that exist in laboratory plasmas, planetary atmospheres, ionosphere, etc.[5].

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## Vibrationally resolved photoelectron angular distributions of ammonia

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We present a theoretical study of vibrationally resolved photoelectron angular distributions for ammonia in both laboratory and molecular frames, in the photon energy range up to 70 eV, where only valence and inner-valence ionization is possible. We focus on the band resulting from ionization of the  $3a_1$  HOMO orbital leading to  $\text{NH}_3^+$  in the electronic ground state, for which the dominant vibrational progression corresponds to the activation of the umbrella inversion mode. We show that, at room temperature, the photoelectron angular distributions for randomly oriented molecules or molecules whose principal  $C_3$  symmetry axis is aligned along the light polarization direction are perfectly symmetric with respect to the plane that contains the intermediate  $D_{3h}$  conformation connecting the pyramidal structures associated with the double-well potential of the umbrella inversion mode. These distributions exhibit symmetric, nearly perfect two-lobe shapes in the whole range of investigated photon energies. In contrast, for molecules where the initial vibrational state is localized in one of the two wells, a situation that can experimentally be achieved by introducing an external electric field, the molecular-frame photoelectron angular distributions (MFPADs) are in general asymmetric, but the degree of asymmetry of the two lobes dramatically changes and oscillates with photoelectron energy. We also show that, at ultracold temperatures, where all aligned molecules initially lie in the delocalized ground vibrational state, the photoelectron angular distributions are perfectly symmetric, but the two-lobe shape is only observed when the final vibrational state of the resulting  $\text{NH}_3^+$  cation has even parity. When the latter vibrational state has odd parity, the angular distributions are much more involved and, at photoelectron energies of 10 eV, they directly reflect the bi-pyramidal geometry of the molecule in its ground vibrational state. These results suggest that, in order to obtain structural information from MFPADs in ammonia and likely in other molecules containing a similar double-well potential, one could preferably work at ultracold temperatures, which is not the case for most molecules.

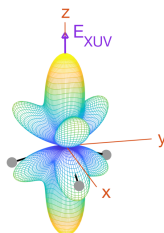


Figure 1: Photoelectron angular distributions of ammonia reflect, under special circumstances, the double-well potential of its umbrella mode.

## Benzene oxidation in collisions with superoxide anions in the gas phase

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Superoxide anion,  $O_2^-$ , is one of the reactive oxygen species (ROS) which are responsible for numerous biochemical processes leading to oxidative damage in living organisms [1] as well as in materials [2]. In particular, 8-oxoguanine is frequently formed by the interaction of ROS with the guanine base in DNA under conditions of oxidative stress, yielding an efficient way of damaging DNA [3].

We have studied in a combined theory and experimental approach the collision of  $O_2^-$  with benzene, as a prototype molecule. We have shown [4,5] that superoxide anions colliding with benzene molecules form massive complexes. In this communication we present quantum chemistry calculations to understand the production of such complexes. We propose a mechanism in which a sudden double ionization of benzene and the subsequent electrostatic attraction between the dication and the anion form a stable covalently bonded  $C_6H_6O_2^+$  molecule, that evolves towards the formation of benzene-diol conformers. These findings lend support to a model presenting a new high energy anion-driven chemistry as an alternative way to form complex molecules.

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## **Mass spectrometry at the limits of biological objects: viruses, bacteria and amyloid fibers**

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Bioparticles consisting of self-organized biomolecular assemblies are ubiquitous in nature. Viruses are a good example of this and are the most abundant and robust biological entities on Earth.

New electrostatic traps (Benner trap) based on charged detection mass spectrometry (CDMS) have recently been set up to carry out fragmentation experiments on selected ions with masses up to several GigaDalton [1]. One of this setup has been developed in the SpectroBio group of iLM at University of Lyon 1, allow coupling with a laser and performing infrared multiphoton dissociation, monitoring fragmentation and determining the activation energy of unimolecular dissociation of bioparticles and whole DNAs [2,3,4].

A large part of this project will be to develop both an analytical chemistry approach to characterize bioparticles by mass spectrometry, and to push the limits of photo-fragmentation induced by laser irradiation on intact viruses or other bioparticles (bacteria or amyloid fibers) to develop new structural characterization tools.

This project is part of the FET-OPEN ARIADNE VIBE (Airborne Ion Analysis with Dissociation and Non-destructive Evaluation of Viruses and Bacteria – Grant agreement 964553) funded by Europe on the characterization of viruses and bacteria using CDMS technique.

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## **Electronic resonances in $N_2^-$**

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The XCHEM method<sup>1</sup> allows the study of the metastable state of the anionic molecular nitrogen molecule and its ultrafast autodetachment into neutral molecular nitrogen. At the core of the XCHEM method lies the Gaussian-B-spline basis (GABS)<sup>2</sup>, used to represent bound and continuum states. It has been successfully applied to cations, such as neon<sup>2</sup>, nitrogen<sup>3</sup> and carbon monoxide<sup>4</sup>. In this communication, we present for the first time results for a diatomic anion, the nitrogen anion.

$N_2^-$  resonant state has been thoroughly studied before and extensive data is available. Therefore, this work serves as a benchmark for the usage of this XCHEM formalism in the study of resonances in anionic species, comparing the results with the aforementioned data that is accessible. XCHEM has never been used before in the study of these anionic states, and for future works it is important to assess the validity of this method.

The results are in close agreement with the theoretical and experimental data, surpassing several methods in the accuracy of the calculation of the  $E_R$  resonant energy and  $\Gamma$  width of this resonant state. These values establish the XCHEM formalism as a valid method for the analysis of these resonant states.

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## Double ionization of S<sub>2</sub>

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Disulfur, S<sub>2</sub>, is a reactive intermediate molecular species, which is of great interest from both a fundamental perspective, due to its similarity to molecular oxygen, and for a number of applied scientific aspects. In particular, it is astrophysically significant, where it is known to be important in the atmospheres of Jovian planets. Whereas the single ionization photoelectron spectrum of S<sub>2</sub> is known from the work of Dyke and coworkers [1] the double ionization photoelectron spectrum of S<sub>2</sub> is still unknown. Previous experiments also reported a surprisingly low energy for doubly ionized S<sub>2</sub> [2], which calls for new, independent experiments.

Using time-of-flight multiple electron and ion coincidence techniques, in combination with a helium gas discharge lamp and synchrotron radiation, the double ionization electron spectrum and fragmentation dynamics of disulfur (S<sub>2</sub>) are investigated. S<sub>2</sub> was produced by resistively heating mercuric sulfide (HgS), whose vapour at a suitably chosen temperature consists primarily of S<sub>2</sub> and atomic Hg. A multi-particle-coincidence technique is particularly advantageous for retrieving spectra of S<sub>2</sub> from ionization of the vapour. The results obtained are compared with detailed calculations performed with highly correlated *ab initio* methods, such as CASSCF followed by MRCI for the electronic structure and potential energy curves of S<sub>2</sub>, and RCCSD(T) for total energies and dissociation limits. Our new experimental findings strongly agree with these theoretical results [3].

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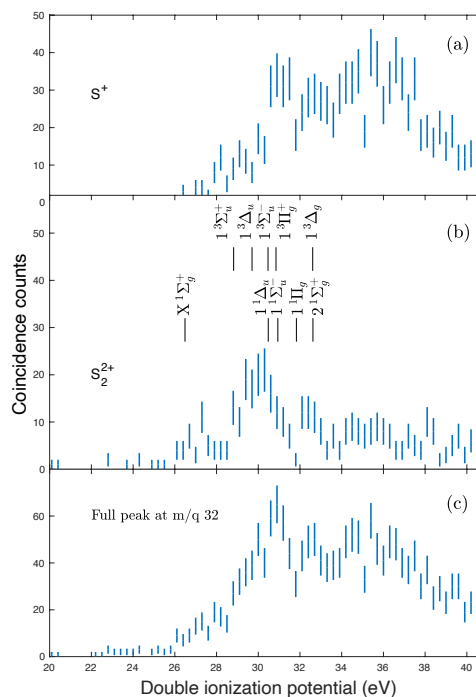


Figure 1: Double ionization electron spectra at the photon energy of 40.81 eV. Each spectrum is based on electron pairs extracted in coincidence with all ions at mass/charge 32 (c), S<sub>2</sub><sup>2+</sup> ion (b) or one of its S<sup>+</sup> fragments (a). The middle panel also shows calculated vertical double ionization energies from the ground state of neutral S<sub>2</sub>.

## Kinetics of the OH+CH<sub>3</sub>NH<sub>2</sub> reaction in the gas-phase as a function of interstellar temperatures

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As the temperature ( $T=10-100$  K) and the gas density ( $n=10^2-10^6$  cm<sup>-3</sup>) are extremely low in the Interstellar Medium (ISM), it is a challenge to experimentally mimic these conditions to study the chemistry of this cold environment. Furthermore, to model the chemical evolution of the ISM astrochemical models are necessary. One of the parameters required by these models are the rate coefficients,  $k(T)$ , for radical-molecule gas-phase reactions, e.g. the reactions of the hydroxyl (OH) radical with interstellar species, such as methylamine (CH<sub>3</sub>NH<sub>2</sub>). Most of them are not known at IS temperatures. For this reason, in this work, the kinetics of the reaction of OH with CH<sub>3</sub>NH<sub>2</sub> have been studied experimentally at ultra-low temperatures. The rate coefficients,  $k(T)$ , were determined using the most powerful pulsed CRESU<sup>1</sup> reactor worldwide [1], which is able to reproduce ultra-low temperatures between 11.7 K and 177.5 K [2] from the uniform supersonic expansion of a buffer gas (He, Ar, N<sub>2</sub> or binary mixtures with N<sub>2</sub>) from a high-pressure reservoir to a vacuum chamber through a convergent-divergent asymmetric device. This device is known as Laval nozzles and were specifically designed to produce a specific temperature. To perform the kinetic study, the pulsed laser photolysis of H<sub>2</sub>O<sub>2</sub> at 248 nm was used to generate OH radicals and the laser induced fluorescence of OH at 308 nm was monitored as function of the reaction time. Recently, our group published  $k(22$  K) for this reaction showing a huge increase of  $k(T)$  with respect to that at room temperature [3]. This increase of the rate coefficient of the OH+CH<sub>3</sub>NH<sub>2</sub> reaction when decreasing temperature is confirmed in the present work over a wide temperature range. In contrast,  $k(T)$  at  $T>550$  K exhibits an Arrhenius behaviour, according to theoretical calculations [4].

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<sup>1</sup> CRESU stands for the French acronym of "Cinétique de Réaction en Ecoulement Supersonique Uniforme"



## An ab initio calculation of electron capture in proton collisions with CO<sub>2</sub>

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Collisions of protons with CO<sub>2</sub> molecules are abundant in the solar wind interaction with planets, moons and comet atmospheres. However, these processes have been the subject of a limited number of experimental works and the only theoretical counterpart available employs a simple two-state ion-atom model (see [1]). In a recent work [2], we aim at calculating the single electron capture (SEC) cross sections in H<sup>+</sup> + CO<sub>2</sub> collisions for energies in the range  $0.1 \leq E \leq 50$  keV. We employ a semiclassical treatment where the ion-molecule relative motion is described by means of projectile classical trajectories, while the electronic degrees of freedom are treated quantally. Our calculations consider the anisotropy of the molecular target, and we perform an average over different molecular orientations to compare with the experimental cross sections; a very good agreement is observed, as shown in Figure 1.

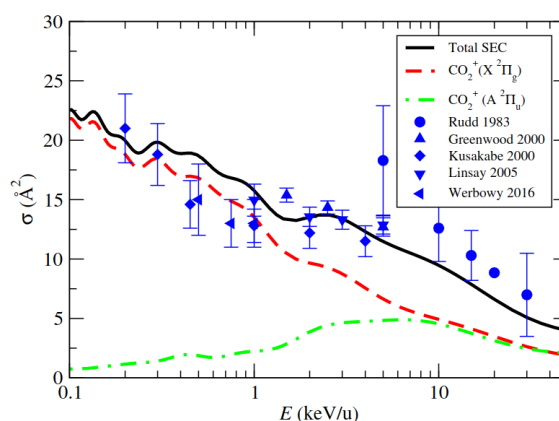


Figure 1: Orientation-averaged SEC cross-section in proton collisions with CO<sub>2</sub> as a function of impact energy,  $E$ . Lines are the present calculations: solid line, total EC; broken lines indicate the production of different cations (indicated in the figure). Symbols are experimental data.

### Acknowledgements

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## An ab initio calculation of electron capture y proton collisions with uracil

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The interaction of protons with the building blocks of DNA is of great interest in view of the increasing number of proton therapy facilities. When these protons enter the biological tissue, they are decelerated down to keV energies, when they induce molecular ionization either by electron capture or electron emission. However, studies of proton collisions with large molecules are much scarce and single electron cross sections (SEC) with uracil have only been measured by Tabet et al [1] at impact energies of 80 keV, where its contribution to the total ionization of the molecule is about 30%. Here, we carried out an ab initio calculation using multielectronic wavefunctions and the non-perturbative semiclassical eikonal method to obtain the orientation-dependent SEC along three families of projectile-molecule orientations (t1, t2 and t3), as detailed in Figure 1. Orientation-averaged results are also shown in Figure 1.

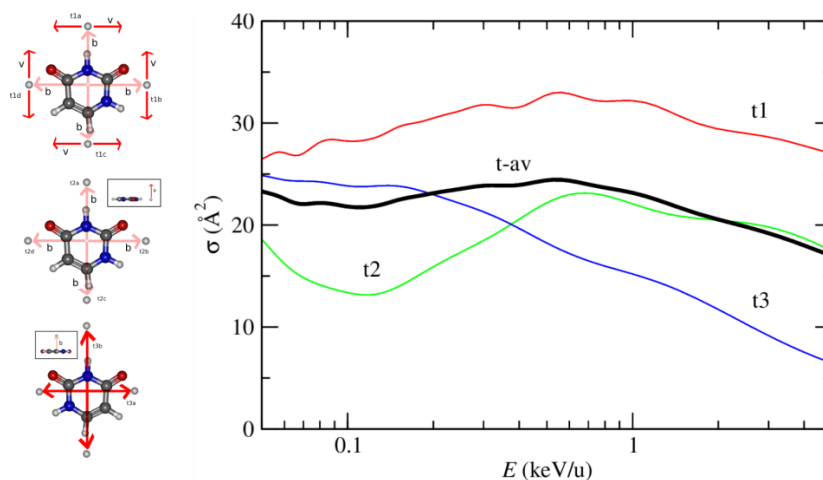


Figure 1: Orientation dependent SEC cross-section in proton collisions with uracil as a function of impact energy,  $E$ . Color lines are the orientation dependent calculations along trajectories indicated in the figure. The oriented averaged results is the thick-black line. The only experimental data [1] available falls above 25 keV.

### Acknowledgements

This work has been partially supported by Ministerio de Economía and Competitividad (Spain), project no. FIS2017-84684-R.

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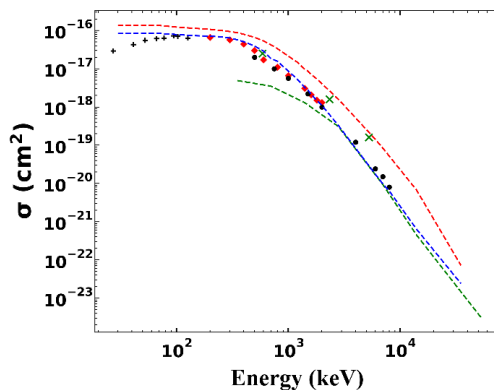
## Ionization and charge exchange cross sections induced in collisions between singly charged ions and He(1s) and N(2p) atoms

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The atomic processes in ion-atom collisions are essential and fundamental in different research areas such as in the interstellar space and in the fusion plasma research [1]. Hence, in order to model and control these processes, accurate cross sections of the induced electron processes must be provided.



**Figure 1.** Total cross sections of the single-electron capture in  $\text{Li}^+\text{-He}(1s)$  as a function of the projectile impact energy. Theory: --- Present CTMC results using model potential --- Present CTMC results using frozen core model, --- Samanta et al. [4]. Experiments: black circle: Woitke et al. [5], red diamond: Pivovaret et al. [6], black plus: Pivovar et al [7], green cross: Dmitriev et al. [8].

In this work we present total cross sections for single-ionization and single charge exchange cross sections in collision between singly charged ions  $A^{q+}$  ( $q = 1$ ) and ground-state helium and nitrogen atoms. We treat the collision problem classically using the three body approximation. The target atoms are described within the single active electron approximation using Garvey model potential where only the outermost electron is involved in the collision dynamics [2]. Regarding the projectile, in the first approximation, it is treated as a frozen core model and the charge of the projectiles are +1 in the entire time of the collision. In the second approximation, the projectile target interaction is described by a model potential which considers the screening effect by the projectile electrons [2]. The scattering problem is solved within the frame of the classical trajectory Monte Carlo (CTMC) [3]. Figure. 1 shows the total cross sections of the single electron-capture process in  $\text{Li}^+\text{-He}(1s)$ . We found that our present CTMC results for both models are in a good agreement with available theoretical and experimental data.

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## Quantum dynamics of the addition of molecular oxygen to organic substrates in absence of cofactors

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Reactions between molecular oxygen and closed-shell organic molecules leading to the formation of stable (closed-shell) adducts involve the change of the spin state of the system, and accordingly should be slow at room temperatures. Some enzymes are capable to catalyze these reactions, even in the absence of cofactors that may promote the intersystem crossing.

One of these reactions is the addition of O<sub>2</sub> to S-methyl-but-3-enethionate that occurs in the active site of the DpgC enzyme. Previous electronic structure calculations<sup>1</sup> showed that this process involves two electron transfer steps, the first of them concomitant with the intersystem crossing. The crossing is produced between a singlet and a triplet state, therefore the spin-orbit coupling becomes an important property to produce the intersystem crossing. The potential energy curves and spin-orbit couplings as a function of R<sub>CO</sub> and  $\varphi$  angle (see Figure 1) are calculated and fitted so that can be used in the quantum dynamics calculations using MCTDH method<sup>2</sup>. The analysis of the flux is used to follow the evolution of the wavepacket along the reaction coordinate (R<sub>CO</sub>, Figure 1).

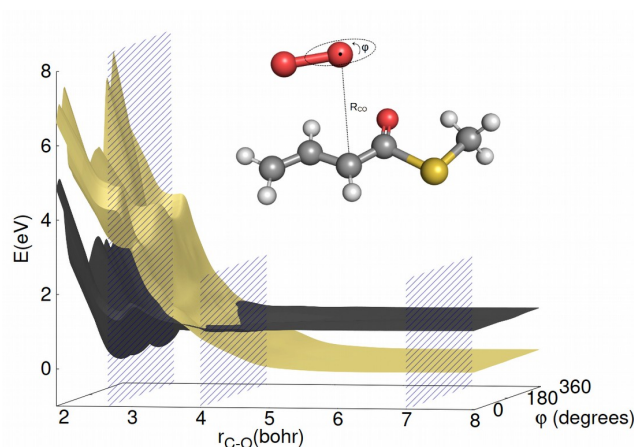


Figure 1: Representation of the 2D PES (as a function of R<sub>CO</sub> and  $\varphi$  for the O<sub>2</sub>+ S-methyl-but-3-enethionate system. The singlet and triplet states are shown in dark grey and golden color, respectively. The planes through which the flux is evaluated are represented in blue color.

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## Excitation and Ionization Cross Sections in H+H Collisions

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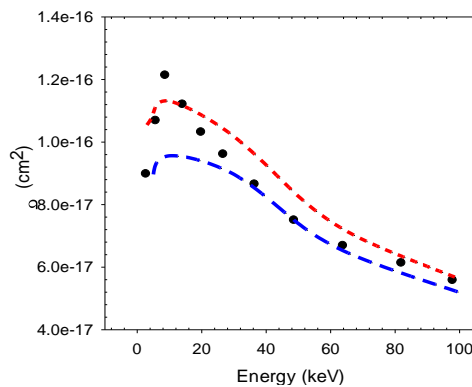
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Classical calculations for determining atomic collision cross sections have received a great deal of interest in the past years in fusion research. Recently, there is a great revival of the CTMC calculations applied in atomic collisions involving four or more particles [1-3]. The CTMC method is a non-perturbative method, where classical equations of motions are solved numerically [1-4]. It was shown, that the quasi-classical trajectory Monte Carlo (QTM) model, where the Kirschbaum and Wilets potential ensures mimicking quantum features of the collisions, improve the results of the standard CTMC model [5].

The main aim of the present work was to develop an accurate theoretical model for the description of inelastic interactions such as ionization, excitation, de-excitation processes for hydrogen-hydrogen type four-body systems.

We present total cross-section data for ionization and excitation in collision between two hydrogen atoms using both the standard 4-body CTMC and the QCTMC method in the projectile energy range between 1.0 keV and 100 keV. According to our knowledge, this is the first time to present cross section data using the QCTMC method for such systems. We used Coulomb potential for describing the interactions among the particles.

Figure 1. shows the projectile ionization cross sections as a function of impact energy. Our results were compared with experimental data. We found reasonably good agreement between the experimental data and our results obtained by QCTMC model, especially at low energies below 25 keV. On the other hand, the standard CTMC calculation shows good an agreement at higher energies above 25 keV, demonstrating that the Heisenberg correction term has stronger influence to the collision dynamics at low energies and it has smaller influence at higher energies.



**Figure 1.** Projectile ionization cross sections in collision between two hydrogen atoms as a function of impact energy. Red short-dashed line: present 4-body QCTMC results. Blue long-dashed line: present standard 4-body CTMC results. Black solid circles: experimental data by McClure [6].

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## Cyanamide radical cation: formation, isomerization and fragmentation

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Cyanamide, NH<sub>2</sub>CN, is a molecule with a large prebiotic potential [1,2]. Since 1975, it has been detected in several astrophysical environments including protostars and starburst galaxies [3]. Cyanamide has also been found in Titan's aerosol analogs (tholins), and it has been proposed as playing a role in the formation of larger nitrogenous organic molecules in Titan's atmosphere [4]. Due to the presence of ionizing radiation and high-energy particles in both the ISM and Titan's upper atmosphere, it is reasonable to assume that cyanamide radical cations, NH<sub>2</sub>CN<sup>+</sup>, play a significant role in these environments.

In the presented study, cyanamide radical cations were prepared by photoionization of neutral cyanamide using VUV photons (beamline DESIRS, synchrotron SOLEIL) in combination with the guided ion beam instrumental setup CERISES [5]. The ionization energy of NH<sub>2</sub>CN and the appearance energies of its fragment ions (11 fragments above *m/z* 11) were measured and compared with both highly accurate (G4 and W1BD level of theory) quantum chemistry calculations and thermochemistry values from literature.

A potential energy surface (PES) of [C, H<sub>2</sub>, N<sub>2</sub>]<sup>+</sup> family isomers (i.e. minima and first-order saddle points) was calculated at B3LYP/cc-pVTZ and MP2(FC)/cc-pVTZ levels of theory. The PES together with the high-resolution electron ionization mass spectra of cyanamide reveals an unexpected complexity of dissociation for such a relatively small molecular system.

### Acknowledgements

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### Magnetically Confined Electron Beam Transmission System: Highly Accurate Total Electron Scattering Cross Section from CO<sub>2</sub>

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Accurate measurements of total cross sections (TCSs) for electron scattering from gaseous molecules are crucial for several major reasons. In particular, they serve as reference values to validate the self-consistency of a given cross section data set. In this sense, accurate measurements of TCSs are very helpful, considering that significant discrepancies between available cross sections are not uncommon. Additionally, at low collision energies, resonance processes which involve the formation of transient negative ions (TNIs) can be experimentally probed independently of their decay pathways. Over the last years, our group has presented TCSs for a vast set of relevant molecules as measured with a state-of-the-art magnetically confined electron beam-transmission experimental system placed at Instituto de Física Fundamental (CSIC, Madrid).<sup>1,2</sup> This apparatus, designed, constructed, and optimized by us, is one of the most accurate ones in providing reliable TCSs for gas-phase molecular targets. Moreover, the small uncertainty (below 5%) and high energy resolution (up to 100 meV) have allowed us to identify many resonant features related to the formation of TNIs for each of the many studied molecule.

In light of our previously obtained results and the experimental system at our disposal, we have revisited simple molecular targets, one of them being CO<sub>2</sub>.<sup>3</sup> In the 1 to 40 eV energy range, we have identified different features related to electron attachment resonances, some of them not reported in previous investigations (see Figure 1).

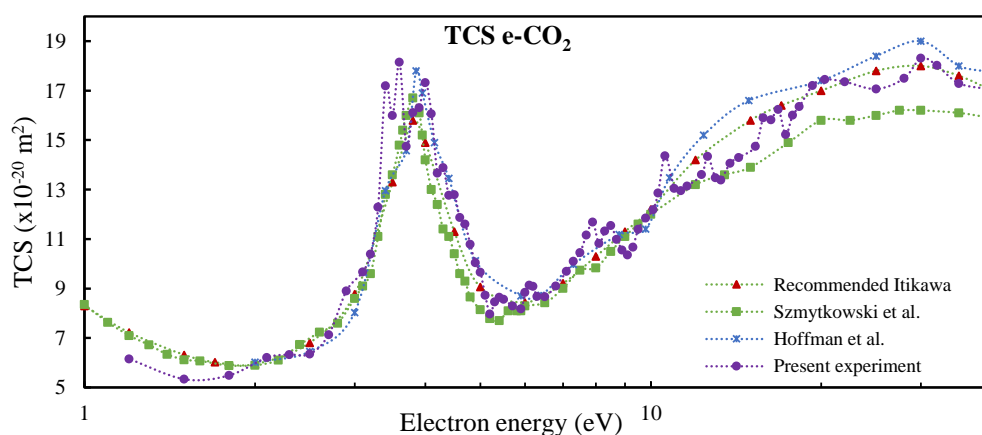


Figure 1. Present total electron scattering cross sections from CO<sub>2</sub> together with the data from refs. 4-6

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## Computational quantum chemistry approaches in CO<sub>2</sub> clathrate-hydrates: from finite-size molecular clusters to extended lattice systems

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Clathrate hydrates are crystalline compounds formed by guest molecules within a three-dimensional host lattice of water cages. These structures have been involved in current technological and industrial applications. Specifically, the CO<sub>2</sub> clathrate has been proposed as a potential molecular material in the fight against environmental problems related to greenhouse gases capture and storage.

The objective of this work is to understand of formation, energetics and structural stability of sI, sII and sH clathrate hydrates to describe the underlying processes at molecular level and determine the guest-host/host-host interactions dominated by hydrogen bonds and van der Waals forces. In particular, we consider two approaches: bottom-up and top-down. The first approach proposes to study the intermolecular interactions in finite-size systems of individual aperiodic cages, such as guest-free and guest-host CO<sub>2</sub> clathrates, and then extrapolate to their entire periodic unit cells. The second approach considers the unit cell that reproduces a periodic crystalline structure, and thus, guest-lattice effects are studied by a systematic evaluation of different density functionals. We consider functionals, including local and non-local dispersion corrections such as the exchange-hole dipole moment (XDM) and the semi-empirical model (DFT-D), as well as vdW-DF and vdW-DF2, respectively.

Our findings show that DFT-D approaches are able to describe properly the underlying interactions, once dispersion corrections are applied. Further, the results obtained allow to generate reference interaction energies from accurate quantum-mechanical calculations by testing different approaches on CO<sub>2</sub>@sI/sII/sH systems. Such studies provide high-quality information with new insights that allow the construction of new reliable data-driven models and in turn have greater control of the properties of this promising material.

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## HOMO-LUMO gap modulation of Indieno [1,2-b] fluorene

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The p-quinodimethane (p-QDM) unit confers to Indieno [1,2-b] fluorene (IF) frameworks antiaromatic character with narrow HOMO-LUMO (HL) gaps, which make these systems more attractive than their aromatic analogs for applications in (opto)electronics. To increase the IFs stability, the highly reactive apical carbons at the five-membered rings are shielded with different protecting groups (-R), which further act as modulators of the properties.<sup>1</sup> Based on previous studies, and through an efficient and versatile engineering strategy, the stability, and the modulation of optoelectronic and magnetic properties of IFs have been accomplished. The first, through the incorporation of 4-substituted-2,6-dimethylphenyl acetylene as a stabilizing group; and the second, taking advantage of the versatility of this group, by varying the electron withdrawing/donating strength of substituent in the 4-position (see figure 1).

In this contribution, we report a reliable theoretical study based on DFT calculations in the gas phase, involving optimized geometries, HOMO-LUMO gaps, DFT-TD vertical excitation energies, diradical character, singlet-triplet gap energies, and nucleus-independent chemical shift indexes (magnetic criteria of aromaticity). Our simulations fully support the experimental results, which show redshifted absorption maxima, corresponding to HL gaps down to 1.5 eV, and diradical character increasing.<sup>2</sup>

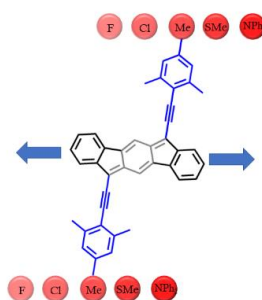


Figure 1: Schematic chemical structure for IFs studied, with protecting and modulator groups.

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## He inclusion in Clathrate-like Frameworks: a first-principles computational study

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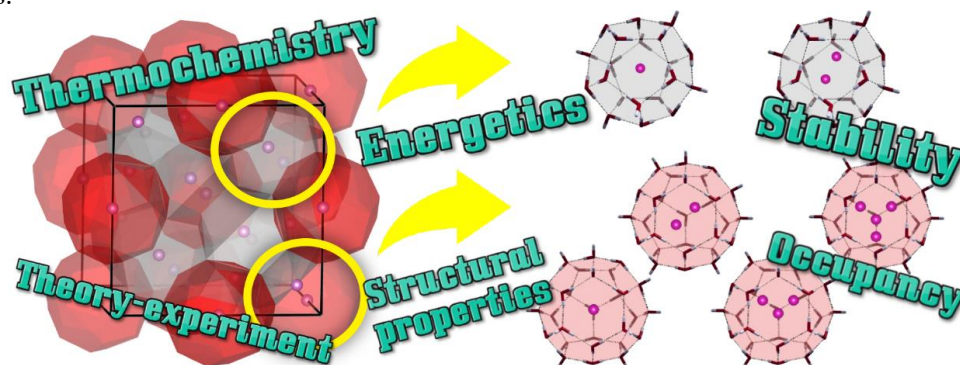
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Clathrate hydrates are in the spotlight due to their interesting properties, as well as their future promising applications. In this context, the computational study of helium clathrate hydrates raises as a motivating and challenging task, since the small size and low reactivity of this noble gas facilitate its removal by pumping from the structure where it is contained. This way, new structures can be synthesized, such as the ultra-low density ices [1].

Focusing on the He@hydrates, we have performed a computational study from the most basic finite-size clathrate-like structures [2-4] to the periodic 3D crystalline frameworks [5,6]. We have first assessed the performance of different DFT-D approaches in comparison with well-converged WF-based data, so as to find the most suitable functional available also for larger structures. In turn, we have analysed the stability of different clathrate-like systems, considering single and multiple cage occupancy, in terms of change in enthalpy, change in Gibbs free energy and change in entropy at a range of T-P conditions comparable to the experiment [7]. Finally, we have explored the effects of the encapsulation of one or several He atoms inside the sI/sII crystals in order to find the most favourable structure and cage occupancy. With this purpose, structural and energetical properties have been computed. All these results allow to acquire a greater knowledge about the interactions that take place in these systems and can benefit research into the development of new data-driven models, as well as the synthesis of new structures.



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## Ultrafast chemical bond studies by X-Ray Spectroscopy

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Among the most prominent ultrafast advances are the new capabilities of the X-ray Free Electron Lasers (XFELs). XFELs produce attosecond/femtosecond X-ray pulses providing a way to study ultrafast electronic processes in matter induced by X-ray photons [1,2]. A second XFEL pulse can be used in order to track the X-ray induced dynamics through X-ray Photoelectron Spectroscopy (XPS). When a core electron is removed from an atom or molecule it turns out into a core-hole state. Those core-hole states decay via Auger transitions. Every inner-shell ionization process is followed by an excitation in the valence resulting in additional states called satellite states. These states are close in energy to the main core-hole state, and it is expected that they have a high contribution in the XPS at the ultrafast regime. Our group collaborates in projects with experimental XFELs groups, providing theoretical support and developing numerical tools to simulate the dynamics of molecular systems. In particular, we have developed a semi-classical model that combines nuclear propagation with XPS calculations. The main objective of using this model is to study the dynamics of the electron together with the motion of the nucleus in molecules under the effect of XFEL pulses.

### Acknowledgements

A.P. and A. M.-G. acknowledge funding from Comunidad de Madrid through TALENTO grant ref. 2017-T1/IND-5432 and programa de empleo juvenil ref. PEJ-2020-AI/IND-18063.

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## Attosecond photoionization time delays in Acetylene

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Attosecond pump-probe spectroscopy techniques offer the possibility to track and control electron dynamics in matter. Among the different techniques available, the RABBITT technique (acronym for Reconstruction of Attosecond Beating By Interference of Two-photon transitions) has been employed to extract photoionization time delays in atoms, and more recently in molecules and solids. Initially conceived as a method for the temporal characterization of trains of attosecond pulses [1], this technique employs an attosecond XUV pulse train in combination with a weak IR field leading to an interferometric signal from which dynamical information on the photoelectron emission can be extracted with attosecond resolution. This information is encoded in the resulting photoelectron spectrum measured as a function of the time delay between the train and the IR field. The spectrum captures the so-called mainbands, resulting from a one-photon absorption induced by the XUV attosecond pulse train, along with the interferometric signal (sidebands) resulting from the absorption of an XUV photon and the absorption or emission of an IR photon. From this signal, it is possible to retrieve the photoionization time-delays. The most recent applications in molecules have shown that the vibrationally resolved RABBITT spectra of diatomic [2] and polyatomic [3] molecules further allows one to capture changes induced by the nuclear motion, as, e.g., on the centrifugal barrier seen by an escaping photoelectron.

We will present our most recent theoretical results applying the RABBITT technique to acetylene. We investigate an energy range where up to four valence-channels ( $X^2\Pi_u$ ,  $A^2\Sigma_g^+$ ,  $B^2\Sigma_u^+$  and  $C^2\Sigma_g$ ) are energetically open. We examine the photoelectron spectra and analyze the dependencies of the resulting photoionization time-delays with the molecular orientation with respect to the light polarization. In particular, following our previous work on  $CF_4$  [4], we show how the RABBITT spectra is significantly modified due to IR-induced transitions between the different cationic states. The theoretical methodology employed for this calculations consisted in solving the time-dependent Schrödinger equation in a basis of Kohn-Sham orbitals and using the exclusive probability formalism to include interchannel couplings [4]. The basis is obtained in the dipole and static-exchange approximations by solving the Kohn-Sham Hamiltonian using a B-spline multicenter approach and the LB94 functional [5]. All the calculations have been performed in the fixed nuclei approximation.

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## Photodissociation control of IBr molecule

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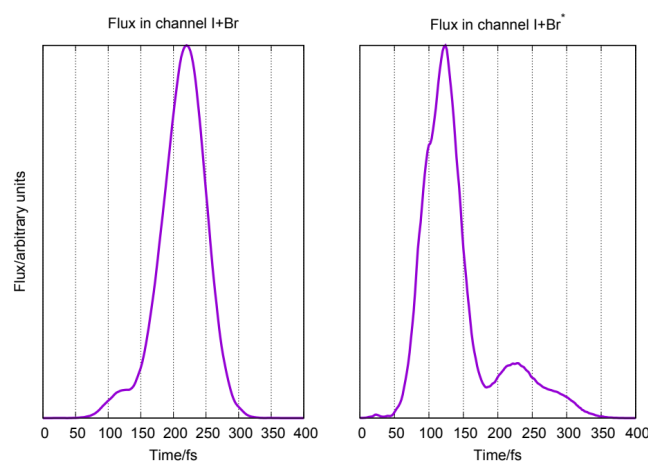
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One of the main goals in Chemistry is the control of chemical reactions. Over the years the use of laser pulses has been one of the strategies used to guide reactions towards different pathways. In the system of IBr, a study of the photodissociation [1] controlled by the application of a time delayed control pulse, claimed an inversion of the branching ratio of dissociation of IBr into the two lowest dissociation channels. In this system, within the spin-orbit excited states, there is an avoided crossing among the states dissociating into two different dissociation channels. The experimental procedure uses a sequence of two pulses, a first one (pump) producing the excitation into the upper manifold of states and a second one (control), non-resonant within the states involved in the avoided crossing, that modifies the potential curves near the crossing enhancing the dissociation into the upper channel.

We have simulated the experiment using time dependent wavepacket propagations in the full system, including all states dissociating into the spin-orbit states of I + Br. The dissociation into the I + Br and I + Br\* channels is analysed using the flux through a surface placed in each channel. The analysis of the fluxes shows that the time need by the system to reach the lower channel is longer than in the upper channel (see Figure below), in agreement with the experiments. However, the time scale differs with the experiments independent of the time delay of the control pulse. Further analysis of the propagations makes us consider that, the enhancement of the flux over the upper channel might be a consequence of late excitation of the wavepacket, after the system has already overpassed the avoided crossing.



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## The key atom for the accurate prediction of the absorption and emission spectra of a 3-input AND molecular logic gate

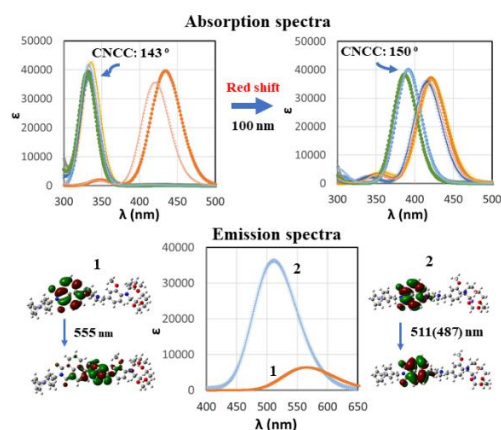
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The development of artificial receptors for sensing and recognition of species, as well as for advanced logic functions, is a significant challenge in the field of molecular information technology.[1-3] In this presentation, we study, via DFT/TD-DFT calculations, the photophysical properties of a 3-input AND molecular logic gate [4] which presents an enhanced fluorescence spectrum. It was found that the geometry conformation at an N atom of the piperazine group is the key factor for the correct calculation of the absorption spectra of the calculated structures. Its geometry is between tetrahedral and planar, while changes in the corresponding CNCC dihedral angle of about 10 degrees can cause significant shifts of the main peak of the absorption spectra up to 100 nm. Moreover, the unusually enhanced fluorescence of a molecular logic gate (MLG) is explained. Finally, we conclude that molecular systems having N atoms, whose geometry is between planar and tetrahedral, can be ideal molecules as sensors and molecular logic gates. Our calculated absorption and emission spectra are in excellent agreement with available experimental data. [5]



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## Collision Induced Deactivation of Microsolvated Cysteine Cations

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Cysteine (C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>S), one of the nonessential amino acids, plays a key role in many important biological processes. In this work, cysteine-water cluster cations Cys(H<sub>2</sub>O)<sub>3,6</sub><sup>+</sup> and Cys(H<sub>2</sub>O)<sub>3,6</sub>H<sup>+</sup> have been prepared by assembly inside He droplets and subsequently probed by tandem mass spectrometry with collision induced activation. Calculations based on the DFT as well as statistical mechanics have been performed in support of the experimental findings.

The theoretical approach applied in this work follows our previous strategy [1,2], which relies on the energetic structure, time propagation and entropy maximization for elucidation of the initial energy redistribution process. Firstly, the geometries of cysteine-water clusters (both protonated and non-protonated) involving three and six water molecules were optimized using the M06-2X functional and the 6-31++G(d,p) basis set. Secondly, for systems with three water molecules ab initio molecular dynamics simulations were carried out with the Atom Centered Density Matrix Propagation (ADMP) method. To treat fragmentation dynamics of large clusters, such as Cys(H<sub>2</sub>O)<sub>6</sub><sup>+</sup>, a less computationally expensive method than ADMP is required. Therefore, the Microcanonical Metropolis Monte Carlo method, in its recent implementation in the M<sub>3</sub>C code [3], was applied for the first time to obtain the fragmentation branching ratios for molecular clusters of such size.

From the obtained results we can see that, in the case of small cysteine-water clusters, the protonation has practically no influence on the binding of water to the central cation. The comparison of the experimentally measured appearance energies of individual fragmentation channels with water dissociation energies from the DFT calculations indicate that clusters do not fragment exclusively by sequential emission of single water molecules, but rather by the release of small water clusters. Through the fitting procedure of the M<sub>3</sub>C-obtained data with experimental relative ion yields we can comment on the energy partitioning after collisional activation. We find that only some of the collision energy redistributes via ergodic process, while the rest is transferred into a non-ergodic channel leading to the loss of a single water molecule from the cluster. Ergodicity-breaking processes exceed the scope of the M<sub>3</sub>C theory.

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## Theoretical investigation on the negative ions formed in collisions of potassium (K) atoms with hexachlorobenzene (C<sub>6</sub>Cl<sub>6</sub>)

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Theoretical study of electron transfer processes involving multiply charged ions and atoms in collision with atomic and molecular targets are in our interest since several years [1-4]. In our recent joint collaboration [4] we have selected hexachlorobenzene (C<sub>6</sub>Cl<sub>6</sub>) which as part of a large group of volatile organochloride compounds, has been used as a pesticide across the globe, and found to be a prevailing environmental pollutant. Given its environmental relevance, a key discussion is essential on its lifetime in the Earth's atmosphere where photolysis and/or reactions with radicals may act as a sink mechanism [5-6].

From the experimental point of view, the electronic state spectroscopy of C<sub>6</sub>Cl<sub>6</sub> is rather absent when probed by electron attachment and/or charge transfer processes. Therefore, the first investigation on the negative ions formed in collisions of hyperthermal neutral potassium atoms (K) with thermal neutral C<sub>6</sub>Cl<sub>6</sub> molecules in the 10–100 eV laboratory frame range has been performed. A novel K<sup>+</sup> energy loss spectrum in the forward scattering direction was obtained revealing the contribution of the most accessible electronic states in the collision processes. A vertical electron affinity of  $(-3.76 \pm 0.20)$  eV was obtained and assigned to a transition from hexachlorobenzene ground state to a  $\sigma_{\text{CCl}}^*$  repulsive state of the temporary negative ion yielding Cl<sup>-</sup> formation. Of relevance, the time-of-flight mass spectra recorded in the wide collision energy region, shows that more than 80% of the total anion yield is due to C<sub>6</sub>Cl<sub>6</sub><sup>-</sup>, C<sub>6</sub>Cl<sub>5</sub><sup>-</sup> and Cl<sup>-</sup> formation.

In our contribution we focus mainly on the interpretation of the experimental data with the help of state-of-the-art methods used for the calculations on the structure of C<sub>6</sub>Cl<sub>6</sub>. The complementary results were obtained to determine the ionisation energy, electron affinity and vertical detachment energy and to look closely at the negative ion where the symmetry of molecule is broken. Additionally, in the presence of a potassium atom, a detailed analysis of the K-C<sub>6</sub>Cl<sub>6</sub> interaction occurring between molecular states involved in this process has been made to determine asymptotic molecular configurations and for analyzing the LUMOs participating in the collision process [4]. The joint experimental and theoretical methodologies employed in these studies are the most comprehensive and unique assignments of the hexachlorobenzene anionic species and the role of C<sub>6</sub>Cl<sub>6</sub> electronic states in collision induced dissociation to date.

**Acknowledgements** This work is a joint collaboration in the frame of the Molecular Dynamics in the GAS phase (MD-GAS) CA18212 COST Action between Universidade NOVA de Lisboa (Portugal), Gdańsk University of Technology (Poland) and Instituto de Física Fundamental, Consejo Superior de Investigaciones Científicas (Spain).

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