



COST Action CA18212

MD-GAS

Molecular Dynamics
in the GAS phase

Dubrovnik, September 25-27, 2023

BOOK OF ABSTRACTS

3rd General Meeting

Sponsors

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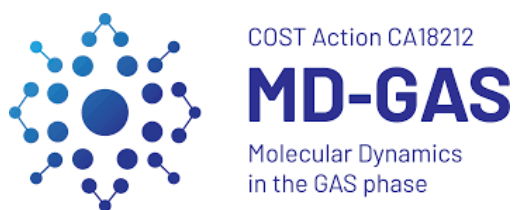


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Foreword

Welcome to the 4th General Meeting of the COST Action MD-GAS!

The MD-GAS action aims to improve the understanding of the interactions between molecules or clusters and photons, electrons, or heavy particles. The scientific program of the 4th General Meeting covers a wide range of these areas. We hope this meeting will be an opportunity to exchange ideas and discuss advances and challenges in describing these interactions from the experimental and theoretical perspective.

Program

Monday, September 25th		
8:45	Opening	
9:00	T1 P. Rousseau	Peptide bond formation in amino acid clusters induced by ion collision and VUV excitation
	T2 P. Slaviček	Water in Highly Excited States: The Race between Proton and Electron Transfer
	T3 J. Fedor	Nuclear dynamics in molecules probed by electron scattering
10:30	Coffee break	
11:00	T4 M. Hochlaf	Unimolecular chemical processes induced by (multi)-photon ionization: theory and experiment
	T5 S. Dujko	Recent advances in the kinetic and fluid modelling of charged-particle swarms and streamer discharges
	HT1 E. Rossich-Molina	Machine Learning meets Molecular Dynamics: Application and case study of an astrochemical relevant system
	HT2 M. Sapunar	Detailed insight into the electronic relaxation of pyrazine revealed by X-ray spectroscopy
12:30	Lunch	
14:30	T6 O. Heber	Molecular ion time-dependent rotational relaxation dynamics probed by photo-electrons in an ion trap
	T7 L. Schwob	X-Ray action spectroscopy of gas-phase biomolecular ions
	HT3 L. Carlini	Investigation of valence and core shells of azobenzene by photo-ionization and photo fragmentation
	HT4 C. E. Tzeliou	Theoretical kinetic study of Criegee intermediates with N ₂ O
16:00	Coffee break	
16:30	Poster session	

Tuesday, September 26th		
9:00	T8 H. T. Schmidt	Mutual-Neutralization experiments using the double electrostatic ion-beam storage ring DESIREE
	T9 P. Ferrari	Laboratory infrared characterization of gas-phase sulfur clusters: solving the astronomic sulfur puzzle?
	T10 M. Łabuda	The role of electron transfer in an investigation on the negative ions formed in collision of potassium with hexachlorobenzene
10:30	Coffee break	
11:00	T11 D. Strasser	Formation of new bonds in ionization & neutralization of isolated molecules
	HT5 D. Cruz Pérez	Pump-probe experiment on gas-phase DNA
	HT6 N. Tańska	The interplay between theory and experiment in the study of electron scattering from methyl formate (HCOOCH ₃)
	HT7 S.Demes	Excitation of hot ammonia rotational levels due to collisions with molecular hydrogen
	HT8 L. Cigrang	Quantum Dynamics of Small Molecules; Methods and Application
12:30	Lunch	
14:30	T12 R. Prosimiti	Data-driven potential models and quantum simulations on ion microhydration
	T13 M. Žitnik	Interferences due to Auger decay of a doubly excited state
	HT9 L. M. Ibele	Investigating photochemical reactions with coupled trajectories
	HT10 K. P. Khakurel	3D Fourier Transform Holography of Randomly Oriented Objects
16:00	Coffee break	
16:30	WG reports and new Action(s)	

Wednesday, September 27th		
9:00	T14 A. Cartoni	Gas Phase Ion Reactivity for Radiation Damage and Atmospheric Chemistry: Two Challenging Topics
	T15 E. K. Campbell	Synthesis and spectroscopic characterisation of molecular ions for astrochemical consideration
	HT11 J. E. Navarro Naverrete	Precise measurements of the electron affinities of C ₆₀ and C ₇₀
	HT12 Gómez	Excited state quantum dynamics on graphene nanoflake models
10:30	Coffee break	
11:00	HT13 Berholts	Photofragmentation dynamics of halogenated nitroimidazole radiosensitizers
	HT14 S. Swain	Fragmentation Dynamics of Coulomb Explosion of N ₂ Using Velocity Slice Imaging Technique
	T16 S. Maclot	Coincidence study of core-ionized adamantane: Site-sensitivity within a carbon cage?
	T17 D. Piekarski	Molecular growth induced by ions and electron: from linear 1,3-butadiene clusters towards 6-member ring compounds
12:30	Lunch	
14:30	T18 E. Erdmann	Collision induced fragmentation and energy redistribution: statistical vs. non-statistical process
	HT15 P. Szabó	When the Arrhenius rate law is not fulfilled: bimolecular collisions through a pre-reaction van der Waals complex
	HT16 M. Michielan	Investigating the Reactivity of Silicon and Sulfur Bearing Species to Unravel the Beyond-2 nd - Period Chemistry
	HT17 B. Milovanović	Cyclic crown ether traps for alkali ions: IQA portrayed reaction pathways
	HT18 A. Prlj	Influence of Ground State Distributions on Calculations of Photolysis Observables
16:00	Closing	

Talks

Peptide bond formation in amino acid clusters induced by ion collision and VUV excitation

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We are living in a molecular universe with more than 200 species identified in space. Moreover complex organic molecular are observed in meteorites and on Saturn moons. One can wonder what is the role of energetic processing by radiation on the molecular growth. Besides the two traditional approaches, namely bottom-up and top-down, recently we have shown that molecular growth can also occurred inside of molecular clusters [1-2].

In the context of the emergence of life, the formation of peptide bonds is a critical step. Using ion beams delivered by GANIL (Caen, France) and VUV photon beam produced at Synchrotron SOLEIL (Saint Aubin, France), we have studied the reactivity inside of amino acids clusters. In neutral clusters of β -alanine, polypeptide are formed after collisions with He^{2+} projectiles [3] while VUV excitation of protonated serine dimer leads to the formation of dipeptide [4].

Acknowledgments: This work is the result of fruitful collaborations with colleagues at Synchrotron SOLEIL, Universidad Autonoma de Madrid, and Bar-Ilan University.

References

- [1] R. Delaunay et al., *J. Phys. Chem. Lett.* 2015 **6**, 1536.
- [2] M. Nihamkin et al., *J. Phys. Chem. Lett.* 2011, **133**, 10100.
- [3] P. Rousseau et al., *Nature Commun.* 2020, **11**, 3818.
- [4] O. Licht et al., *Angew. Chem. Int. Ed.* 2023, **62**, e202218770.

Water in Highly Excited States: The Race between Proton and Electron Transfer

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I will first focus on the experimental observation of the ultrafast processes following the interaction of molecules with high-energy radiation. The simplest process is the proton transfer of water upon upper valence ionization, arguably the fastest acid-based reaction [1]. Subsequently, I will delve into the interplay between proton and electron processes, such as formation of solvated electrons [2], intermolecular Coulombic decay (ICD) and Electron Transfer Mediated Decay (ETMD) [3,4]. Doubly charged systems will be discussed as well [5].

In the next part, I will briefly discuss less conventional approaches for modelling the dynamics of highly excited systems. In particular, I will discuss applicability of the fragmentation approaches, the constrained density functional theory and especially the electronic force field approach, modelling the electrons classically. The talk will conclude with broader considerations. Numerous novel phenomena have recently emerged in the field of X-ray molecular science. However, this knowledge has yet to permeate other research areas, such as radiation chemistry, biophysics, and astrochemistry. Are the new processes really relevant?

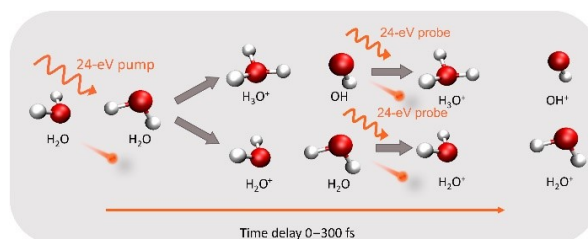


Figure 1: Probing proton transfer in water with X-ray free electron laser.

Acknowledgments: The project was supported Czech Science Foundation, grant number 21-26601X.

References

- [1] K. Schnorr, M. Belina, S. Augustin, H. Lindenblatt, Y. Liu, Severin Meister¹, Thomas Pfeifer¹, G. Schmid, R. Treusch, F. Trost, P. Slavíček, R. Moshhammer, *Science Advances*, 2023, **9**, eadg786a.
- [2] V. Svoboda, R. Michiels, A. C. LaForge, J. Med, F. Stienkemeier, P. Slavíček, H.J. Wörner, *Science Advances* 2020, **6**, eaaz0385
- [3] C. Richter, D. Hollas, C.M. Saak, M. Förstel, T. Miteva, M. Mucke, O. Björneholm, N. Sisourat, P. Slavíček, U. Hergenbahn, *Nature Communications* 2018, **9**, 4988.
- [4] S. Thürmer, M. Ončák, N. Ottosson, R. Seidel, U. Hergenbahn, S. E. Bradforth, P. Slavíček, B. Winter, " On the nature and origin of dicationic charge-separated species formed in liquid water on X-ray irradiation" *Nature Chemistry* 2013, **5**, 590.
- [5] J. Zhou, M. Belina, S. Jia, X. Xue, X. Hao, X. Ren, P. Slavíček, *J. Phys. Chem. Lett.* 2022, **13**, 10603–10611.

Nuclear dynamics in molecules probed by electron scattering

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One of the central tasks in AMO physics is to specify how the atomic nuclei move, for example, upon a vertical excitation by an external trigger. In this talk I will focus on the excitation mediated by collisions of molecules with free electrons. The interaction time of an electron with the kinetic energy in the chemical range (units of eV) is, in the direct scattering regime, typically too short for any nuclear dynamics. The situation changes if quasi-bound states embedded in the continuum are formed in the collision. Such states – electronic resonances and virtual states – have often autodetachment lifetime comparable with the timescale of nuclear motion. Probing various decay channels of the continuum states thus provides information about the nuclear dynamics.

The main experimental tools are a two-dimensional electron energy loss spectroscopy and a velocity-map-imaging dissociative electron attachment spectroscopy. The first technique provides information about the initial states of nuclear motion via measuring the energies of detached electrons, prior to molecular dissociation. The second technique provides information about the kinematics and dynamics of anionic fragments and thus about the final stage of the nuclear motion. I will provide an overview of effects which are revealed by the combination of these two techniques. The examples include an extremely non-Born-Oppenheimer dynamics of the vibronic coupling through continuum [1], vibrational autodetachment mediated by a presence of dipole-bound states [2], or distant-symmetry control of the bond cleavage [3].

References

- [1] J. Dvořák et al., Vibronic coupling through continuum e + CO₂ system, *Phys. Rev. Lett.* 129 (2022) 013401
- [2] C. Anstöter et al., Mode-Specific Vibrational Autodetachment Following Excitation of Electronic Resonances by Electrons and Photons, *Phys. Rev. Lett.* 124 (2020) 203401
- [3] Ragesh Kumar T. P. et al., Distant Symmetry Control of Electron-Induced Bond Cleavage, *J. Phys. Chem. Lett.* 13 (2022) 11136

Unimolecular chemical processes induced by (multi)-photon ionization: theory and experiment

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The dissociation of doubly charged OCS^{2+} and SO_2^{2+} ions is examined. These doubly charged ions are formed by photoionization of the neutral molecule at 40.81 eV or by ultrafast multi ionization processes. For interpretation we use high level quantum chemical calculations on isomeric structures and their potential energy surfaces.

For SO_2^{2+} , we find experimental evidence for electronic-state-selective production of O_2^+ from SO_2 , a chemical constituent of many planetary atmospheres and one which played an important part on Earth in the Great Oxidation Event. These experimental findings are analyzed with the aid of advanced ab initio computations resulting in the following model: First, the single photon double ionization of SO_2 forms the SO_2^{2+} dication. The O_2^+ production involves isomerization of SO_2^{2+} by a roaming mechanism leading to efficient formation of the O_2^+ ion in form of dissociative double ionization of SO_2 , which can be converted to abiotic O_2 by electron neutralization. This formation process may contribute significantly to the abundance of O_2 and related ions in planetary atmospheres, such as the Jovian moons Io, Europa and Ganymede. It represents an alternative to and may compete with the well-established abiotic O_2 production pathways via the photodissociation of water vapor by extreme ultraviolet (XUV) light [2-3] or the near ultraviolet (NUV) photochemistry of titanium (IV) oxide (titania) [4]. We suggest that this sort of ionic pathway for the formation of abiotic O_2 involving multiply-charged molecular ion decomposition may also exist for other atmospheric and planetary molecules. Further details can be found in [5].

For OCS^{2+} , the dominant dissociation channel of $[\text{OCS}]^{2+}$ is charge separation forming $\text{CO}^+ + \text{S}^+$ ion pairs, found here to be formed with low intensity at a lower-energy onset and with a correspondingly smaller kinetic energy release than in the more intense higher energy channel previously reported. We explain the formation of $\text{CO}^+ + \text{S}^+$ ion pairs at low as well as higher ionization energies by the existence of two predissociation channels, one involving a newly identified COS^{2+} metastable state. We conclude that the dominant $\text{CO}^+ + \text{S}^+$ channel with 5.2 eV kinetic energy release is reached upon $\text{OCS}^{2+} \rightarrow \text{COS}^{2+}$ isomerization, whereas the smaller kinetic energy release (of ~ 4 eV) results from the direct fragmentation of OCS^{2+} ($X^3\Sigma^-$) ions. Dissociation of the COS^{2+} isomer also explains the existence of the minor $\text{C}^+ + \text{SO}^+$ ion pair channel. We suggest that isomerization prior to dissociation may be a widespread mechanism in dications and more generally in multiply charged ion dissociations. Further details can be found in [6].

Acknowledgments: This work was carried out while M.H. was Waernska Guest Professor at Gothenburg U (Sweden). We thank the Helmholtz Zentrum Berlin, the Swedish Research Council (VR; grant # 2018-03731, 2020-05293) and the Knut and Alice Wallenberg Foundation, Sweden (grant # 2017.0104), the Swedish National Infrastructure for Computing (SNIC) at the Chalmers Centre for Computational Science and Engineering (C3SE) and PCMI of CNRS, CEA and CNES. This article is based

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References

- [1] F. Tian et al. *Earth Planet. Sci. Lett.* 385, 22 (2014).
- [2] R. Wordsworth, R. Pierrehumbert. *Astrophys. J. Lett.* 785, L20 (2014).
- [3] R. Luger, R. Barnes. *Astrobiology* 15, 119 (2015).
- [4] N. Narita et al. *Sci. Rep.* 5, 13977 (2015).
- [5] M. Wallner, M. Jarraya, E. Olsson, V. Ideböhn, R.J. Squibb, S. Ben Yaghlane, G. Nyman, J.H.D. Eland, R. Feifel, and M. Hochlaf. *Science Advances* **8**, eabq5411 (2022).
- [6] M. Jarraya, M. Wallner, S. Ben Yaghlane, E. Olsson, V. Ideböhn, R. J. Squibb, J. Palaudoux, G. Nyman, M. Mogren Al-Mogren, J.H. D. Eland, R. Feifel, and M. Hochlaf. *Phys. Chem. Chem. Phys.* **25**, 19435 (2023).

Recent advances in the kinetic and fluid modelling of charged-particle swarms and streamer discharges

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In this work we review the progress achieved over the last decade in the fundamental kinetic theory of charged-particle swarms with the focus on numerical techniques for the solution of Boltzmann's equation, as well as on the development of the fluid equation based models of streamer discharges. We present a time-dependent multi term solution of Boltzmann's equation for charged-particle swarms in varying configurations of electric and magnetic fields [1]. The capacity of a theory and associated computer code will be illustrated by considering the effects of anisotropic scattering on electron transport properties in CO and electron transport processes in strongly attaching gases in the presence of electric and magnetic fields.

The kinetic theory for solving the Boltzmann equation will be followed by a fluid equation description of streamer discharges. First, we present our 1.5D classical fluid model of Resistive Plate Chambers (RPCs) which is used for timing and triggering purposes in many high energy physics experiments [2]. The model is used to investigate the avalanche to streamer transition in RPCs in the presence of space charge effects and photoionization. Second, we will also discuss our high-order fluid model for streamer discharges in noble gases and the extension of a theory to model the electron transport and streamer propagation in liquid rare gases [3].

In the final segment of this presentation, we will discuss our recently developed axisymmetrical model of a streamer discharge. The model is developed within the AMReX, a C++ software framework that supports the development of block-structured adaptive mesh refinement algorithms for solving systems of partial differential equations with complex boundary conditions [4]. The validity of the model and associated code is tested by comparing its results with those of the Afivo-streamer code [5] in the N₂-O₂ and N₂-CH₄ mixtures. In particular, we study the propagation of streamers in N₂-CH₄ mixtures with the aim of investigating the possibility for the occurrence of lightning in the atmosphere of Titan, the largest satellite of Saturn [6].

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References

- [1] S. Dujko, R.D. White, Z.Lj. Petrović and R.E. Robson, *Phys. Rev. E* 2010, **81**, 046403.
- [2] D. Bošnjaković, Z.Lj. Petrović and S. Dujko, *J. Phys. D: Appl. Phys.* 2016, **49**, 405201.
- [3] I. Simonović, N.A. Garland, D. Bošnjaković, Z.Lj. Petrović, R.D. White and S. Dujko, *Plasma Sources Sci. Technol.* 2019, **28**, 015006.
- [4] W. Zhang et al., *J. Open Source Software*, 2019, **4(37)**, 1370.
- [5] J. Teunissen and U. Ebert, *J. Phys. D: Appl. Phys.* 2017, **50**, 474001.
- [6] C. Köhn, S. Dujko, O. Chanrion and T. Neubert, *Icarus* 2019, **33**, 294 – 305.

Molecular ion time-dependent rotational relaxation dynamics probed by photo-electrons in an ion trap

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Hot gaseous ions are common in many systems ranging from chemical reactions, plasma, and atmospheric science to interstellar medium. A fundamental difficulty is understanding the way such a system's internal dynamics evolve as a function of time in nonequilibrium conditions with the environment. For a practical example, such a nonequilibrium condition in molecules is expected in the diffused interstellar medium.

We are reporting on a new experiment incorporating a hot molecular ion source that produces hot OH⁻ anions, an Electrostatic Ion Beam Trap (EIBT) and a Velocity Map Imaging (VMI) electron spectrometer. This experiment can follow internal molecular dynamics as a function of trapping time in the EIBT using a coincidence between particle detectors, the VMI spectrometer, and lasers [1].

The rotational distribution of hot OH⁻ molecules distribution ($J < 50$) is measured as a function of trapping time in room-temperature environment. It was found that the Boltzmann distribution only reasonably describes the system (temperature), and a full-dynamic model using master equations is a better description in the first second after the ion production. However, although the temperature is not a suitable parameter, the actual internal energy distribution dynamics behavior during the observed time (0-3s) is proximate to the Boltzmann distribution. The contribution of the black body radiation to the internal dynamics starts to be influential on time longer than 1 second in our experiment [2].

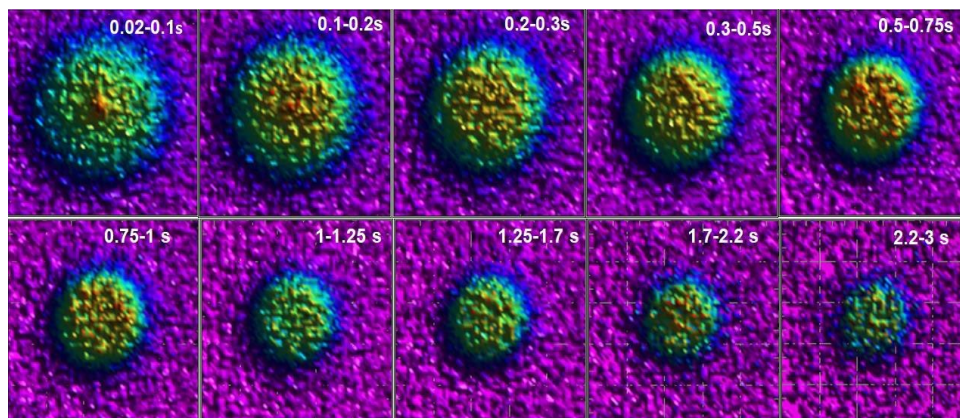


Figure 1. VMI time-dependent images of photoelectron distribution.

References

- [1] K. Saha et al. Review of Scientific Instruments **88** (2017) 053101
- [2] A. Shahi et al. Scientific Reports **12** (2022) 22518

X-Ray action spectroscopy of gas-phase biomolecular ions

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Over the past decades, peptides and proteins have been investigated in the gas phase using state-of-art mass spectrometric techniques combined to electrospray ionization sources. In order to obtain new insights into the electronic and structural properties of such biomolecules, X-ray action spectroscopy experiments, also called NEXAMS (near-edge X-ray absorption mass spectrometry), which are based on the resonant photoexcitation of core electrons, have been carried out at synchrotron facilities, which offer a broad photon energy range and a high photon flux. It has been used successfully to unravel different aspects of the photodissociation of peptides and to probe conformational features of proteins. It is a current question to which extent the resonant photoabsorptions are sensitive toward effects of conformational isomerism, tautomerism, and intramolecular interactions in gas-phase peptides. Additionally, in the soft X-ray regime, the high degree of localization of the deposited energy allows getting a deeper understanding on the dissociation processes. However, identifying products of site-selective dissociation in large biomolecules is challenging at the carbon, nitrogen, and oxygen edges because of the high number of these atoms and related chemical groups. Probing the inner shells of a single sulfur atom within a biomolecule as the one and only excitation site is a promising way to overcome this obstacle. I will present here an overview of recent synchrotron-based experimental studies on the X-ray action spectroscopy of model peptides, carried across at the carbon, nitrogen, and oxygen K-edges as well as sulfur L-edge.

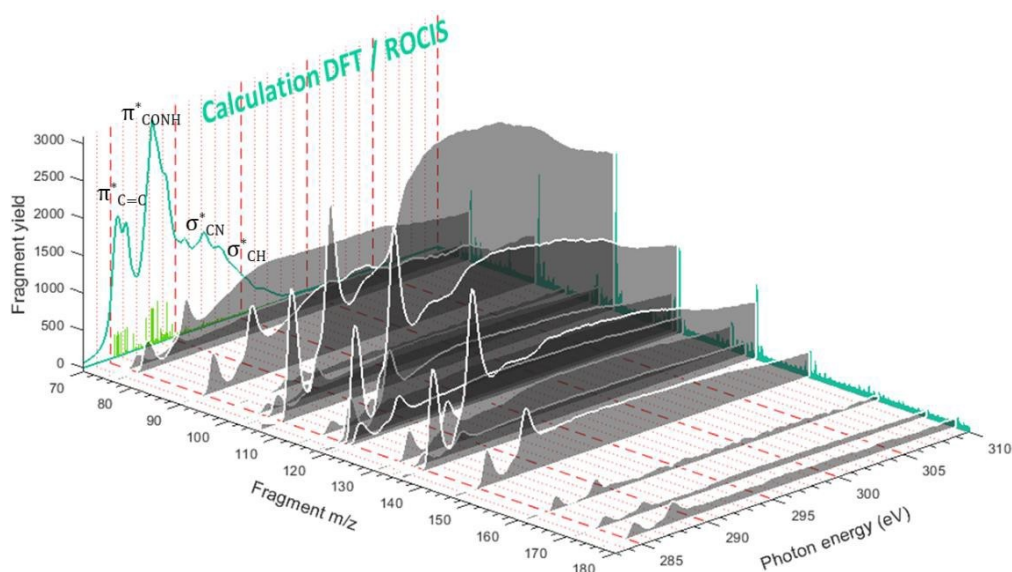


Figure 1: NEXAMS spectra of protonated methionine enkephalin at the carbon K-edge and comparison with DFT/ROCIS calculation.

Mutual-Neutralization experiments using the double electrostatic ion-beam storage ring DESIREE

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Mutual Neutralization (MN) is the fundamental process in which charge is transferred between two ions of opposite charge states leading to the formation of two (or more in the case of molecular ions) neutral products: $A^+ + B^- \rightarrow A + B$. As a fundamental charge-recombination mechanism, MN affects all plasma environments cool enough to sustain a non-negligible anion population. In particular, it has been demonstrated that MN with atomic hydrogen anions is important for the quantum-level distribution of metals in stellar atmospheres that can not generally be assumed to be in thermal equilibrium [1]. Therefore, the detailed study of MN processes with control of both the initial and final quantum levels are essential for a correct determination of stellar elemental composition based on astronomical observations. We perform experimental studies of MN at the cryogenic double electrostatic ion-beam storage-ring facility, DESIREE, Stockholm University [2]. I will describe the setup and the experimental procedure and discuss results of MN experiments with H^- ions for stellar atmosphere applications [3–5] as well as other atomic MN processes [6,7], and will further discuss preliminary results of studies of MN with molecular ions where full advantage of the combination of the long-time storage offered by the extreme vacuum and the merged-beams geometry is taken.

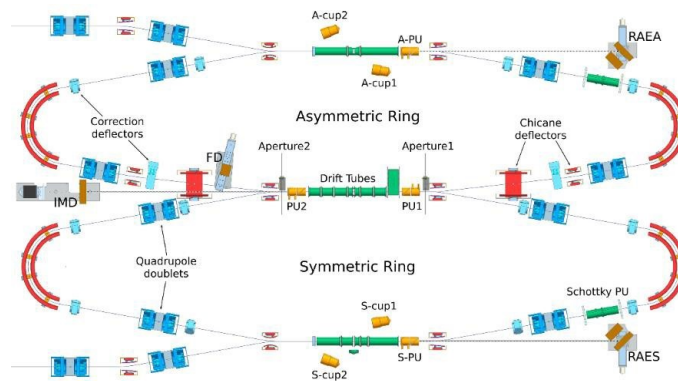


Figure 1: Schematic of the Double Storage Rings of DESIREE

Acknowledgments: This work was performed at the Swedish National Infrastructure, DESIREE (Swedish Research Council Contracts No. 2017-00621 and No. 2021-00155) and is a part of the project “Probing charge- and mass-transfer reactions on the atomic level,” supported by the Knut and Alice Wallenberg Foundation (2018.0028).

References

- [1] P. S. Barklem, A. Belyaev, and M. Asplund, *Astron. Astrophys.* 2003, **409**, L1
- [2] R. D. Thomas et al. *Rev. Sci. Inst.* 2011 **82**, 065112; H. T. Schmidt et al. *Rev. Sci. Inst.* 2013 **84**, 055115
- [3] G. Eklund et al. *Phys. Rev. A* 2020 **102**, 012823
- [4] G. Eklund et al. *Phys. Rev. A* 2021 **103**, 032814
- [5] J. Grumer et al. *Phys. Rev. Lett.* 2022 **128**, 033401
- [6] M. Poline et al. *Phys. Chem. Chem. Phys.* 2021 **23**, 24607
- [7] M. Poline et al. *Phys. Rev. A* 2022 **106**, 012812

Laboratory infrared characterization of gas-phase sulfur clusters: solving the astronomic sulfur puzzle?

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Compared to diffuse interstellar environments and photon-dominated regions in space, the atomic sulfur concentration in dense molecular clouds and planet forming disks is depleted by a factor of 100 [1,2]. In contrast, abundant sulfur was recently detected in the atmosphere of an exoplanet [3], showing the efficient incorporation of sulfur into forming planets. In this respect, the chemical pathway of sulfur from diffuse interstellar regions, through clouds to planets, remains elusive and is often referred to as the sulfur puzzle. Hypotheses to account for the missing atomic sulfur include the formation of sulfur-bearing molecules, although the concentration of sulfur-based molecules currently observed in space is far from sufficient to account for all atomic S loss [4], or the embedding of sulfur in grain mantles at low temperatures and high densities [5]. A third alternative is the formation of sulfur clusters, but a fundamental step to elucidate on this possibility is relevant spectroscopic data. Here we show the first experimental far-IR spectra of neutral and charged (anionic and cationic) sulfur clusters, employing the light provided by the free electron laser FELIX (Nijmegen, The Netherlands). The experimental spectra of the investigated species show a remarkably good agreement with quantum chemical calculations, allowing us to predict abundance limits for detection with the recently commissioned James Webb Space Telescope (JWST). This could spur a targeted observational search of sulfur clusters, and the possibility of solving the sulfur mystery in dense molecular clouds and star-forming regions.

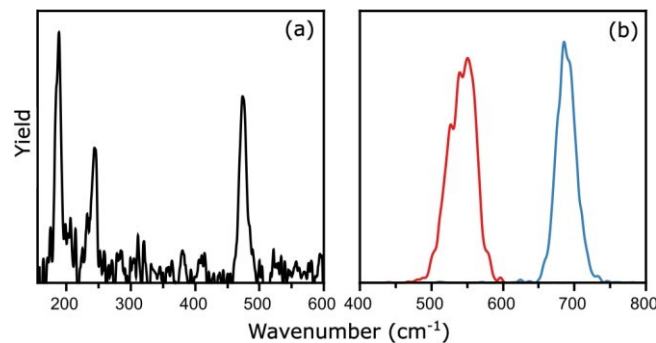


Figure 1: Infrared spectrum of S₈ (a), S₄⁺ (b, blue) and S₄⁻ (b, red).

References

- [1] D. V. Mifsud, Z. Kaňuchová, P. Herczku, S. Ioppolo, Z. Juhász, S. T. S. Kovács, N. J. Mason, R. W. McCullough, B. Sulik, *Space Sci. Rev.* 217 (2021) 14.
- [2] Le Gal, R., et al. 2021 *ApJS* 257, 12
- [3] S.-M. Tsai et al., *Nature* 617 (2023) 483.
- [4] J. R. Goicoechea, A. Aguado, S. Cuadrado, O. Roncero, J. Pety, E. Bron, A. Fuente, D. Riquelme, E. Chapi-llon, C. Herrera, C. A. Duran, *A&A* 647 (2021) A10.
- [5] Cazaux, S. et al.: 2022 *A&A* 657, A100

The role of electron transfer in an investigation on the negative ions formed in collision of potassium with hexachlorobenzene

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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 (C₆Cl₆) 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 C₆Cl₆ 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 C₆Cl₆ molecules in the 10–100 eV laboratory frame range has been performed. A novel K⁺ 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 ± 0.20) eV was obtained and assigned to a transition from hexachlorobenzene ground state to a σ_{CCl}^* repulsive state of the temporary negative ion yielding Cl⁻ 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 C₆Cl₆⁻, C₆Cl₅⁻ and Cl⁻ 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 C₆Cl₆. 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-C₆Cl₆ 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 C₆Cl₆ 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).

References

- [1] M. C. Bacchus-Montabonel, M. Łabuda, Y. Tergiman, J. Sienkiewicz, *Phys. Rev. A*, **72**, 052706 (2005)
- [2] M. Łabuda, J. González-Vázquez, F. Martín, L. González, *Chemical Physics* **400**, 165 (2012)
- [3] E. Erdmann, M.-C. Bacchus-Montabonel and M. Łabuda, *Phys. Chem. Chem. Phys.*, **19**, 19722 (2017)
- [4] S. Kumar, T. Kilich, M. Łabuda, G. García, P. Limão-Vieira, *Phys. Chem. Chem. Phys.*, **24**, 366 (2022)
- [5] W. W. Brubaker and R. A. Hites, *Environ. Sci. Technol.*, **32**, 766 (1998)
- [6] S. L. Simonich and R. A. Hites, *Science.*, **269**, 1851 (1995)

Formation of new bonds in ionization & neutralization of isolated molecules

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Ionization is a powerful trigger for structural rearrangement and formation of new chemical bonds. It is particularly important for the chemical evolution of isolated low temperature molecules. Using 3D coincidence imaging methods we explore different types of molecular dynamics, with emphasis on mechanisms involving charge transfer dynamics. Recently, we studied dynamics initiated by double-ionization of several organic species.[1-3] In a combined experimental and theoretical effort, we reveal a rich variety of competing proton and electron transfer mechanisms leading to different Coulomb explosion product channels. Furthermore, I will briefly present new experimental results from mutual-neutralization of $\text{H}_3\text{O}^+ + \text{OH}^-$, also exhibiting competing electron-transfer and proton-transfer mechanisms.



Figure 1: Coincidence fragment imaging is a powerful tool for

References

- [1] Krishnendu Gope et al, An “inverse” harpoon mechanism .Sci. Adv.8,eabq8084 (2022).
- [2] Krishnendu Gope et al, Sequential mechanism in H_3^+ formation dynamics on the ethanol dication, Phys. Chem. Chem. Phys., 25, 6979-6986 (2023)
- [3] Dror Bittner et al, Sequential and concerted C–C and C–O bond dissociation in the Coulomb explosion of 2-propanol, J. Chem. Phys. 157, 074309 (2022)

Data-driven potential models and quantum simulations on ion microhydration

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Dissolved ions in aqueous media are ubiquitous in many physicochemical processes, playing a crucial role in the structure of the water molecules network. A thorough understanding of the underlying forces from small clusters to bulk solutions still remains elusive. Thus, we introduced a systematic analysis of the interaction energies obtained from high-level electronic structure methodologies, to assess various dispersion-corrected density functional approaches, as well as ab initio-based data-driven potential models for halide ion–water clusters [1]. Following a bottom-up data-driven potential approach, we have then looked into both classical and quantum behavior of poly-hydrated halides, employing an evolutionary programming procedure and classical/ quantum path-integral molecular dynamics simulations [2]. Our results on the ongoing conflicting distribution of different ions in aqueous environments, as well as the transition from nanoscale clusters to macroscopic condensed phases will be discussed (see Figure 1).

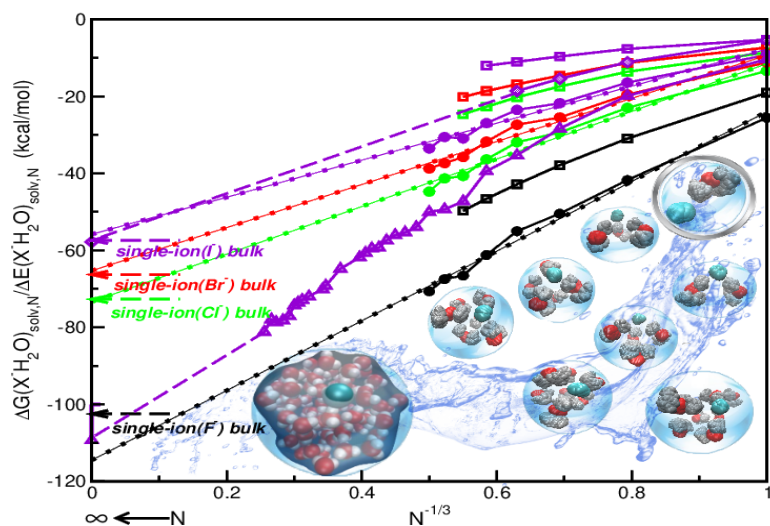


Figure 1. Computed single-ion solvation energetics of halide-water systems as a function of N solvating water molecules. Linear trends in the large cluster size regime and comparison with experimentally determined single-ion bulk solvation free energies are also shown.

Acknowledgements: This work has been supported by MICINN grant No, PID2020-114654GB-I00 and COST action CA18212 (MD-GAS). Authors acknowledge the SGAI-CSIC/IFF” and CESGASupercomputing centre for allocation of computer time.

References

[1] <https://doi.org/10.3390/molecules27051654>

[2] <https://doi.org/10.1039/D2CP01396G>

Interferences due to Auger decay of a doubly excited state

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Auger decay of doubly excited atomic resonances causes a non-trivial modulation of absorption spectrum above the core-hole ionization threshold because it interferes with both, the direct photoionization leading to the low-energy photoelectron continuum, and the shake-up Auger photoelectron recapture leading to the high-energy Auger electron continuum. The effects of both, the participator and spectator Auger coupling are clearly seen in our study of the isolated $1s^{-1}3p^{-1}4s^2$ 1P resonance in argon [1].

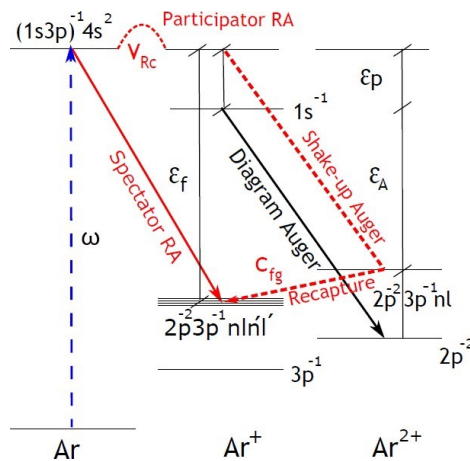


Figure 1: The scheme of non-radiative electronic transitions triggered by photoexcitation of $1s^{-1}3p^{-1}4s^2$ state of argon. The kinetic energies of the K-shell photoelectron and of the resonant and the non-resonant K-L₂² electrons are denoted by ε_p , ε_f and ε_A , respectively.

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References

[1] M. Kavčič et al., *Phys. Rev. Lett.* **102**, 143001 (2009)

Gas Phase Ion Reactivity for Radiation Damage and Atmospheric Chemistry: Two Challenging Topics

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The study of the radiation damage and atmospheric chemistry represents several challenge due to the difficulty to reproduce in the laboratories the real conditions of biological environments and of atmosphere [1,2]. To gain insights into these complex processes, a combination of gas phase experimental measurements and theoretical calculations are performed. As regard the issue of radiation damage in the aqueous medium, radiation generates radicals and ions such as H_2O^+ , OH^+ , and O^+ , which can react with DNA's building blocks. Even when these ions are initially produced with significant kinetic energy by the primary radiation, they quickly lose energy through collisions with surrounding molecules in the media and react with low kinetic and internal energy ranging from meV to a few tens of eV. In order to simulate this low energy regime the talk presents the first gas phase experimental investigation of ion-molecule reactions involving the H_2O^+ and OH^+ ions, generated by photoionization with synchrotron radiation, with the furan (c-C₄H₄O) molecule, a template for deoxyribose sugar in DNA [3]. The results indicate that the reaction favors charge exchange (CT) over proton transfer (PT), with both processes having high cross sections at low energies. At higher energies, the dissociation of protonated furan dominates over the dissociation of ionized furan, suggesting that c-C₄H₅O⁺ is more prone to fragmentation compared to c-C₄H₄O⁺.

Moving to atmospheric chemistry, the reactivity of carbon dioxide (CO_2^+) and nitrous oxide (N_2O^+) radical cations, produced by synchrotron radiation to simulate cosmic rays, is discussed by a combined experimental and theoretical investigation.

Overall, the talk will highlight the significance of experimental measurements and theoretical calculations in understanding radiation damage and atmospheric chemistry.

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References

- [1] E. Alizadeh and L. Sanche *Chem. Rev.* 2012, **112**, 5578–5602.
- [2] V. Kumar, S. K. Dhaka, M. H. Hitchman, S. Yoden, *Sci. Rep.* 2023, **13**, 3707.
- [3] D. Ascenzi *et al.* submitted to PCCP 2023

Synthesis and spectroscopic characterisation of molecular ions for astrochemical consideration

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Recent advances in laboratory methods using cryogenic traps have enabled gas phase measurement of the electronic spectra of large molecular ions of astrochemical interest at temperatures below 10 K. Routine tagging of virtually any cation with helium atom(s) has led to a relatively straightforward route to obtain spectroscopic information on buffer gas cooled molecular ions [1]. This enabled the first identification of a molecular carrier of some of the enigmatic diffuse interstellar bands (DIBs) to be made [2]. Experiments combining laser ablation synthesis with ion storage at 3 K have enabled the spectroscopic detection of molecules for which a traditional organic synthesis route does not exist [3]. In this talk I will present some of our recent studies on the electronic spectra of fullerenes and analogues [4,5] and related molecular ions [6,7].

References

- [1] E. K. Campbell, *Mol. Phys.* 2020, **118**, e1797918 and references therein.
- [2] J. P. Maier, E. K. Campbell, *Int. J. Mass Spectrom.* 2018, **434**, 116 and references therein.
- [3] E. K. Campbell, P. W. Dunk, *Rev Sci. Instrum.* 2019, **90**, 103101.
- [4] E. K. Campbell *et al.* *ApJ*. 2020, **897**, 88.
- [5] J. Rademacher *et al.* *Mol. Phys.* 2023, e2173507.
- [6] E. S. Reedy *et al.* *Mol. Phys.* 2021, **120**, e1989070.
- [7] J. Rademacher, E. S. Reedy, E. K. Campbell, *J. Phys. Chem. A*. 2022, **126**, 2127.

Coincidence study of core-ionized adamantane: Site-sensitivity within a carbon cage?

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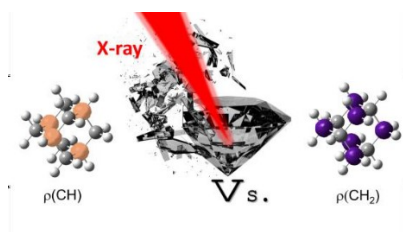
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Adamantane (C₁₀H₁₆) is the prototypical diamondoid molecule, which due to their high stability are of high interest both in astrophysics, and nanotechnologies. A recent series of photoionisation experiments have been performed in various facilities to reveal the fragmentation dynamics of adamantane cations.

The initial experiment was done at Lund University using femtosecond XUV pulses produced via high-order harmonic generation and ion/electron spectroscopy [1]. As a main result we were able to show that the doubly charged adamantane molecule is metastable and will spontaneously dissociate. But, preceding dissociation, the cage structure will open and hydrogen migration(s) will occur.

Recently, we investigated the fragmentation dynamics of adamantane dications produced after core-ionization at the carbon edge followed by Auger decay using X-rays of the synchrotron SOLEIL [2,3]. The combination of high-resolution electron spectroscopy, energy-resolved electron-ion multi-coincidence spectroscopy and different theoretical models allows us to give a complete characterization of the processes involved after ionization. We show that energy- and site-sensitivity is observed even for a highly-symmetric molecule that lacks any unique atomic site.



References

- [1] S. Maclot, J. Lahl, J. Peschel, H. Wikmark, P. Rudawski, F. Brunner, H. Coudert-Alteirac, S. Indrajith, B. A. Huber, S. Díaz-Tendero, N. F. Aguirre, P. Rousseau, and P. Johnsson, *Scientific Reports* (2020), 10, 2884
- [2] S. Ganguly, M. Gisselbrecht, P. Eng-Johnsson, R. Feifel, P.A. Hervieux, Z. Alfaytarouni, R. F. Fink, S. Díaz-Tendero, A. Milosavljevic, P. Rousseau and S. Maclot, *Phys. Chem. Chem. Phys.* 2022, **24** 28994
- [3] S. Ganguly, M. Gisselbrecht, P. Eng-Johnsson, R. Feifel, S. Díaz-Tendero, E. Muchová, A. R. Milosavljević, P. Rousseau and S. Maclot, *Molecules* 2023, **28**, 5510

Molecular growth induced by ions and electron: from linear 1,3-butadiene clusters towards 6-member ring compounds

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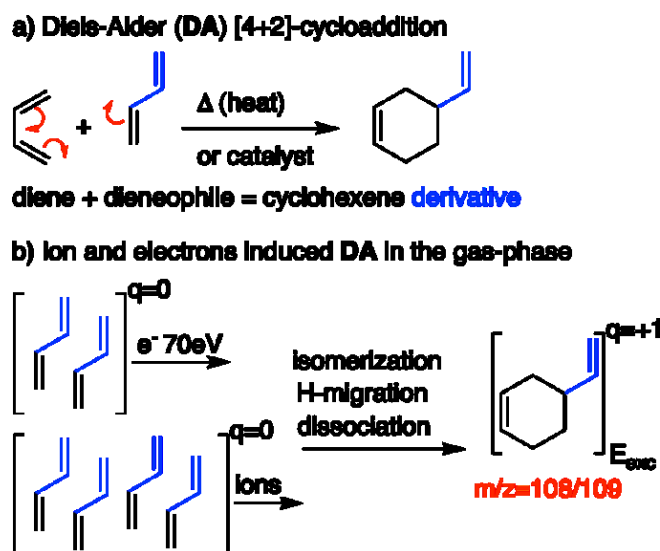
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Molecules embedded into clusters present an explicit environmental effect on encapsulated target molecules, especially when their reactivity is induced with e.g. highly-charged ions. The interaction of ions with clusters of fullerenes, polycyclic aromatic hydrocarbons (PAHs), and biomolecules, is stabilized with a protective effect due to the presence of an environment around the one excited molecule [1]. This is explained by a redistribution of energy and charge between the different residues in the cluster. In addition, the presence of an environment can induce an additional reactivity within the cluster itself, such as hydrogen transfers [2] or molecular growth processes [3], that is not observed in the individual molecule fragmentation. Based on *ab initio* molecular dynamics and potential energy surface calculations we postulate that cosmic radiation can induce Diels-Alder (DA) reaction in the outer space, transforming the clusters of small linear unsaturated hydrocarbons into more stable, long-lived cyclic species.



Some of the peaks observed by us e.g. with mass over charge ratio, $m/z=68^+$ and $m/z=79^+$ have been previously proposed as PAHs precursors, cyclic or bicyclic singly charged species, that have been observed in outer-space [4]. The production of a long-live cyclic structure from an initial linear neutral 1,3-butadiene cluster has been accounted for the DA-like mechanism, allowing to easily form 4-vinylcyclohexene radical cation, precursor of subsequent fragmentations.

Figure 1: a) general scheme of Diels-Alder mechanism and b) our approach.

References

- [1] B. Manil, L. Maunoury, B.A. Huber, J. Jensen, H.T. Schmidt, H. Zettergren, H. Cederquist, S. Tomita, P. Hvelplund, *Phys. Rev. Lett.* 2003, **91**, 215504.
- [2] A. Domaracka, M. Capron, S. Maclot, J-Y. Chesnel, A. Méry, J-C. Pouilly, J. Rangama, L. Adoui, P. Rousseau, B.A. Huber, *Journal of Physics: Conference Series* 2012, **373**, 012005.
- [3] H. Zettergren, P. Rousseau, Y. Wang, F. Seitz, T. Chen, M. Gatchell, J.D. Alexander, M.H. Stockett, J. Rangama, J.Y. Chesnel, and others, *Phys. Rev. Lett.* 2013, **110**, 185501.
- [4] M. J. Abplanalp, R.I. Kaiser, *Astrophys. J* 2020, **889**, 3.

Collision induced fragmentation and energy redistribution: statistical vs. non-statistical process

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The main aim of this work is to investigate and understand a complex problem of the evolution of a molecule following deposition of energy by collision with ions/photons/atoms. If the amount of energy is sufficient, the excited molecule can subsequently undergo ionization and/or fragmentation through a radiationless transition of energy to rovibrational degrees of freedom. Hence, we propose to study the fragmentation separately from the excitation process.

In a statistical fragmentation pattern the deposited energy is statistically redistributed across all internal degrees of freedom. Conversely, non-statistical fragmentation channels do not follow a statistical redistribution of energy and lead to fragment yields that exceed expected values calculated by statistical theories.

In this work we present a theoretical investigation combined with experimental results in two systems: ion- and photon-induced fragmentation of the furan molecule [1] as well as dissociation of cysteine-water clusters induced by collisions with Ar atoms [2]. Our theoretical approach consists of three complementary methodologies: (1) *ab initio* molecular dynamics simulations, (2) exploration of the Potential Energy Surface (PES) with Density Functional Theory, and (3) a statistical Microcanonical Metropolis Monte Carlo method [3] in its recent implementation in the M₃C code [4]. The main results of M₃C technique are fragment yields as a function of the internal energy.

The good comparison between theoretical and experimental breakdown curves of furan cation obtained by the statistical theory and PEPICO measurements suggests the efficient coupling between electronic and vibrational degrees of freedom and the adequacy of the approximation of the ultrafast redistribution of energy in the electronic ground state in this system. However, in the case of cysteine-water clusters, we observe high intensity of the single molecule evaporation channel in CID experiments which is not consistent with the M₃C results. This discrepancy suggests a non-ergodic process, where a single molecule of a weakly bound cluster takes away a significant amount of the collision energy.

References

- [1] E. Erdmann et al., *Phys. Chem. Chem. Phys.* 2021, **23**, 1859-1867
- [2] L. Tiefenthaler et al., *Phys. Chem. Chem. Phys.* 2023, **25**, 5361-5371
- [3] S. Díaz-Tendero, P.-A. Hervieux, M. Alcamí, and F. Martín, *Physical Review A* 2005, **71**, 033202
- [4] N. F. Aguirre, S. Díaz-Tendero, P.-A. Hervieux, M. Alcamí, and F. Martín, M3C (Microcanonical Metropolis Monte Carlo), 2020, <https://github.com/nfaguirrec/M3C>

Hot Topic

Machine Learning meets Molecular Dynamics: Application and case study of an astrochemical relevant system

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The infrared (IR) spectrum of a molecule serves as its molecular fingerprint and is thus widely used in chemistry as a mean of molecules' identification. In astrochemistry, IR spectroscopy is a main tool for molecular recognition, thus the ability to produce calculated spectra is crucial for comparison purposes. Indeed, calculation of the frequencies beyond the harmonic approximation is an active research area and there exist different theoretical approaches for it, e.g. TOSH, VPT2, VCI [1-3]. One of the disadvantages of these methods, is that they provide discrete spectra that need to be smoothed out if one aims to make a comparison with experimental results. An alternative to these static methods, is the calculation of the IR spectrum from the dipole auto-correlation function computed during *ab initio* Molecular Dynamics (AIMD) simulations. AIMD is a powerful tool for the study of the time evolution of a chemical system and that allows for the exploration of the potential energy surface. Aside its usefulness, AIMD has a significant computational cost; at each time step of a given trajectory it is needed to calculate the *ab initio* force acting on each of the atoms. This cost increases with the level of theory and the system size. Furthermore, the computation of the IR spectrum from AIMD requires the use of small-time steps and long trajectories increasing the computational cost. To overcome these limitations, forces can be alternatively calculated by means of Machine Learning (ML). Here, we interface sGDML[4] model with Q-Chem [5] software and calculate the DACF as well as the velocity auto-correlation function. We benchmark the length of the trajectories that is needed to have a converged IR spectrum and compare the results from traditional AIMD method and AIMD with ML calculated forces.

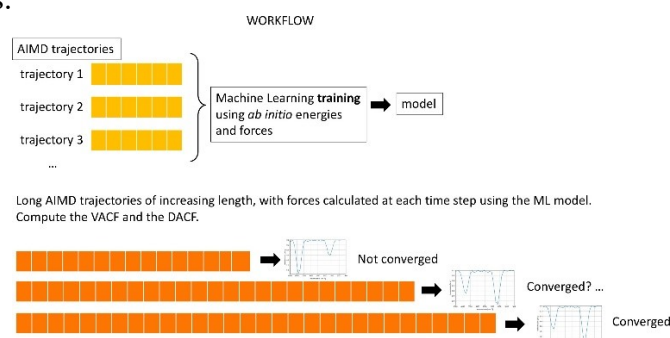


Figure 1: Workflow to calculate autocorrelation functions from AIMD with ML predicted forces.

References

- [1] Hanson-Heine M. W. D., George M. W. and Besley N. A. *J. Chem. Phys.* 2012, **136**: 224102.
- [2] Adel A. and Dennison D. M. *Phys. Rev.* 1933, **43**, 716-723.
- [3] Whitehead R. J. and Handy N. C. *J. Mol. Spect.* 1975, **55**, 356-373.
- [4] Chmiela S., Sauceda E. H., Poltavsky I., Muller K.-R. and Tkatchenko A. *Comput.Phys. Commun.* 2019, **240**, 38-45.
- [5] Y. Shao *et al.*, Advances in molecular quantum chemistry contained in the Q-Chem 4 program package, *Mol.Phys.*, 2015, **113**, 184 -215.

Detailed insight into the electronic relaxation of pyrazine revealed by X-ray spectroscopy

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We use X-ray spectroscopy at both the carbon and the nitrogen *K*-edge to directly compare and elucidate the pathways of electronic relaxation of UV-excited pyrazine in gas and solution phases. This extends recent gas phase experiments at the carbon *K*-edge which have for the first time conclusively shown the involvement of the 1A_u ($n\pi^*$) state in the electronic relaxation of pyrazine [1]. These spectra are explained through a detailed analysis of mixed quantum-classical nonadiabatic dynamics simulations followed by high level calculations of XAS spectra. While the simulated spectra predict a slightly ($\sim 30\%$) faster relaxation, we achieve good overall agreement with the experimental results. We find that electronic relaxation from the S_2 $^1B_{2u}$ ($\pi\pi^*$) state induces population oscillations between the $^1B_{3u}$ ($n\pi^*$) and 1A_u ($n\pi^*$) states in the gas phase that have been predicted by theory [2], but have not been observed so far in experiment. We also see that these oscillations are entirely suppressed in aqueous solution.

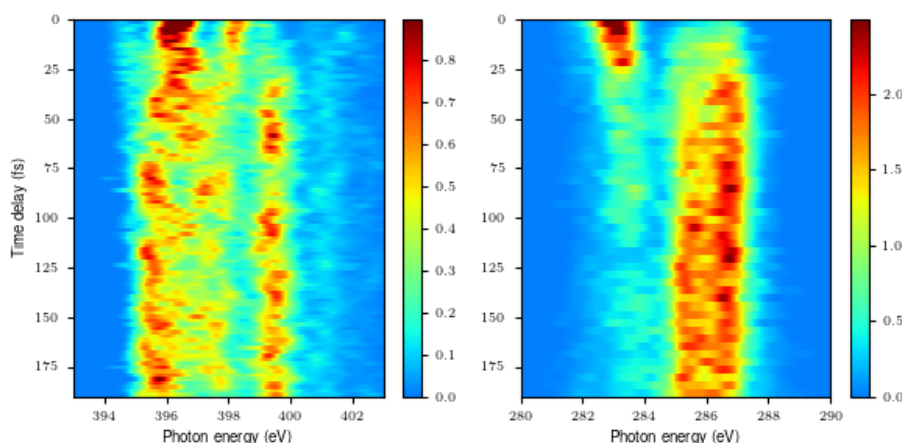


Figure 1: Simulated TRXAS spectra of pyrazine at the carbon and nitrogen *K*-edge

References

- [1] V. Scutelnic, S. Tsuru, M. Pápai, Z. Yang, M. Epshtein, T. Xue, E. Haugen, Y. Kobayashi, A. I. Krylov, K. B. Møller, S. Coriani and S. R. Leone. *Nat. Commun.* 2021, **12**(1), 6-13.
- [2] M. Sala, B. Lasorne, F. Gatti and S. Guérin, *Phys. Chem. Chem. Phys.* 2014, **16**(30), 15957.

Investigation of valence and core shells of azobenzene by photo-ionization and photo-fragmentation

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A class of molecules of high technological interest are the so-called molecular photo-switches. These molecules show structural, optical and electronic properties that can be tuned and controlled reversibly by light flashes and can be exploited for many applications, such as molecular motors, peptide folding or optical storing. Therefore, they hold a high potential for future nanometer-scale devices [1].

The Azobenzene (AB) molecule and its derivatives can be considered prototypes of molecular photo-switches. The *trans*-isomer of AB can be efficiently converted into the *cis*-isomer after interaction with UV light and the *cis* form can be isomerized back to the *trans* with visible light. As a consequence, the full investigation of the photo-physical properties of AB is of great interest to achieve a better understanding of the systems itself as well as of the processes there are involved.

The electronic and structural changes of the AB isolated *trans*-isomer after light absorption can be obtained by means of high resolution synchrotron radiation spectroscopies [2]. In this work, the valence and core shells as well as the absorption K edge of carbon and nitrogen of AB molecule have been investigated by combining photo-ionization and photo-fragmentation experiments and accurate quantum chemical calculations [3]. XPS, NEXAFS, photoelectron-photoion coincidence (PEPICO) measurements, and mass spectra (MS) across the C and N K-edges have been carried out at the Gas Phase Photoemission (GAPH) beamline [4] of the Elettra synchrotron radiation facility in Trieste. The results allowed to fully characterize the XPS and NEXAFS spectra and pinpointed that transient signals will appear in a background-free regions suggesting that both the carbon and nitrogen K edges are suitable candidates for exploring the photoinduced dynamics of AB.

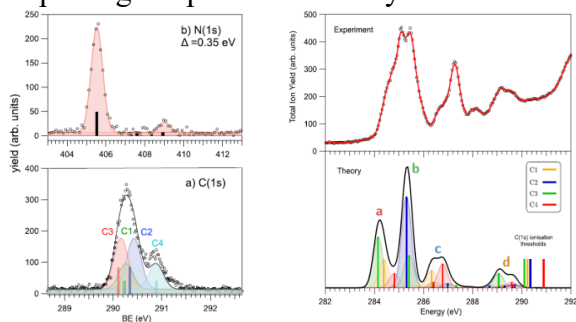


Figure 1: *Left side* – XPS spectra (open dots) of nitrogen 1s (top) and carbon 1s (bottom) with experimental fits (full areas) and theoretical predictions (vertical bars). *Right side* – Carbon K-edge NEXAFS spectra. The experimental data are reported in the top panel, while the theoretical results are depicted in the bottom panel.

References

- [1] J. D. Harris et al., Proc. Natl. Acad. Sci. U. S. A. 115, 9414–9422 (2018).
- [2] J. R. Rouxel et al., J. Chem. Theory Comput. 18, 605–613 (2022).
- [3] P. Bolognesi et al. J. Chem. Phys. 158, 054201 (2023).
- [4] R. R. Blyth et al., J. Electron Spectrosc. Relat. Phenom. 101-103, 959 (1999).

Theoretical kinetic study of Criegee intermediates with N₂O

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Criegee intermediates (carbonyl oxides) are key intermediates in the ozonolysis of alkenes in the atmosphere. These reactions proceed initially by the formation of a primary ozonide (POZ) by addition of O₃ on a double bond, followed by decomposition of the POZ into a Criegee intermediate and a carbonyl compound. [1] Nitrous oxide (N₂O) is a major greenhouse gas and a potential ozone-depleting substance. N₂O is very long-lived in the troposphere, however it reacts photolytically with O(¹D) forming NO resulting in the destruction of the ozone layer. The concentration of N₂O in atmosphere is increasing continuously in the 21st century, [2] and it is thus critical to investigate the reactions in atmosphere where it is involved as well as to find ways to reduce its concentrations.

In this work, we study theoretically the reaction of N₂O with the CH₂OO Criegee intermediate. This reaction has not been studied before. The kinetic of this reaction is compared to the corresponding ones of the Criegee intermediate with NO and SO₂ and the self-reaction of CH₂OO. [1] For this purpose, high-level quantum chemistry methods (DFT/CAS/CCSD(T)) are employed to study the energy profile of the reaction. Additionally, the mechanism of this reaction is studied searching for characteristic points on the energy path, i.e., minima and transition states. Moreover, *ab initio* molecular dynamics simulations are performed to give insight into the time evolution of the system. The kinetics of the reaction will be studied using kinetic Monte Carlo methodology, which is implemented in the AutoMeKin software package. [3-6]

References

- [1] L. Vereecken, H. Hardera and A. Novellia, *Phys. Chem. Chem. Phys.* 2012, **14**, 14682-14695.
- [2] T. L. Nguyen, A. R. Ravishankara and J. F. Stanton, *Chem. Phys. Lett.* 2018, **708**, 100-105.
- [3] E. Martínez-Núñez, G. L. Barnes, D. R. Glowacki, S. Kopec, D. Pelaez, A. Rodriguez-Fernandez, R. J. Shannon, J. J. P. Stewart, P. G. Tahoces and S. A. Vazquez, *J. Comput. Chem.* 2021, **42**, 2036-2048.
- [4] E. Martínez-Núñez, *J. Comput. Chem.* 2015, **36**, 222-234.
- [5] E. Martínez-Núñez, *Phys. Chem. Chem. Phys.* 2015, **17**, 14912-14921.
- [6] J. J. P. Stewart, MOPAC2016, Stewart Computational Chemistry: Colorado Springs, CO, USA, [HTTP://OpenMOPAC.net](http://OpenMOPAC.net), 2016.

Pump-probe experiment on gas-phase DNA

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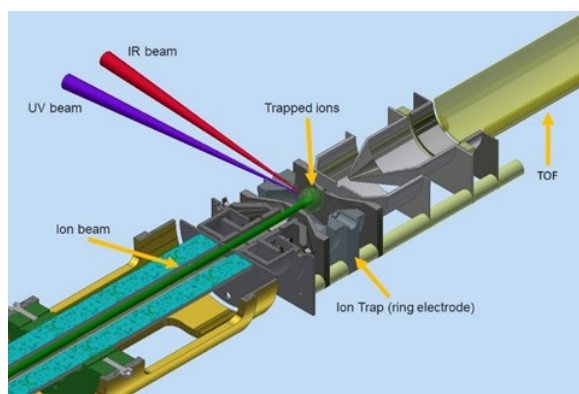
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The formation of the G-quadruplex DNA from DNA monomers proceeds via a complex self-assembly process. We study these systems because of their presence in the telomere of the human genome and because they allow DNA replication [1]. In addition, G4 is also found in regular DNA. The in-vivo folding of DNA strands rich in guanine, into G-quadruplex takes hours [2], which is why the reverse process, i.e., melting of G-quadruplexes is usually investigated experimentally. To study the very first femtoseconds and picoseconds of this melting process, it is straightforward to employ a gas-phase pump-probe approach. Here, we employ an UV pump laser pulse to start the G4 unfolding process and an IR probe pulse. We have previously shown that G4 structures based on by 5'-TTGGTT-3' monomers can be melted by fs IR laser pulses [3], leaving the constituent monomers intact. Interaction of the same laser pulse with monomer ions, however, leads to fragmentation. It is the yield of the monomer fragments that will be used as an observable.

To first understand the response of 5'-TTGGTT-3' monomer anions upon interaction with the pump-probe pulses, we investigated the dependence of ionization and fragmentation as a function of pump-probe delay in a radiofrequency ion trap. We interfaced both laser beams with the ion cloud. Firstly, multiple UV photons of 4.82 eV are absorbed and ultimately heat the system up, triggering the unfolding process; secondly, the IR beam (1030 nm) fragments the system. The photoproducts generated by the combined pump-probe interaction are then analyzed and assigned according to their m/z ratio.



Tandem mass spectrometer, Paultje.

References

- [1] M.L. Bochman, K. Paeschke and V.A. Zakian, *Nat Rev Genet* 2012, **13**, 770-780.
- [2] R.D. Gray and J.B. Chaires, *Nucleic Acids Research* 2008, **36**, 4191-4203.
- [3] X. Wang, (2022). Photon induced charge and structural dynamics in gas-phase DNA. PhD thesis, University of Groningen.

The interplay between theory and experiment in the study of electron scattering from methyl formate (HCOOCH₃)

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Methyl formate (HCOOCH₃) has been detected towards many interstellar sources, including hot, and prestellar cores, though its formation route is not fully understood. Low-energy electrons are thought to play an important role in inducing chemical reactions occurring in interstellar ices. We present the comparison of experimental and calculated cross sections for electron scattering on methyl formate. Measurements of the absolute *grand*-total cross sections (TCS) were performed with the linear transmission method [1] for energies ranging from 0.2 up to 300 eV. Integral elastic cross section (ECS) was calculated up to 15 eV with the R-matrix approach implemented in the UKRmol+ suite [2].

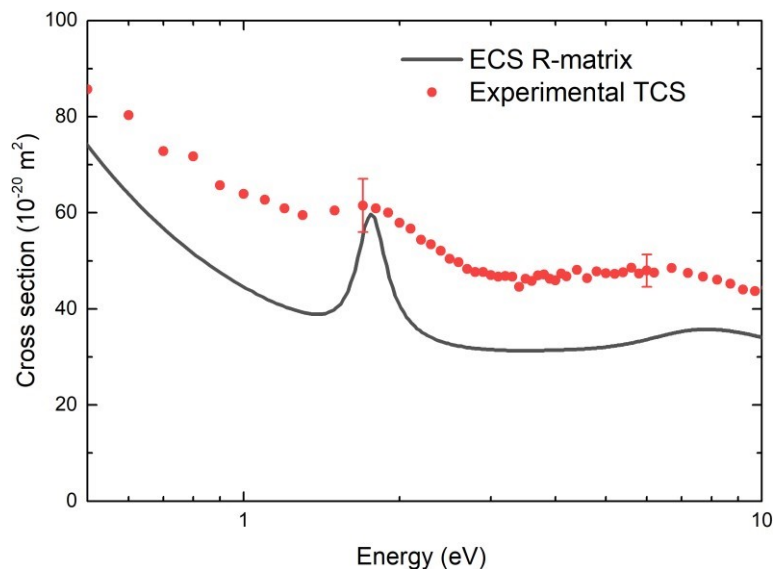


Figure 1: Present experimental TCS and calculated ECS for electron scattering on HCOOCH₃ [3].

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References

- [1] Cz. Szymkowski and P. Możejko *Vacuum* 2001, **63**, 549-554.
- [2] Z. Mašin, J. Benda, J. D. Gorfinkiel, A. G. Harvey and J. Tennyson *Comput. Phys. Commun.* 2020, **249**, 107092
- [3] N. Tańska, E. Bandeira, A. S. Barbosa, K. Wójcik, S. Dylnicka, E. Ptasińska-Denga, Cz. Szymkowski, M. H. F. Bettega and P. Możejko, submitted

Excitation of hot ammonia rotational levels due to collisions with molecular hydrogen

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We report rotationally state-selective collisional data for the (de)excitation of NH₃ induced by H₂ [1]. The computations were performed within the close-coupling formalism by the HIBRIDON scattering code [2]. The cross sections are calculated up to 4700 cm⁻¹ kinetic energies and the corresponding rate coefficients are derived up to 500 K, with a total number of 33 *ortho*- and 62 *para*-NH₃ states included. The collisional propensity rules have been analysed. Rate coefficients were also computed following an averaging over the thermal H₂ relative populations, which exhibit significantly larger magnitudes than the corresponding state-to-state collisional data in the case of NH₃ transitions with large internal energy difference, due to the strong rotational energy transfer and near-resonance effects between the colliders.

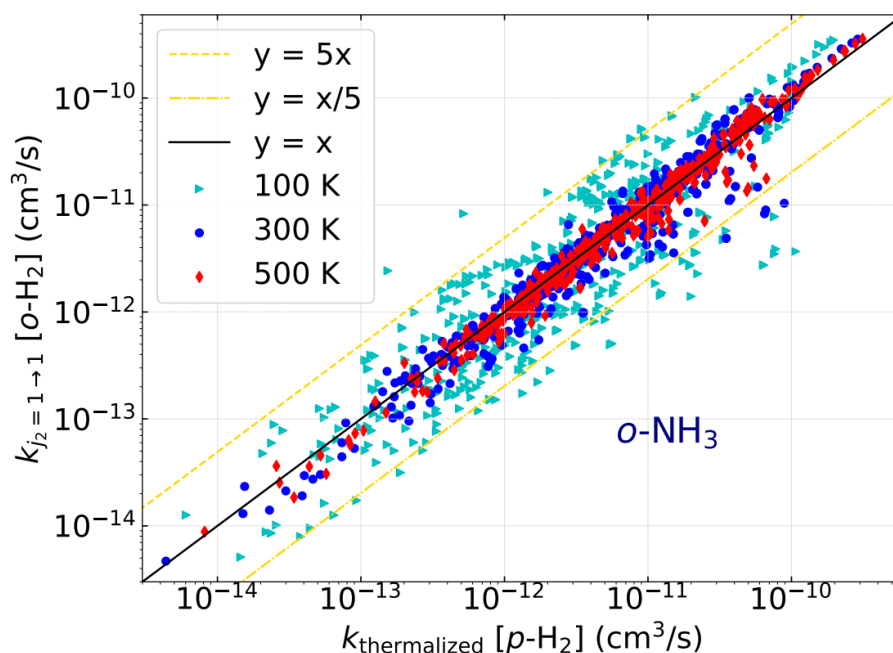


Figure 1: Ratio of the *ortho*-NH₃ rate coefficients as computed in collisions with thermally averaged *para*-H₂ ($j_2=0,2$) vs. ground-state *ortho*-H₂ ($j_2=1$) at 100, 300 and 500 K.

Acknowledgments: We acknowledge financial support from the European Research Council (Consolidator Grant COLLEXISM, Grant Agreement No. 811363)

References

- [1] S. Demes, F. Lique, J. Loreau, A. Faure, *Mon. Not. Roy. Astron. Soc.* 2023, **524**, 2368-2378.
- [2] M. Alexander, P. Dagdigan, H.-J. Werner, J. Klos *et al.*, *Comp. Phys. Comm.* 2023, **289**, 108761.

Quantum Dynamics of Small Molecules; Methods and Application

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The use of high level, multidimensional quantum dynamics methods such as MCTDH [1] and vMCG [2] can be used to provide an accurate description of a time-evolving system by approximately solving the Time-Dependent Schrödinger Equation. The inclusion of non-adiabaticity in these simulations makes it possible to understand excited state dynamical processes such as photodissociation. In this talk, a brief introduction to some of the Quantum Dynamics methods will be given, along with applications in the form of a study of the dissociation pathways of photo-excited methanol. These results rely on the on-the-fly calculation of the potential energy surfaces along all of the normal modes. From there, the branching ratios (and timescales) of the photodissociation reaction are determined. The ultimate aim of this project is to model the photodissociation in an astrochemically interesting environment, and some work towards that goal is also presented in the form of a new methodology for describing explicit environment interactions.

This talk will focus on the applicability of QD methods to solve chemically interesting problems and will touch on the difficulties one might encounter when trying to use these tools (such as electronic structure calculations) and the limitations associated with them (such as the scaling with system size).

References

- [1] H.-D. Meyer, U. Manthe, L. S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990)
- [2] G. W. Richings, I. Polyak, K. E. Spinlove, G. A. Worth, I. Burghardt, B. Lasorne, *Int.Rev.Phys.Chem.* **34**, 269 (2015)

Investigating photochemical reactions with coupled trajectories

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The exact factorization of the electron-nuclear wavefunction proposes to represent the dynamics of a molecule in the excited state as a single time-dependent nuclear wavefunction, evolving under the action of a single time-dependent potential energy surface and a single time-dependent vector potential [1]. Concepts, such as conical intersections, transition dipole moments and molecular Berry phases, do not arise in this formalism.

The single, time-dependent scalar and vector potentials provide a ready framework for describing the nuclear dynamics through trajectories. I will introduce coupled trajectory formalisms (coupled trajectories mixed quantum classical -- CT-MQC [2], and coupled trajectories Tully surface hopping -- CT-TSH [3]) that can be applied to accurately describe the nonadiabatic dynamics of molecular systems.

We investigated the photoisomerization of a three-dimensional model of the Retinal chromophore [4]. We described the photoinduced cis/trans isomerization process with different coupled trajectory methods accounting for the effects of different couplings as well as varied photoexcitation processes.

References

- [1] A. Abedi, N. T. Maitra, E. K. U. Gross *Phys. Rev. Lett.* 2010, **105**, 123002.
- [2] S. K. Min, F. Agostini, I. Tavernelli, E. K. U. Gross *J. Phys. Chem. Lett.* 2017, **8**, 3048–3055.
- [3] C. Pieroni, F. Agostini *J. Chem. Theory Comput.* 2021, **17**, 5969–5991.
- [4] E. Marsili, M. Olivucci, D. Lauvergnat, F. Agostini *J. Chem. Theory Comput.* 2020, **16**, 6032–6048.

3D Fourier Transform Holography of Randomly Oriented Objects

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Coherent diffraction imaging (CDI) is a lens-less imaging technique practiced at FELs and synchrotron for three-dimensional imaging of molecules, clusters and crystals. In CDI typically, the diffraction patterns are recorded and the phase is obtained through the phase retrieval algorithm [1]. CDI experiments where a reference particle is used with the object can encode the phase information in the diffraction patterns. Fourier transforming such diffraction can generate real space images. Such CDI method is called Fourier transform holography (FTH) [2]. In typical FEL experiments the FEL pulse intercepts the object in random orientations, therefore using the traditional data treatment protocols for assigning orientation to each diffraction pattern from the sample with reference object is not possible which limits the feasibility of 3D FTH. Here we present a new algorithm to get the orientation of randomly oriented samples with the reference object and pave the way forward for the 3D FTH. The algorithms are numerically validated and will be tested with the experimental data in future.

Acknowledgments: The author would like to thank the cost action MD-GAS for the support to present this research.

References

- [1] Jianwei Miao et al. „Beyond crystallography: Diffractive imaging using coherent x-ray light sources. *Science* 348, 530-535 (2015).
- [2] Gorkhover, T., Ulmer, A., Ferguson, K. et al. Femtosecond X-ray Fourier holography imaging of free-flying nanoparticles. *Nature Photon* 12, 150–153 (2018).

Precise measurements of the electron affinities of C₆₀ and C₇₀

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The electron affinities (EAs) of the C₆₀ and C₇₀ molecules have been a matter of disagreement in the literature [1-5]. The most precise values reported from Photodetachment Threshold Spectroscopy (PTS) experiments, with anions that are stored in room temperature storage rings, are 2.666(1) eV and 2.676(1) eV [2] for C₆₀ and C₇₀, respectively. In contrast, the most precise Photoelectron Spectroscopy (PES) experiments, with anions cooled in cryogenic controlled traps, are 2.6835 (6) eV (C₆₀) [4] and 2.765 (10) eV (C₇₀) [5]. The reason for this large discrepancy has been attributed to uncertainties related to spectrometer calibrations in the PES experiments [3], and elevated temperatures in the storage ring experiments such that hot band contributions cannot be neglected when determining the electron detachment energy using PTS [4].

By conducting PTS experiments at the Double Electrostatic Storage Ion Ring ExpERiment (DESIREE), we were able to determine the threshold detachment energy and how it is affected by hot band contributions. The cryogenic operation of DESIREE, which delivers a background pressure of 10³ He/cm³ (at 13 K) [6], allows the fullerene anions to cool down on time scales ranging up to 200s. The threshold energy corresponding to the EA was determined by monitoring how the hot band contributions to the photodetachment cross section becomes less important as the anions cool when they are stored, while the signal from the actual EA threshold remains constant. By using an NMF (Non-negative Matrix Factorization) decomposition technique, the EAs are determined to be 2.683(4) eV and 2.77085(10) for C₆₀ and C₇₀, in agreement with the PES experiments [4,5]. This supports the interpretation in Ref. 4, i.e. that hot band contributions are the reason for the disagreement between the PES and PTS experiments.

In follow-up experiments, we aim to use a depletion laser technique, based on the experiments of the hitherto most precise EA measurement of any atomic species [8], to eliminate the contribution from long-lived excited states and improve the measurement of the EA of C₆₀ and C₇₀ with unprecedented precision.

References

- [1] R. Smalley *et al.*, *Chem. Phys. Lett.* 1991 **182** 5
- [2] C. Brink *et al.*, *Chem. Phys. Lett.* 1995 **233** 52
- [3] K. Støchkel and J. U. Andersen, *J. Chem. Phys.* 2013 **139** 164304
- [4] D.L. Huang *et al.*, *J. Chem. Phys.* 2014 **140** 224315
- [5] X.B Wang *et al.*, *Phys. Rev. Lett.* 2006, **96**, 143002
- [6] H.T. Schmidt *et al.* *Rev. Sci. Instrum.* 2013, **84** 055115
- [7] M. Kristiansson *et al.* *Nat. Comm.* 2022 **13** 5906

Excited state quantum dynamics on graphene nanoflake models

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In this work, we study the deactivation pathways that take place after the UV excitation to the excited state manifold of coronene and circumcoronene, small moieties used as simplified models for graphene quantum dots, nanoflakes and poliaromatic hydrocarbons (PAHs). We use the wavepacket method ML-MCTDH[1] to study the time evolution of the states as well as their lifetimes.

The full-dimensional non-adiabatic dynamics results show that the different absorption spectra are only due to electronic delocalisation effects that change the excited state energies, but their structural dynamics are identical. Breathing and tilting motions drive the decay dynamics of the electronic states independently of the size of the aromatic system.[2] This promising result allows the use of coronene as a model system for the dynamics of larger polycyclic aromatic hydrocarbons (PAHs) such as graphene sheets or nanoflakes.[3]

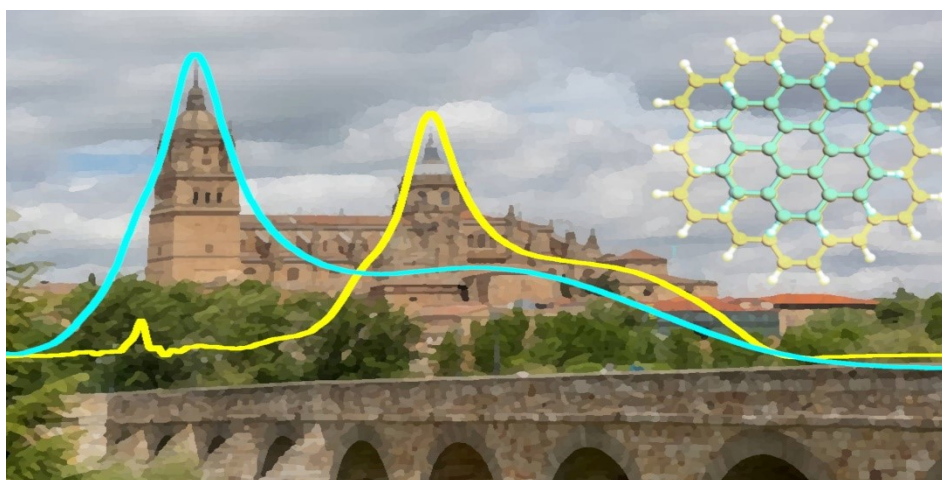


Figure 1: Absorption spectra of coronene and circumcoronene computed as the Fourier transform of the autocorrelation function from dynamics starting from the $1B_{3u}$ excited state. In the background, the cathedral of the city of Salamanca, Spain. The x axis has units of nm.

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References

- [1] H. Wang and M. Thoss, *The Journal of Chemical Physics* 2003, **119**, 1289-1299.
- [2] A. Martín Santa Daría, L. Gonzalez-Sanchez and S. Gómez (under revision)
- [3] D. López-Díaz, A. Solana, J. García-Fierro, M. Merchán, M. Velázquez, *Journal of Luminescence* 2020, **219**, 116954.

Photofragmentation dynamics of halogenated nitroimidazole radiosensitizers

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In a series of gas-phase experiments, we have investigated the photofragmentation processes of iodine- and bromine-enhanced nitroimidazole-based radiosensitizer model compounds at varying photon energies. Radiosensitizers are compounds used in radiotherapy to make tumor cells more sensitive to the radiation treatment. Unlike traditional nitroimidazole radiosensitizers used in clinics, the studied molecules possess a dual functionality, featuring improved photoabsorption capabilities due to the inclusion of high-Z elements and the ability to generate species relevant to cancer sensitization upon photofragmentation¹. This dual functionality holds promise for the development of more effective sensitizers for future applications.

Despite the fact that the investigated radiosensitizers are not in their natural environment, gas phase experiments provide valuable control over the occurring fragmentation reactions, thereby offering insights into radiosensitization mechanisms¹⁻⁴. We have employed the following advanced experimental techniques: photoelectron-photoion-photoion coincidence spectroscopy (performed at MAX IV, FinEstBeAMS beamline) and near-edge X-ray absorption mass spectrometry (performed at BESSY II, UE52_PGM beamline). To assess the differences in the fragmentation dynamics, we compared the results with non-halogenated references. Furthermore, we explored the impact of incorporating a single water molecule into the system on its fragmentation behavior. This experiment was performed at the P01 beamline at PETRA III synchrotron using the ion trap setup to record mass spectra of the halogenated molecule and its water adduct under hard X-rays.

Acknowledgments: This work was supported by the Estonian Research Council grant (MOBTP1013). We acknowledge the synchrotron facilities MAX IV (FinEstBeAMS beamline), BESSY II (UE52_PGM beamline), and PETRA III (P01 beamline) for the granted beamtime and helpful beamline staff.

References

- [1] Pihlava, L.; Berholts, M.; Niskanen, J.; Vladyka, A.; Kooser, K.; Stråhlman, C.; Eng-Johnsson, P.; Kivimäki, A.; Kukkk, E. *Phys. Chem. Chem. Phys.* **2023**, *25* (18), 13004–13011.
- [2] Bolognesi, P.; Casavola, A. R.; Cartoni, A.; Richter, R.; Markus, P.; Borocci, S.; Chiarinelli, J.; Tošić, S.; Sa'adeh, H.; Masič, M.; Marinković, B. p.; Prince, K. c.; Avaldi, L. *J. Chem. Phys.* **2016**, *145* (19), 191102.
- [3] Itälä, E.; Niskanen, J.; Pihlava, L.; Kukkk, E. *J. Phys. Chem. A* **2020**, *124* (27), 5555–5562.
- [4] Meißner, R.; Kočišek, J.; Feketeová, L.; Fedor, J.; Fárnik, M.; Limão-Vieira, P.; Illenberger, E.; Denifl, S. *Nat. Commun.* **2019**, *10* (1), 2388.

Fragmentation Dynamics of Coulomb Explosion of N₂ Using Velocity Slice Imaging Technique

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The invention of the momentum imaging technique has revolutionized the field of molecular collisions and light-matter interaction. The adaptation of the Velocity Slice Imaging (VSI) technique in photo-dissociation study as well as in low-energy electron collision experiments has brought forward new facets of these processes [1]. In this technique, only the central slice of the Newton sphere, which contains the ions emitted on the plane of the collision, is detected and gives the full angular and translational energy information. The detection of central slices can be done by pulsing the position-sensitive detector in such a way that the detector remains active only during the arrival of the central slice of the desired ion [2]. For the very first time in ion-molecule collision studies, we have used VSI technique to probe the fragmentation dynamics of the Coulomb explosion of N₂.

A large volume of work has been reported in the literature about the fragmentation dynamics of the Coulomb explosion of the different charge states of the molecular nitrogen ion, mostly by using recoil ion momentum spectroscopy. Using VSI technique, we have measured the angular distribution as well as the kinetic energy of the fragments formed in the collision of 120 keV Ar⁸⁺ beam with supersonic gas beam of N₂ (Fig.1a). The kinetic energy (KE) spectrum of the fragment N⁺ formed in the decay of N₂²⁺ shows two distinct peaks at 3.75 eV (1st) and 5.15 eV (2nd) respectively (Fig.1b), which is similar to previous reported measurements. However we have observed a KE-dependent angular distribution in which, the 1st peak shows an isotropic distribution, whereas for the 2nd peak, the angular distribution indicates that the perpendicular orientation of the parent molecular ion with respect to the projectile beam is more favored for the charge symmetric decay of N₂²⁺ (Fig.1c). Extended interpretation of this finding is needed, as the KE-integrated angular distribution for N⁺ reported in the literature is given without distinction of the various dissociative processes.

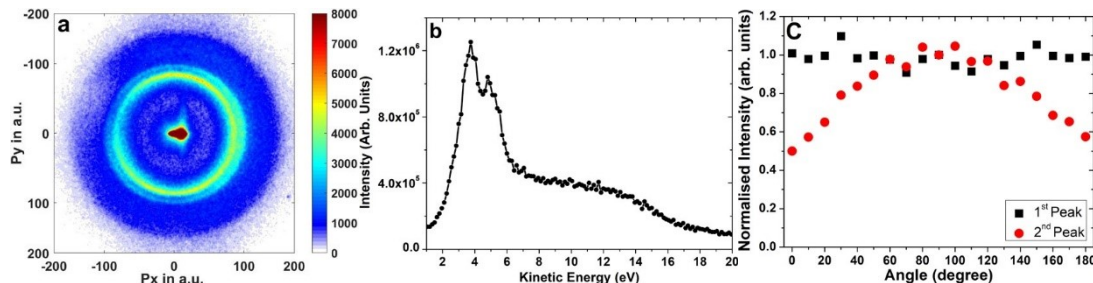


Figure 1: VSI (a), Kinetic energy distribution (b) and Angular distribution (c) of the fragment N⁺.

References

- [1] Akshay Kumar, Suvasis Swain, and Vaibhav S. Prabhudesai, Nat. Comm. **14**, 2769-2776.
- [2] Dave Townsend, Michael P. Minitti and Arthur G. Suits, Rev. Sci. Instrum. **74**, 2530-2539.

When the Arrhenius rate law is not fulfilled: bimolecular collisions through a pre-reaction van der Waals complex

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A vast majority of gas-phase chemical reactions proceed via reaction intermediates, supported by potential wells. The kinetic and dynamical signatures of a complex-forming reaction can be quite distinct from those of direct reactions. The reaction path of these reactions is often barrier-less or contains a "submerged" barrier, which may result in a significant deviation from the Arrhenius law. Negative temperature dependence of the rate constant can be observed for many of these reactions, or sometimes even the sign of the activation energy changes with the temperature. While the dynamics of reactions with direct mechanism is well established, our knowledge and understanding of complex-forming reactions is still far from complete.

Many of such complex-forming reactions take place between free radicals (mainly hydrocarbon radicals) which are the main substances of flames. The kinetics of prototypical hydrocarbon radicals provides the major source for the determination of the heats of formation (C-H bond energies) for alkyl radicals. Despite the importance of this information and the number of experimental studies that have been done so far on hydrocarbon radicals, considerable disagreement can be found among the derived heats of formation based on distinct experimental works.

$HBr + CH_3 \rightarrow Br + CH_4$ and $HBr + OH \rightarrow Br + H_2O$ are the prototypes of this class of reactions characterized by a van der Waals complex and a "submerged" barrier to H-atom abstraction. In our studies, we performed quantum state resolved quasiclassical trajectory calculations on accurate global potential energy surfaces to understand the origin of its unique Arrhenius behavior. Besides the characterization of the dynamics, we also calculated the accurate rate constants in a wide temperature range to diminish the uncertainty of kinetic models [1-3].

References

- [1] S. D. Gao, X. Xin, D. Wang, P. Szabo, G. Lendvay, *Phys. Chem. Chem. Phys.*, (2022), 24, 10548
- [2] B. Csorba, P. Szabo, S. Goger, G. Lendvay, *J. Phys. Chem. A*, (2021), 125, 38, 8386
- [3] S. Góger, P. Szabo, G. Czako, G. Lendvay, *Energy & Fuels*, (2018), 32, 10100

Investigating the Reactivity of Silicon and Sulfur Bearing Species to Unravel the Beyond-2nd-Period Chemistry

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Chemistry plays a remarkable and widespread role in space, even in the face of challenging and extreme environmental conditions. Gaining a comprehensive understanding of how molecules are formed and destroyed is crucial to unraveling the past, characteristics, and development of astronomical entities where these compounds have been detected. Therefore, gathering a solid theoretical and experimental knowledge on such processes, encompassing neutral and/or ionic species, becomes indispensable.

Mimicking and extending the combined chemical-astronomical approach used to investigate the chemistry of the so-called interstellar Complex Organic Molecules (iCOMs) [1, 2], which interest is strongly related to the development of prebiotic molecules in space, we aim to shed light on the chemical processes involving species containing beyond-the-2nd-period elements. Many of them are indeed significantly abundant in space and some of their compounds (e.g., SiO, SiS, H₂CS, CH₃SH) have been already detected [3]. By understanding this chemistry, we can collect valuable data on species responsible for prebiotic molecules (beyond iCOMs) and the incorporation of Si into the refractory core of dust particles, ultimately contributing to the birth of planetesimals and planets.

Numerous reactions involving these elements are documented in accessible databases (e.g., KIDA and UMIST); however, some entries suffer from incompleteness or inaccuracies, such as unstable isomers incorrectly identified as primary products, or rate constants lacking temperature dependence. Moreover, experimental data, when available, is frequently sourced from older studies. To critically revise such information, we now illustrate preliminary findings from laboratory experiments investigating the reactivity of various Si- and S-bearing species in the gas phase.

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References

- [1] P. Caselli, C. Ceccarelli, *A&ARev.* 2012, **20**, 56.
- [2] E. Herbst, E.F. van Dishoeck, *ARA&A.* 2009, **47**, 427–480.
- [3] <http://www.astro.uni-koeln.de/cdms/molecules>

Cyclic crown ether traps for alkali ions: IQA portrayed reaction pathways

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Sodium and potassium ions have crucial roles in various physiological processes within the human body, and their imbalance has been linked to a range of problematic health conditions. Detection of these ions in blood samples relies on optical and electrochemical sensing. These sensors need to meet specific criteria, including high sensitivity and strong selectivity. Crown ethers are recognized as effective traps for alkali ions due to their oxygen atoms oriented inward, attracting positively charged particles. Cyclic crown ethers that demonstrate selective preference for Na⁺ and K⁺ ions are already synthesized. [1] Furthermore, notable spectral changes are observed upon ion capture. Apart from the favorable cavity dimensions, the remarkable selectivity of these ethers arises from significant interactions between the metal ions and polar solvent molecules. [2] While long-range electrostatic forces facilitate ion-trap recognition, different characteristics define the interaction between the ions and their respective hosts. In this sense, Na⁺ resembles a point charge, whereas the high polarizability of K⁺ results in pronounced quantum effects. This research aims at providing comprehensive mechanistic insights as well as energetic changes along ion capture reaction pathways. The reaction pathways are resolved by constructing minimum energy paths with constraints imposed in the form of the coordination number (CN) of the alkali cation with respect to crown's coordinating oxygen atoms. Afterwards, Interacting Quantum Atoms (IQA) methodology is employed to examine intra- and inter-fragment interactions along the reaction pathways. IQA has been proven successful in describing various systems featuring non-covalent interactions. Additionally, we utilize Relative Energy Gradient (REG) analysis which helps in identification of the driving forces for ion-trap complex formation. In this particular case, dominant Na⁺-crown interaction is electrostatic, while the nonclassical interaction plays a significant role for K⁺-crown complexes. However, REG analysis reveals that classical contributions govern not just Na⁺ complexation (CN = 4.8), but also K⁺-crown formation in the small region along the reaction path close to the final point (CN = 5.4).

Acknowledgments: This work was financially supported by the Ministry of Education, Science, and Technological Development of the Republic of Serbia within the framework of contract number: 451-03-47/2023-01/200146. B. M. acknowledge the COST Action CA18212 (Molecular Dynamics in the GAS phase (MD-GAS)).

References:

- [1] A. Giovannitti, C. B. Nielsen, J. Rivnay, M. Kirkus, D. J. Harkin, A. J.P. White, H. Sirringhaus, G. G. Malliaras and I. McCulloch, *Adv. Funct. Mater.* 2015, 26, 514-523.
- [2] M. Hercigonja, B. Milovanović, M. Etinski and M. Petković, *J. Mol. Liq.* 2023, 381, 121791.

Influence of Ground State Distributions on Calculations of Photolysis Observables

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Nonadiabatic molecular dynamics offers a powerful tool to study the excited-state dynamics of molecular systems beyond the Born-Oppenheimer approximation. The key to any nonadiabatic dynamics simulation is the definition of the initial conditions, ideally representing the initial molecular quantum state of the system of interest. We provide a detailed analysis of how initial conditions may influence the calculation of experimental observables by focusing on the photochemistry of methylhydroperoxide, the simplest and the most abundant organic peroxide in the atmosphere. Following our protocol for the determination of photolysis observables of transient atmospheric molecules,[1] we investigate the outcomes of trajectory surface hopping simulations for distinct sets of initial conditions sampled from different approximate quantum distributions: harmonic Wigner distribution and ab initio molecular dynamics using a quantum thermostat. We show how the choice of initial conditions critically affects photoabsorption cross-sections, photolysis quantum yields, and translational kinetic energy maps, in particular when low-frequency normal modes are coupled to the photophysics of a molecule.[2,3]

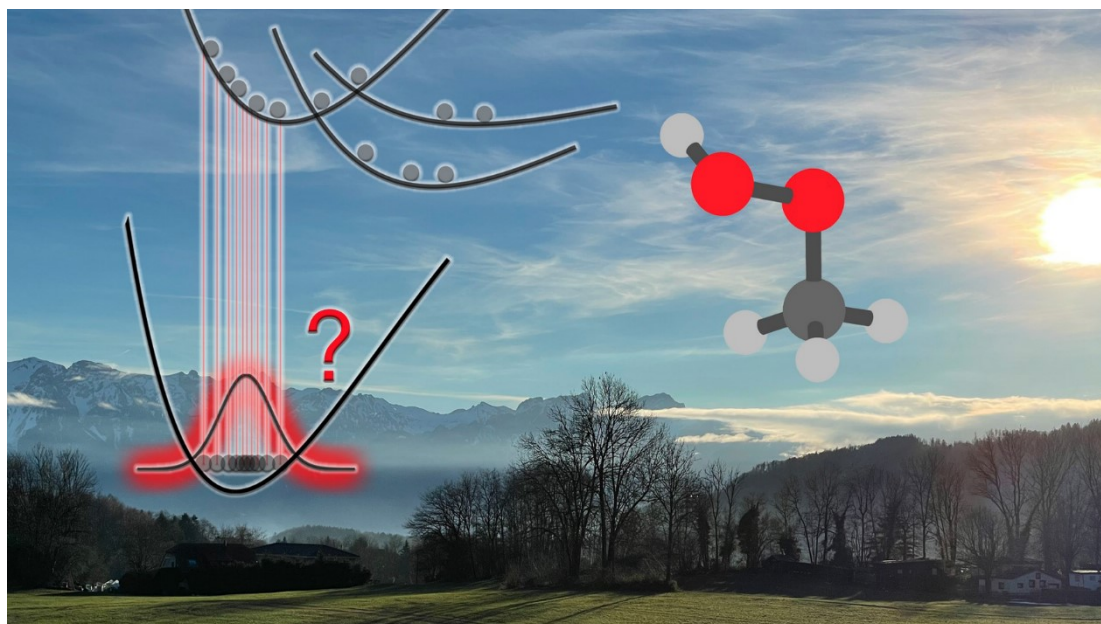


Figure 1: Scheme of molecular photoexcitation and excited state dynamics

References

- [1] A. Prlj, L. M. Ibele, E. Marsili and B. F. E. Curchod, *J. Phys. Chem. Lett.* 2020, **11**, 5418-5425.
- [2] A. Prlj, E. Marsili, L. Hutton, D. Hollas, D. Shchepanovska, D. R. Glowacki, P. Slaviček and B. F. E. Curchod, *ACS Earth Space Chem* 2022, **6**, 207-217.
- [3] A. Prlj, D. Hollas and B. F. E. Curchod, *J. Phys. Chem A* 2023, accepted (*arXiv:2304.03644v2*).

Posters

Predicting the Environmental Impact of Pesticides by Theoretical Calculations

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In this communication we present the development of the SEPIA Expert System based exclusively in theoretical calculations to predict the Environmental Impact of Pesticides (SEPIA stands from Sistema Experto de Predicción del Impacto Ambiental, in Spanish)

SEPIA is a powerful tool that can be used to perform risk assessment and, in the development, and design of new safer pesticides. Its main goal is to use state-of-the-art theoretical calculations to predict physico-chemical and ecotoxicological properties and to identify potential degradation products in different environments. It consist in 5 modules to evaluate a) the structure of most stable conformers in different media, b) evaluation of electronic properties using high level DFT calculations, c) prediction of degradation products by means of Molecular Dynamic calculation, d) QSAR and Machine Learning models to predict final properties of interest for the industry and regulatory agencies e) a large open access database with all the results obtained in the calculations. At this moment, this database contains the conformation of 500 different pesticides and results of 60.000 individual DFT calculations and we expect to incorporate in the systems around 600 active substances in a near future. All predicted properties are also available at the web site www.sepia-pesticides.es

A critical aspect to evaluate environmental impact is to identify potential degradation products. Part of the system implies the evaluation the fragmentation dynamics of ionized forms and the degradation products obtained under solar irradiance to simulate environmental conditions. Some examples of the calculation performed to predict dissociation products under the presence of solar radiation will be presented for Tralkoxydim pesticide. Molecular Dynamic calculations of the fragmentation of protonated forms will be presented for a family of triazole-containing fungicides. Collaboration with experimental groups is crucial to verify the theoretical predictions.

A chemist's guide to DESIREE: recurrent fluorescence in polycyclic aromatic hydrocarbons

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DESIREE (Double ElectroStatic Ion Ring ExpERiment) is a cryogenic ion-storage ring experiment at Stockholm University in which electrostatic fields are used to store ions on long timescales (tens of seconds) by selecting ions of a particular m/z and controlling their orbit in the ring. The principle of these ion-storage ring experiments is to monitor the dissociation of charged and vibrationally-hot species, through detection of neutral fragments, as a function of storage time. Some of the present authors have studied the photophysics of selected radical cationic polycyclic aromatic hydrocarbons (PAHs) that have either recently been identified in the interstellar medium (*e.g.* cyanonaphthalene, indene, and cyanoindene)[1,2,3], or are related to PAH formation (*e.g.* azulene and naphthalene). These studies[4,5] have observed two important stabilisation pathways that help to account for the unexpectedly high abundance of the PAHs identified in the interstellar medium – infrared cooling and recurrent fluorescence. Here, we give an overview, from a chemist's perspective, of the two single-ring experiments (spontaneous neutralisation and photo-induced neutralisation) used to study these radical cationic PAHs, and of the properties of the stabilisation pathways.

References

- [1] B. McGuire, R. Loomis, A. Burkhardt, et al., *Science*, 2021, **371**, 1265–1269
- [2] A. Burkhardt, K. Long, K. Lee, et al., *Astrophys. J. Lett.*, 2021, **913**, L18
- [3] M. Sita, P. Changala, C. Xue, et al., *Astrophys. J. Lett.*, 2022, **938**, L12
- [5] J. Lee, M. Stockett, E. Ashworth, et al., *J. Chem. Phys.*, 2023, **158**, 174305
- [6] M. Stockett, J. Bull, H. Cederquist, et al., *Nat. Commun.*, 2023, **14**, 395

Relaxation dynamics of the naphthalene-azulene radicalcation couple

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Naphthalene and azulene (Figure 1) are isomeric polycyclic aromatic hydrocarbons (PAHs) and are topical in the context of astrochemistry due to the recent discovery of substituted naphthalenes in the Taurus Molecular Cloud-1 (TMC-1). This poster summarises studies at DESIREE (Double ElectroStatic Ion storage Ring ExpERiment) on the thermal- and photo-induced isomerisation, dissociation, and radiative cooling dynamics of naphthalene (Np^+) and azulene (Az^+) radical cations produced in an ECR source [1]. DESIREE is a cryogenic electrostatic ion storage ring, affording “molecular cloud in a box” conditions. Measurement of the cooling dynamics and kinetic energy release distributions for neutrals formed through dissociation, until several seconds after hot ion formation, are consistent with the establishment of a rapid (sub-microsecond) $\text{Np}^+ \rightleftharpoons \text{Az}^+$ quasi-equilibrium. Dissociation by C_2H_2 -elimination proceeds predominantly through common Az^+ decomposition pathways. Simulation of the isomerisation, dissociation, recurrent fluorescence, and infrared cooling dynamics using a coupled master equation, combined with CCSD(T)/cc-pVTZ potential energy surface calculations, reproduce the trends in the measurements. The data support that radiative cooling *via* recurrent fluorescence, predominately through the $\text{D}_0 \leftarrow \text{D}_2$ transition in Np^+ , efficiently quenches dissociation for vibrational energies up to ≈ 1 eV above dissociation thresholds. These radiative cooling dynamics parallel recent DESIREE measurements on 1-cyanonaphthalene cations [2]. Overall, measurements support the suggestion that small cations, such as Np^+ , may be more abundant in space than previously thought. We are currently applying similar methods to investigate the cooling dynamics of other PAH cations, including those for indene, indenyl, and 2-cyanoindene.

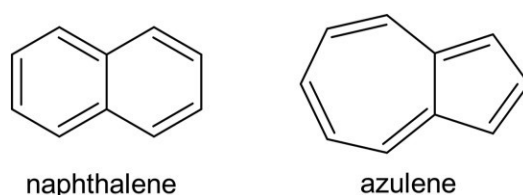


Figure 1: Molecular structures of naphthalene and azulene. The radical cations are denoted Np^+ and Az^+ .

References

- [1] J. Lee, M. Stockett, E. Ashworth, J. Navarro Navarrete, E. Gougoula, D. Garg, M. Ji, B. Zhu, S. Indrajith, H. Zettergren, H. Schmidt, J. Bull, *J. Chem. Phys.*, 2023, **158**, 174305
- [2] M. Stockett, J. Bull, H. Cederquist, S. Indrajith, M. Ji, J. Navarro Navarrete, H. Schmidt, H. Zettergren, B. Zhu, *Nat. Commun.*, 2023, **14**, 395

Functional protein dynamics of RNA-bound h-Argonaute2: a Molecular Dynamics Study

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MicroRNAs (miRNAs) are single-stranded and noncoding RNAs (ncRNAs) that regulate expression of thousands of genes in plants and animals upon the so-called miRNA silencing process. By forming RNA-induced silencing complexes (RISCs) with Argonaute 2 (Ago2), a member of Argonaute protein family, miRNA is used as the guide to identify complementary target mRNA and causes specific gene silencing via translational repression and degradation [1,2].

ESI-MS experiments are normally carried-out in water/organic solvent which can strongly influence the conformational stability of Ago-RNA complex respect to its physiological environment. Therefore, the definition of suitable experimental conditions requires a prior evaluation of the behavior of the complex in similar solution environment employed in ESI-MS experiment. 2 μ s Molecular Dynamics simulations in NPT ensemble were performed on specific Ago-miRNA-mRNA model structure. The conformational space of the complex has been sampled in water solvent and in a mixture of Water/Methanol (70:30), which is the standard solution employed in ESI-MS. Principal components analysis (PCA) was performed on C α atoms of Ago-Protein in order to reduce the conformational space explored, selecting directions having the maximum variance. The Free Energy Landscape at right side of figure 1 exhibits an irregular shape suggesting a high degree of freedom of Ago Protein. Water system shows a local minimum at the extreme side of PC1. Eigenvectors results related to water system show a torsion of PAZ and MID domain along PC1 as highlighted by red arrows direction. The PC2 eigenvectors, instead, exhibit a departure motion between PAZ and MID domains that can expose the RNA chain to solvent attack.

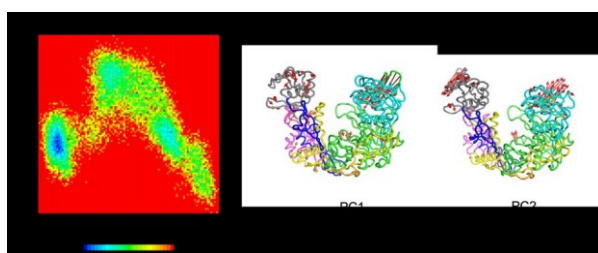


Figure 1 .Right PC1vsPC2 free energy landscape. Left Eigenvectors along PC1 andPC2 for simulation performed in water. Red arrows show the direction of motion along first and second PCs

References

- [1] Nature 2004, 431, 350–355, doi:10.1038/nature02871.v
- [2] Cell 2012, 150, 100–110, doi:10.1016/j.cell.2012.05.017.

Efficient molecular oxidation in collisions with superoxide anions

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Benzene is one of the simplest and more stable aromatic ring molecules. It has been considered a prototype for the study of chemical reactions involving biomolecules. On the other hand, oxygen 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[1,2]. In this context, oxidative processes in benzene have been extensively studied from different points of view such e.g. in atmospheric reactions[3,4]. Ascenzi et al.[5] showed that oxygen-benzene reactions in atmospheric pressure plasmas induce energetically disfavored chemical processes leading to formation of phenol cations ($C_6H_5OH^+$) and neutral phenol (C_6H_5OH). Additionally, relevant ion chemistry processes in the interstellar medium (ISM) have been reported from low-energy anion induced reactions with different types of hydrocarbons yielding increasingly complex molecules[6].

In this communication, we present gas-phase energetic interactions of a superoxide anion with a benzene molecule leading to an unexpectedly and quite efficient oxidation process of the neutral molecule[7,8]. The experimental conditions provide binary collisions between the incoming projectile (O_2^-) and the neutral target molecule (C_6H_6), where no positive ions with higher mass-to-charge ratio (m/z) than that of the parent ion ($m/z=78$ u) are expected to be formed. However, the mass/charge analysis of the collision products reveals the presence of a prominent feature at $m/z \sim 110$ u for specific impact energies between 200 and 900 eV.

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References

- [1] Marx J 1987 *Science* **235** 529
- [2] Shigdel UK *et al.* 2020 *Nat Commun* **11** 4437
- [3] Norrish RGW 1956 *Proc R Soc London A Math Phys Sci* **234** 160
- [4] Lay TH *et al.* 1996 *J Phys Chem* **100** 6543
- [5] Ascenzi D *et al.* 2006 *J Phys Chem A* **110** 7841
- [6] Larsson M *et al.* 2012 *Rep Prog Phys* **75** 066901
- [7] Guerra C *et al.* 2021 *Sci Rep* **11** 23125
- [8] Guerra C *et al.* 2022 *Int J Mol Sci* **23** 1266

CHEMI-IONIZATION PROCESSES WITH THE CREATION OF QUASI-MOLECULAR COMPLEXES IN ATOM - RYDBERG ATOM COLLISIONS

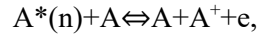
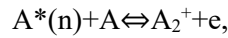
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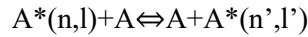
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In this work we will consider inelastic processes in atom Rydberg-atom collisions with formation of molecules and quasi molecules, in particular chemi-ionization and (n-n') mixing. The chemi-ionization reactions (associative ionization and non-associative ionization) are processes of the type:



where A and A⁺ are atoms and atomic ions in their ground states and A*(n) is an atom in a highly excited (Rydberg) state with the principal quantum number n ≥ 2. Moreover, the Rydberg state distribution in a weakly ionized hydrogen plasma may be as well strongly influenced by (n-n')-mixing processes in A*(n) + A collisions i.e. excitation/deexcitation processes



provoked by the same resonant mechanism as the processes of chemi-ionization.

The considered processes are treated as the result of the almost resonant energy conversion within the electron component of a quasi-molecular complex, created during thermal atom Rydberg-atom collisions. It will be demonstrated that the inclusion of (n-n') mixing in the calculation, influences significantly on the values of chemi-ionization rate coefficients, particularly in the lower part of the block of the Rydberg states.

We will also demonstrate the significance of chemi-ionization processes for solar and stellar atmospheres investigation as well as for broad line region around active galactic nuclei.

Understanding Cyanine Chromophores: Photochemistry, Photophysics, and Stability

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Cyanines are well-known chromophores, acting among others as infrared-absorbing tools for fluorescent labeling of nucleic acids and proteins, and photosensitizers in photodynamic therapy, biosensors, or imaging agents (see Figure 1) [1]. In our work, we present two theoretical studies concerning on cyanines: a description of their photophysical behavior, and an exploration of their newly discovered truncation mechanism.

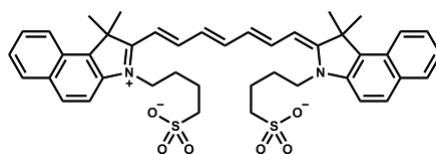


Figure 1: Structure of Indocyanine Blue – a cyanine derivative approved for medical usage by Food and Drug Administration (FDA).

The photophysical description of cyanines poses several challenges. It was shown that commonly used DFT-based approaches fail due to a strong reorganization of the electron density upon excitation [2,3]. In addition, our study reveals another issue: When calculating spin-orbit coupling matrix elements (SOCMEs), one arrives at their strong dependence on the vibrational motion [4]. Such a phenomenon – the **spin-vibronic coupling** – then turns out to be a crucial factor in determining the rates of intersystem crossing of cyanines.

Synthetic approaches aiming to modify cyanines typically target the terminal parts of a cyanine chain. Prof. Klán and his co-workers recently discovered a new way towards a **shortening of the chain itself**. Our theoretical exploration found a significant role of **entropy**, which remarkably changes the picture when moving from the electronic energy surface to free energies. A discussion about the involvement of the entropic terms in the calculations occurs in the community (e.g., [5]). Our results support the view [6] that no special treatment is necessary when an appropriate level of theory is used (DLPNO-CCSD(T) in our case).

Acknowledgments: We thank Prof. Petr Klán and his colleagues from Masaryk University in Brno for collaboration and for providing the experimental data on the cyanine truncation process and the photophysical properties of cyanine derivatives.

References

- [1] A. P. Gorke, R. R. Nani, and N. J. Schnermann, *Org. Biomol. Chem.* 2015, **13**, 7584–7598.
- [2] B. Le Guennic, D. Jacquemin, *Acc. Chem. Res.* 2015, **48**, 530–537.
- [3] L. Štacková, E. Muchová et al., *J. Org. Chem.* 2020, **85**, 9776–9790.
- [4] R. Tovtik, E. Muchová et al., *J. Org. Chem.* 2023, **88**, 6716–6728.
- [5] S. Liu, X. Zhu et al., *Phys. Chem. Chem. Phys.* 2023, **25**, 913–931.
- [6] Z. Liu, C. Patel et al., *Phys. Chem. Chem. Phys.* 2017, **19**, 30647–30657.

Role of Hydrophobic Interactions in DNA Recognition: Insights from Molecular Dynamics Simulations of DHX36 Helicase and Parallel G-Quadruplexes

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Intricate DNA and RNA structures, such as G-quadruplexes (G4s), require specialized helicases to ensure cellular stability and proper function. DHX36, a DEAH-box helicase, plays a crucial role in gene expression and replication by recognizing and unwinding parallel G4s in an ATP-dependent manner. To understand the molecular basis of DHX36's high affinity and specificity for parallel-type G4s, we employed all-atom molecular dynamics simulations and computed binding free energies. Our findings highlight the essential role of hydrophobic interactions in the recognition process. Two key G4-interacting subdomains of DHX36, DSM and OB, were identified to exhibit high G4 affinity, and they work in a coordinated manner to recognize two distinctive features of parallel G4s: the exposed planar face of a guanine tetrad and the unique backbone conformation of a continuous guanine tract. Notably, the DSM-mediated interactions, primarily reliant on extensive van der Waals contacts between the GXXXG motifs and hydrophobic residues of DSM and a flat guanine plane, emerged as the main contributor to the binding free energy. Interestingly, our results demonstrate that the sterically more accessible 5'-G-tetrad facilitates more favorable van der Waals and hydrophobic interactions, leading to the preferential binding of DSM to the 5'-side. On the other hand, OB primarily binds to G4 through polar interactions by flexibly adapting to the 5'-terminal guanine tract, forming several strong hydrogen bonds with the backbone phosphate groups. Additionally, our investigations revealed a third DHX36/G4 interaction site, encompassing a flexible loop that was previously absent in the crystal structure. Altogether, our study underscores the critical role of hydrophobic interactions in facilitating DHX36's specific recognition of parallel-type G4 structures, shedding light on the molecular mechanisms underlying DNA recognition by this essential helicase.

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Scaling laws for the cooling dynamic of catacondensed PAH cations

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Synopsis Our aim in this study is to establish scaling laws for the internal energy dependent dissociation and radiative cooling rates as functions of the size of polycyclic aromatic hydrocarbons (PAHs) and their nitrogen substituted species. This kind of scaling laws could be used for modelling their survival probabilities in space.

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of organic molecules based on two or more fused hexagonal aromatic carbon rings with hydrogen atoms attached at their outer rims. They are found and formed in a wide variety of environments. In the case of extraterrestrial environments, PAHs are believed to be an important component in interstellar dust and gas and as such are responsible for infrared emission features that dominate the spectra of many galactic and extragalactic sources [1]. PAHs can be categorised as peri- or cata-condensed defined by the arrangement of those rings. Here, we choose to focus on catacondensed PAHs cations such as naphthalene (C₁₀H₈), anthracene (C₁₄H₁₀) and tetracene (C₁₈H₁₂) but also nitrogen substituted PAHs (PANHs) such as acridine (C₁₃H₉N) and phenazine (C₁₂H₈N₂).

When exposed to high-energy photons, PAH molecules may be electronically excited; thus increasing their internal temperature considerably by rapidly redistributing the absorbed energy among all available vibrational states. On longer timescales, they can then relax, by either fragmenting or emitting photons. Emission of IR photons (vibrational de-excitations) is typically a very slow process occurring on timescales exceeding seconds, while Recurrent Fluorescence (RF) or so called Poincaré fluorescence have been shown to effectively stabilize internally hot PAHs on millisecond timescales [2, 3]. In the RF process, vibrational excitation is converted into electronic excitation (inverse internal conversion - IIC) followed by relaxation to the electronic ground state through photon emission.

For the catacondensed PAHs considered in the present study, the emitted photons are in the 1,5-2,5 eV range, which leads to an efficient cooling and a much higher survival probability than cooling via IR emission alone. Key ingredients determining the RF rate are the energy of the excited state being populated in IIC and the oscillator strength for the electronic transition. As these scale with the size of the catacondensed PAHs, we aim to find a simple scaling law for the RF rate by combining theoretical and experimental results from the literature and from novel studies carried out at electrostatic storage ring facilities in Lyon [4] and in Stockholm [5] by members of the present collaboration (see Fig.1). In a similar fashion, we aim to establish a scaling law for the dissociation rate. With these in hand, the survival probabilities for any catacondensed PAH may be determined as a function of internal energy and used in, e.g., astrophysical modelling.

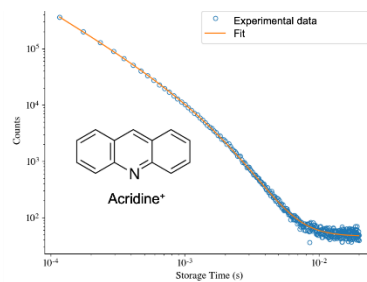


Figure 1. Spontaneous decay curve of acridine cations stored in DESIREE.

References

- [1] Tielens 2008 *Ann. Rev. Astron. Astrophys.* **46** 289
- [2] Martin S et al. 2013 *Phys. Rev. Lett.* **110** 063003
- [3] Stockett et al. 2023 *Nat. Commun.* **14** 395
- [4] Bernard et al. 2019 *J. Chem. Phys.* **150** 054303
Bernard et al. 2023 *PCCP* accepted

Molecular dynamics of spherical metal and metal oxide nanoparticles

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Nanoparticles are used in many technological areas. Due to their shape in molecular structures gas phase dynamics can be modelled rather simply on the nanoscale. The complexity increases rapidly when aggregation phenomena are studied and the interaction with electrons or photons are to be considered.

In the present study, photoionization energies and electron affinities of single nanoparticles for metals and metal oxides in gas phase considering the size and shape (spherical) of the nanoparticles are studied. For large nanoparticles with increasing size and complexity little is known experimentally on the photoionization energies and electron affinities as well as their resonance states. Scattering is not in the current framework of the molecular dynamics software implemented, however, we seek to develop the open source code accordingly to study in future the electron-molecule scattering dynamics of nanoparticles.

Furthermore, time-resolved infrared dynamics through molecular dynamics simulations of H atom connected metal and metal oxide nanoparticles is utilised, where the frequencies are calculated in each time step of simulation. The calculation of the vibrational modes and couplings between the phonons of the nanoparticles' metal atoms and the motion of the H atoms is analysed.

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References

[1] K. Kotsis in PCCP themed collection: Molecular Dynamics in the Gas Phase, *PCCP* 2023, to be submitted.

Using X-ray Absorption Spectroscopy to investigate Nucleotides

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The combination of soft-ionisation techniques, like electrospray ionisation, with radio-mass spectrometric techniques, including radiofrequency ion filtering and trapping, is a powerful tool for studying ions in a well defined state. Biomolecules such as proteins and DNA can thus be investigated without any influences from their solvent environment. Understanding the photoprotection mechanisms in DNA requires, in a bottom-up approach, a detailed understanding of their basic constituents, namely the nucleotides, and their electronic and structural properties and the dissociation mechanisms involved after radiation damage. Activating them with VUV, UV or X-rays from synchrotron facilities helps us gain more insight into their intrinsic properties. In particular, soft X-ray absorption being element specific makes it ideal to probe the different absorption edges and study the resonant photo-absorption in the C, N, O and P inner shells. It is important to understand the role that charge states can have on nucleotides and whether they influence the charge and energy transfer processes within the molecular ion. When developing an overall picture of the system, it is equally important to describe the role of the sugar and phosphate moieties and whether their presence near the nucleobases affects the photoabsorption and the stability of the system.

Experiments were performed on a protonated oligonucleotide chain of the 4 bases Guanine (G), Cytosine (C), Adenine (A) and Thymine (T) connected to the sugar and phosphate backbone. The near-edge X-ray absorption mass spectra were measured at the C, N, O K-edges and P L-edges. Fragmentation mechanism and resonant electronic transitions within the oligonucleotide will be discussed. These experiments were performed at UE52_PGM Ion Trap end station at the BESSY II synchrotron.

Electron-impact excitation and fragmentation of dielectric gases

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Perfluorinated dielectric gases C₄F₇N and C₅F₁₀O were designed as environmentally-friendly alternatives to SF₆ in gas-insulated equipment, but their interactions with free electrons remain poorly understood. Our research addresses this gap by investigating electron-impact excitations and subsequent neutral dissociations of these molecules employing a combination of experimental and theoretical approaches. [1] Most importantly, we implemented a novel computational protocol enabling the calculation of inelastic electron scattering cross sections at a cost comparable to optical oscillator strength calculations. This methodology combines the Born approximation with highly correlated target wave functions. By calculating the photoabsorption and electron energy-loss spectra and contrasting the results with experimental data, we showed that photoabsorption spectra are dominated by $\pi\pi^*$ transitions at higher energies, while low-energy transitions become much more pronounced in the case of forward-direction electron scattering. Furthermore, the electron-impact spectra were shown to converge to the case of photoabsorption for increasing residual energies of forward-scattered electrons. However, the Born approximation, even with the inclusion of the exchange interaction, exhibited limitations in describing backscattering cross sections. To study the time evolution of different initial excited states, non-adiabatic molecular dynamics simulations were employed, revealing non-statistical distributions of neutral fragments formed immediately after the excitation event.

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References

[1] T. Ovad, M. Sapunar, Š. Sršeň, P. Slavíček, Z. Mašín, N. C. Jones, S. V. Hoffmann, M. Ranković, J. Fedor, *The Journal of Chemical Physics* 2023, **158**, 014303.

Reactive collisions between electrons and BeH⁺ at high energy

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Our previous study of dissociative recombination (DR), vibrational excitation (VE) and vibrational de-excitation (VdE), based on the multichannel quantum defect theory (MQDT), presented in [1]-[4], is extended to collision energies above the dissociation threshold, taking into account the dissociative excitation (DE), occurring above the dissociative threshold of the molecular ion. By the scaling law, additional dissociative curves have obtained and they have been included in all calculations. We produced cross sections and rate coefficients (Fig.1) for DR, DE, VE and VdE useful for the detailed kinetics modeling, either in astrophysics, or in the cold plasma close to the wall of the fusion devices.

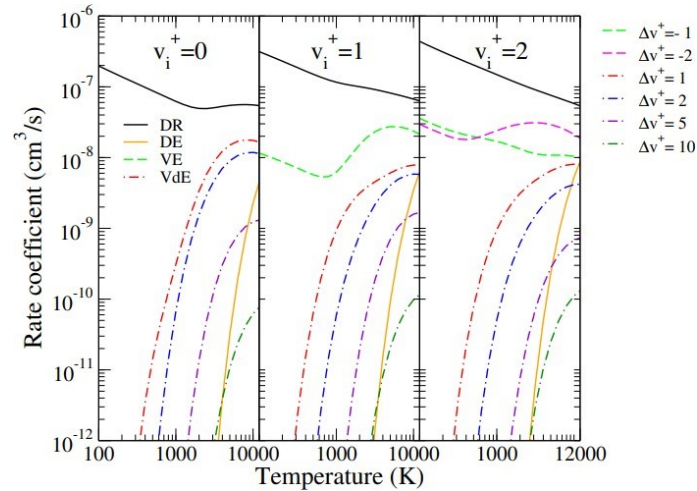


Figure 1: Rate coefficients of BeH⁺ for $v_i^+ = 0, 1, 2$. All competitive reactive processes where $\Delta v^+ = v_f^+ - v_i^-$.

References

- [1] S. Niyonzima S, F. Lique, K. Chakrabarti, Å Larson Å, A. E. Orel A E and I. F. Schneider I F, *Phys. Rev. A* 2013, **87**, 022713.
- [2] S. Niyonzima, S. Ilie, N. Pop, J. Zs. Mezei, K. Chakrabarti, V. Morel, B. Peres, D.A. Little, K. Hassouni, A. Larson, A.E. Orel, D. Benredjem, A. Bultel, J. Tennyson, D. Reiter, I.F. Schneider, *Atomic Data and Nuclear Data Tables* 2017, **115-116**, 287.
- [3] S. Niyonzima, S., et al., *Plasma Sources Sci. Technol.* 2018, **27**, 025015.
- [4] N. Pop et. Al., *Atomic Data and Nuclear Data Table* 2021, **139**, 101414.

Mutual neutralization with manipulated initial quantum level distributions

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The Double ElectroStatic Ion-Ring ExpEriment (DESIREE) was designed to enable studies of mutual neutralization (MN) with ions in their ground states [1,2,3]. In this work, we demonstrate the ability to measure MN with ions in specific excited states. DESIREE combines the ability for long time storage and manipulation of ions with the merged-beams configuration for low-energy MN studies. We used these combined properties to perform MN experiments with Si⁻ beams with or without a significant contribution from the excited metastable levels. Si⁻ ions in excited levels can be eliminated by photodetachment at a wavelength of 900 nm that will leave the ground state ions unaffected as applied recently in a measurement of the oxygen electron affinity [4]. By performing MN measurements with and without the metastable component, we can extract the contributions from the ground and metastable state ions separately.

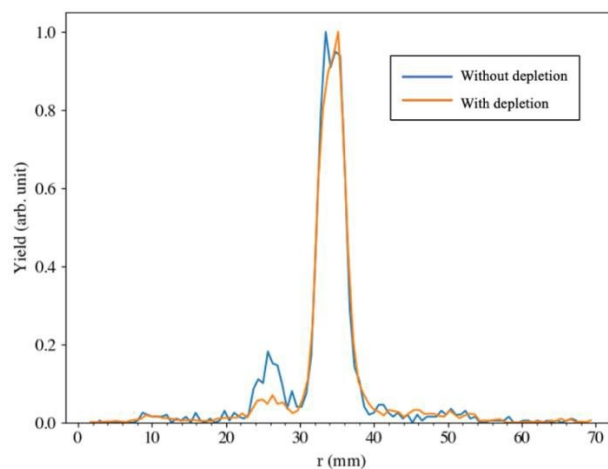


Figure 1 Yield of neutral pairs as a function of the separation r between the atomic products when their centre-of-mass reaches the detector plane. For the blue curve, the laser was not used and the metastable levels were populated, while for the orange curve, the metastable population was eliminated by photodetachment prior to the MN measurement.

Acknowledgments: This work was performed at the Swedish National Infrastructure, DESIREE (Swedish Research Council Contracts No. 2017-00621 and No. 2021-00155).

References

- [1] G. Eklund *et al*, Phys. Rev. A (2020) **102**, 012823 <https://doi.org/10.1103/PhysRevA.103.032814>
- [2] J. Grumer *et al*, Phys. Rev. Lett. (2022) **128**, 033401 <https://doi.org/10.1103/PhysRevLett.128.033401>
- [3] M. Poline *et al*, PCCP (2021) **23**, 24607 <https://doi.org/10.1039/D1CP03977F>
- [4] M. K. Kristiansson *et al*, Nat. Comm. (2022) **13**, 5906 <https://doi.org/10.1038/s41467-022-33438-y>

Dataset for the electron-impact processes involving small molecular ions: influence on the atom excited states population

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In this contribution we report the new data for electron-impact processes involving some small molecular ions. Collisional processes under study may affect atom excited-state populations, i.e. Rydberg state populations as well as ionization level, and optical characteristics of diverse environments. [1,2]. We present rate coefficients for electron-impact processes involving potassium, sodium, lithium and hydrogen molecular cations in domains of higher principal quantum numbers and temperatures up to 12 000 K. The dataset, could be used for various applications, such as plasma chemistry or experiments, for modelling atmospheres of diverse environments such as the interstellar medium, planets and also in the plasma fusion area [3,4].

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References

- [1] Pop, N., et al. *Atomic Data and Nuclear Data Tables* 2021, **139**, 101414.
- [2] Albert, D-, et al., *Atoms* 2020, **8.4**, 76.
- [3] Marinković, B.P.; Srećković, V.A.; Vujčić, V.; Ivanović, S.; Uskoković, N.; Nešić, M.; Ignjatović, L.M.; Jevremović, D.; Dimitrijević, M.S.; Mason, N.J. *Atoms* 2019, **7**, 11
- [4] V.A. Srećković et al., *Data*, 2022, **7(9)**, 129

Ionization and radiative stabilization of an interstellar Polycyclic Aromatic Hydrocarbon molecule

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The Aromatic Infrared Bands observed throughout the Interstellar Medium have long been associated with the vibrational modes common to gas-phase Polycyclic Aromatic Hydrocarbon (PAH) molecules. In the past few years, astronomers using powerful radio telescopes have begun identifying specific PAHs in space based on their unique rotational fingerprints [1]. At the dawn of this new era, we find challenges to the established understanding of the interstellar carbon cycle. The observed abundances of small PAHs like 1-cyanonaphthalene (CNN, C₁₀H₇CN) in the Taurus Molecular Cloud (TMC-1) are underpredicted by state-of-the-art astrochemical modeling by 4-6 orders of magnitude [1]. To help refine these models, we have investigated the stability of 1-CNN against destruction in ionizing collisions, the main destruction channel included in current models, and by VUV photons, which are present even in dark clouds like TMC-1 due to H⁺ recombination.

We used the DESIREE cryogenic electrostatic ion-beam storage ring to determine the absolute dissociation and radiative cooling rate coefficients for 1-CNN cations up to 400ms after collisional ionization [2,3]. We found that Recurrent Fluorescence (RF), the emission of optical photons from thermally excited electronic states, efficiently stabilizes 1-CNN⁺ formed with up to 5 eV of vibrational excitation. This closes some of the destruction channels included in current models and should bring predicted abundances closer to observations. Crucially, Herzberg-Teller (H-T) vibronic coupling was found to enhance the RF rate by two orders of magnitude.

Photoionization of 1-CNN was investigated at the CiPo beamline of the Elettra synchrotron [4]. Prompt autoionization from the plasmon resonance, a pile-up of electronic transitions of the neutral to states well above the detachment threshold, was found to dominate the photophysics for $h\nu = 11.5 - 16.0$ eV. We expect the plasmon-enhanced ionization efficiency of 1-CNN to lead to a higher charge fraction in TMC-1

While we have focused on 1-CNN, H-T coupling, RF and plasmon resonances are typical of PAHs and may have significant influence on their stability in space.

References

- [1] B. McGuire et al. *Science* 2021 **371**, 1265.
- [2] M. H. Stockett et al. *Nature Communications* 2023 **14**, 395.
- [3] J. E. Navarro Navarrete et al. *Faraday Discussions* 2023 **Accepted**, DOI:10.1039/D3FD00005B.
- [4] J. N. Bull et al. *Journal of Chemical Physics* 2023 **158**, 241101.

Ionization and Charge Exchange Cross Sections of Hydrogen Molecule by electron, positron and C^{4+} Impacts

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The understanding of the ionization and charge exchange processes in ion-atom and ion-molecule collisions is of fundamental interest in fields ranging from atmospheric and interstellar physics to radiation damage of solids, surfaces and biological systems. The molecule target holds additional challenges both in experiments and theories due to the many-body character of the collision system.

In this work, we present classical simulations of the ionization and charge exchange cross sections of hydrogen molecule by electron, positron and C^{4+} impacts. We use the classical trajectory Monte Carlo method to obtain the cross sections. For sake of simplicity we apply the three body approximation, i.e. the projectile is one body and the hydrogen molecule is two body. Based on these arguments, in the framework of the hydrogenic approximation the active target electron is initialized around the effective nuclear charge of $Z_{\text{eff}}=1.165$ with effective binding energy of $E_B=0.567$ a.u.

We found that although maybe our model is crude for the description of the hydrogen molecule, the obtained cross sections are close to the previous experimental and theoretical data.

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Interaction of Singly Charged Sodium Ion with Nitrogen Atom: Total and Differential Ionisation Cross Sections

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The electron processes play a significant role in radiation physics, the study of atomic and molecular structures, fusion plasma, and other research domains. In tokamak, atoms are used as a neutral diagnostic beams, such as helium and nitrogen [1].

In our work, we present total and differential cross sections for single ionization in collision between Na^+ ions with N(2p) atom.

We modelled the collision system as a three body system using Garvey model potential [2]. The target is separated into a single active electron and nitrogen core (i.e., nitrogen nucleus and its remaining non-active electrons), the projectile Na^+ with its electrons are considered as a single particle. This model potential invokes the effective charge for a given particle, hence, it considers the screening effect of the non-active electrons. The equations of motion of the collision system are solved numerically using classical trajectories Monte Carlo CTMC method [3].

We present total ionization cross sections as a function of the impact energy in the energy range between 10 keV to 100 MeV. Moreover, we present single and double differential cross sections for impact energy range of 30-60 keV as a function of the ejected electron energies and angles.

We found that the dominant contribution of the electron yield is given by electrons with energies below 10 eV and ejection angles under 20 degrees. Moreover, electrons ejected with energies larger than 20 eV have shown very small angular dependence [4].

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References

- [1] Patel M et al., 2021 *Vacuum* **192** 110440.
- [2] Garvey R.H. et al., 1975 *Phys .Rev. A* **12** 1144.
- [3] Tőkési K. et al., 1994 *Nucl. Instrum. Methods Phys. Res. B: Beam Interact. Mater. At.* **86** 201.
- [4] Al-Ajaleen M and Tőkési K, *Scientific Reports* | (2023) **13**:14080.

A&M data: DCS for electron silver excitation

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For the creation of simulations and models of intricate physical/chemical processes as well as for the interpretation of information obtained from observations and measurements, such as those of laboratory plasma, planetary atmospheres, and the ionosphere [1, 2], atomic and molecular (A&M) data and databases have become crucial [3, 4]. Our understanding of electron atom/molecule collision processes continues to increase thanks to recent and upcoming improvements in experimental methods, theoretical modeling, and interdisciplinary collaboration. These developments have implications for both fundamental science and a range of technical and astrophysical applications ranging from the chemistry of the interstellar medium, to ionizing radiation in the body and DNA damage [5,6]. Here we present new renormalized differential cross sections (DCSs) for electron excitation of the silver atom from the ground $4d^{10}5s^2S$ state to the first combined resonant $4d^{10}5p^2P_{1/2,3/2}$ state at 20 and 40 eV electron impact energies. Renormalization of the obtained results [7] was done in accordance with the results obtained using relativistic convergent close coupling (RCCC) computation [8].

References

- [1] Campbell L., Brunger M. J., *Plasma Sour. Sci. Technol.* 2013, **22** 013002.
- [2] Dubernet M. L. et al., *J. Phys. B.* 2016, **49** 074003.
- [3] B. P. Marinkovic et al., *Eur. Phys. J. D* 2017, **71**, 158-166.
- [4] B. P. Marinkovic et al., *Atoms* 2019, **7**, 11-24.
- [5] R. Srivastava and D. V. Fursa, “Atoms” Special Issue (Electron Scattering from Atoms, Ions and Molecules). *Atoms* 2023, **11**, 31.
- [6] K. Ebel and I. Bald, *Phys. Chem. Lett.* 2022, **13**, 4871–4876.
- [7] S. D. Tošić, V. Pejčev, D. Šević, R. P. McEachran, A. D. Stauffer and B. P. Marinković, *Phys. Rev. A* 2015 **91**, 052703.
- [8] K. McNamara, D. V. Fursa and I. Bray, *J. Phys. B* 2018 **51**, 085203.

Computational study on the thermochemistry and chemical bonding of the HN_3 , H_2N_4 , HNC_2^{2-} and $\text{H}_2\text{N}_2\text{C}_2^{2-}$ species

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Over the past decades, demand for sodium azide (NaN_3), the principal active ingredient in automobile air bag inflators, has rapidly risen, while its accidental environmental releases have increased [1]. NaN_3 is readily hydrolyzed to yield hydrazoic acid, HN_3 , a volatile substance that partitions strongly to the gas phase under atmospheric conditions. Even at low concentrations of 6.5 ppm (m/v) NaN_3 in the aqueous phase, the gas-phase concentration of HN_3 in the atmosphere reaches the threshold limit value of

0.11 ppmv.[2] Thus, it is important to investigate the HN_3 reactions, molecular structure and photophysical properties [2-4].

In this presentation, the chemical bonding, the molecular structure, the photophysical properties, and dissociation energies of the HN_3 and H_2N_4 molecules with respect to $\text{HN} + \text{N}_2$ molecules are studied. Furthermore, the isoelectronic HNC_2^{2-} and $\text{H}_2\text{N}_2\text{C}_2^{2-}$ anions are calculated, and their thermochemical stability has been studied. At first a DFT conformation analysis of the four species was carried out for the singlet, triplet and quintet spin states. Subsequently, the most important conformers have been studied via CCSD, QCISD, and MRCISD methodologies. Finally, selected potential energy curves have been plotted with respect to $\text{HN} + \text{N}_2$ (or C_2^{2-}) products. It is very interesting that despite the expected similarities in the isoelectronic HN_3 and HNC_2^{2-} or in the isoelectronic H_2N_4 and $\text{H}_2\text{N}_2\text{C}_2^{2-}$, they exhibit many differences regarding the chemical bonding and the type of their ground state, see Figure 1.

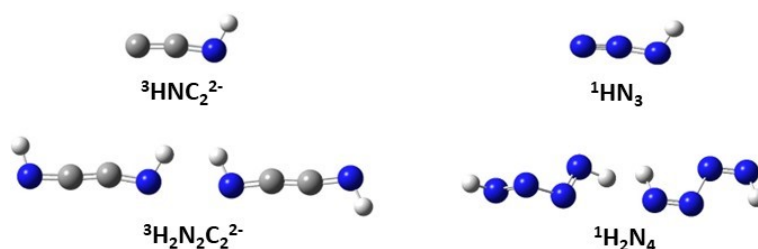


Figure 1: Minimum Energy Structure of HN_3 , H_2N_4 , HNC_2^{2-} and $\text{H}_2\text{N}_2\text{C}_2^{2-}$ species.

References

- [1] Betterton, E. A. Environmental fate of sodium azide derived from automobile airbags. *Crit. Rev. Environ. Sci. Technol.* 2003, **33**, 423-458.
- [2] J. J. Orlando, G. S. Tyndall, E. Betterton, J. Lowry, S. Stegall, *Environ. Sci. Technol.* 2005, **39**, 1632-1640.
- [3] M. N. Glukhovtsev, R. D. Bach, S. Laiter, S., *Int. J. Quantum Chem.* 1997, **62**, 373- 384.
- [4] D. Furman, F. Dubnikova, A. C. T. van Duin, Y. Zeiri, R. Kosloff, *J. Phys. Chem. C* 2016, **120**, 4744-4752.

Theoretical study of Fe_xS_y and MoS_y molecular systems

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Iron–sulfur and molybdenum-sulfur clusters comprise an important functional motif in the catalytic centers of biological systems, capable of enabling important chemical transformations at ambient conditions. This remarkable capability derives from a notoriously complex electronic structure that is characterized by a high density of states that is sensitive to geometric changes.[1-4]

In the first part of the presentation, the ground and low-lying states of the diatomic and triatomic FeS , FeS_2 , MoS , MoS_2 molecules in the gas phase are presented.[3,5] Their bond distances, dissociation energies, and spectroscopic data are calculated via multireference and coupled cluster methodologies, while their bonding is analyzed.

In the second part, how these four molecules, which are model systems of iron and molybdenum complexes and material, are involved in them is discussed and analyzed. Specifically, how, specific states of diatomic and triatomic systems are involved in complexes such as $[\text{Fe}_x\text{S}_y(\text{SCH}_3)_y]^q$ and $\text{Fe}_7\text{MoS}_9\text{C}$, i.e., model systems for iron-sulfur and molybdenum sulfur clusters of rubredoxin and of nitrogenase,[2,4] and in 2D- MoS_2 material.[5] The interactions of the model systems within the 2D material are analyzed.

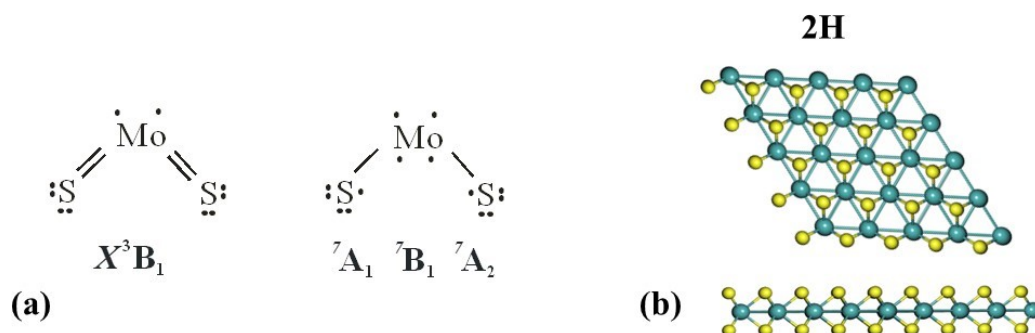


Figure 1: (a) Bonding in the MoS_2 triatomic molecule and (b) 2D- MoS_2 material.

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References

- [1] S. Sharma, K. Sivalingam, F. Neese, G. K.-L. Chan, *Nature Chem.* 2014, **6**, 927-933.
- [2] D. Tzeli, S. Raugai, S. S. Xantheas, *J. Chem. Theory Comput.* 2021, **17**, 6080-6091.
- [3] D. Tzeli, I. Karapetsas, D. M. Merriles, J. C. Ewigleben, M. D. Morse, *J. Phys. Chem. A* 2022, **126**, 1168-1181.
- [4] C. Mejuto-Zaera, D. Tzeli, D. Williams-Young, N. M. Tubman, M. Matoušek, J. Brabec, L. Veis, S. Xantheas, W. A. de Jong, *J. Chem. Theory Comput.* 2022, **18**, 687-702.
- [5] M. A. Mermigki, I. Karapetsas, D. Tzeli, (submitted)

Fragmentation of pyrene molecules following double ionization by 70 eV electron impact

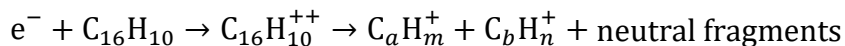
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We have used coincident mass spectrometry to study the fragmentation of doubly-ionized pyrene molecules. The experiment and the data acquisition have been described in our paper on double ionization of anthracene [1]. A beam of pyrene is produced by a resistively heated oven and is crossed by a pulsed electron beam (0.2 μ s, 13.26 kHz) to ionize the molecules. Positively charged fragments are mass analysed using a reflectron time of flight mass spectrometer. A field programmable gate array (National Instruments cRIO9075) is used for recording mass spectra on an event by event basis. We have developed a detailed model of the coincidence data acquisition, fully accounting for the effects of detector dead time and random coincidences, to reliably obtain the map of true coincidences from the file with event by event data.

The fragmentation processes are:



In the coincidence map we observe that fragmentations with an even total number of carbon atoms, $a + b = \text{even}$, are generally significantly stronger than fragmentations with an odd total number of carbon atoms, $a + b = \text{odd}$. No fragmentations are observed for groups with $a + b = 15$.

In most groups, the fragmentations in which each of the fragments has 2 or 3 hydrogen atoms are the strongest. The strongest fragmentations are in the groups $(a, b) = (4, 6)$, $(4, 8)$, $(4, 12)$ and $(5, 7)$ and in these four groups the strongest fragmentations are $C_4H_2^+ + C_{6,8,12}H_2^+$ and $C_5H_3^+ + C_7H_{2,3}^+$. The diagonal groups $(6, 6)$ and $(7, 7)$ also contain a few strong fragmentations, but because of detector dead time these fragmentations are not fully resolved.

In the groups $(6, 10)$, $(5, 11)$, $(4, 12)$, $(3, 12)$ and $(2, 14)$ the largest fragment can have 5 to 8 hydrogen atoms, for example $C_4H_2^+ + C_{12}H_{6,8}^+$ and $C_3H_{2,3}^+ + C_{13}H_7^+$. Very few fragmentations produce a fragment with only one hydrogen atom. The only fragmentations producing a fragment with only one carbon atom are $CH_3^+ + C_{15}H_7^+$ and $CH_3^+ + C_{15}H_7^{++}$.

References

[1] P. J. M. van der Burgt and M. L. Gradziel *Eur. Phys. J. D* 2022, **76**, 60-1-11.

ACol – Database of collisional processes of excitation, ionization and recombination

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We present new additions to the ACol database for atomic collisional processes of excitation and ionization [1] and newly added recombination (both dissociative and electron-ion). The dataset consists of rate coefficients for various species (H, He, K, Li, Na...), involving atoms, ions and molecular ions. ACol database and web service can be reached at <http://servo.aob.rs/acol>, and it complies to A&M community standards, specifically VAMDC [2] protocols. The data for excitation coefficients were obtained by quantum calculations at conditions which satisfied resonant mechanism method. This dataset covers the area important for low temperature plasma modeling from astrophysical and laboratory standpoint [3]. Future development includes adding more species of different metals and connecting to the VAMDC (https://portal.vamdc.org/vamdc_portal/) distributed e-ecosystem.

References

- [1] Vujčić, V., Srećković, V.A. and Jevremović, D., 2022. *New database for collisional excitation/ionization processes of astrophysical interest*. *Contrib. Astron. Obs. Skalnaté Pleso*, 52(3), pp.71-77.
- [2] Albert, D., Antony, B. K., Ba, Y. A., Babikov, Y. L., Bollard, P., Boudon, V., ... & Zwölf, C. M. (2020). *A decade with VAMDC: Results and ambitions*. *Atoms*, 8(4), 76.
- [3] Srećković, V. A., Ignjatović, L. M., Jevremović, D., Vujčić, V., & Dimitrijević, M. S. (2017). *Radiative and collisional molecular data and virtual laboratory astrophysics*. *Atoms*, 5(3), 31.