Universität Potsdam

4th DEA CLUB MEETING

BOOK OF ABSTRACTS

19th to 21st June

Potsdam, Germany, 2024

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Local Organizers

- João Ameixa
- Daniela Höpfner
- Ilko Bald

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- Sibylle Rüstig

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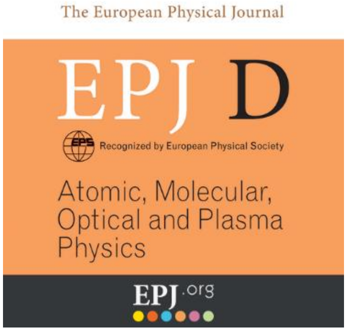

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Contents

General Information

Welcome to the 4th DEA Club Meeting! We are thrilled to extend our warm invitation to researchers in the field of electron-molecule collisions to join us for this prestigious conference. The 4th DEA Club Meeting serves as a pivotal platform for both experimentalists and theoreticians to convene, exchange ideas, and present groundbreaking research in dissociative electron attachment.

Date and Venue:

The conference will be held from June 19th to June 21st, 2024, at the MAXX Hotel Sanssouci Potsdam. Situated in the heart of Potsdam, Germany, this venue offers a tranquil yet centrally located setting conducive to productive discussions and networking.

Conference Focus:

The 4th DEA Club Meeting is dedicated to exploring the latest advancements in electron-molecule collision research, with a specific emphasis on dissociative electron attachment. Attendees will have the opportunity to engage with cutting-edge research findings, participate in stimulating discussions, and forge collaborations that transcend geographical boundaries.

Social Events

Guided City-Tour

An entertaining journey through the past with a glimpse into the Potsdam of tomorrow. For several years, Potsdam's historic center has been shining with new splendor, featuring the Nikolai Church, the Barberini Museum, and the State Parliament housed in the shell of the old city palace. Through the baroque inner city, the route passes Potsdam's shopping street, the "Broadway," to the Dutch Quarter. Small shops, cafés, and bars characterize the flair of this unique Dutch settlement.

Schedule: Thursday, 20.06.204, 17:00-19:00

Meeting point: Luisenplatz, at the fountain.

Endpoint: Holländisches Viertel, near the Restaurant Tomasa.

Language: English.

Conference Dinner

The conference dinner will take place on the evening of the second day at the elegant Restaurant Tomasa, Kurfürstenstraße 52, located in the heart of Potsdam’s historic Dutch Quarter.

Date: Thursday, 20.06, 19:00

The evening will begin with a welcome aperitif, where guests can enjoy a selection of drinks and starters served at the table. The reception will be followed by a one-course dinner, featuring a choice of meat, fish, vegetarian or vegan options selected from the menu, and a refreshing dessert.

We look forward to welcoming you to this memorable dinner and celebrating the success of our meeting together.

Conference Program

Wednesday – Day 1 – Morning Sessions- 19.06.2024

08:45-09:00 **Welcome Address and Opening Remarks**

Session 1	***Electron-Induced Chemistry and Charge Transfer Dynamics***		**Chair: João Ameixa**
09:00-09:30	**Keynote Lecture**	Paulo Limão-Vieira	NOVA University Lisbon, Portugal
	"Current trends in negative ion formation from charge transfer experiments"		
09:30-09:50	**Lecture**	Oddur Ingólfsson	University of Iceland, Iceland
	“Electron induced gas phase fragmentation and deposit formation from Au(I) FEBID precursors. Role of secondary and tertiary reactions in electron beam induced deposition.”		
09:50-10:10	**Lecture**	Mónica Mendes	NOVA University Lisbon, Portugal
	"Electron-induced chemistry in EUVL photoresist materials: study on perfluorophenyl trifluoromethanesulfonate"		
10:10-10:30	**Lecture**	Lisa Mc-Elwee White	University of Florida, USA
	"Electron-Induced Chemistry of π-Facial Ligand Complexes: From Cp to Methyl Acrylate"		
10:30-11:00	**Coffee Break**		

Session 2	***Electron-driven molecular dissociation dynamics***		**Chair: Juraj Fedor**
11:00-11:30	**Keynote Lecture**	Sang Kyu Kim	Korea Advanced Institute of Science and Technology, South Korea
	"Dynamics of the Nonvalence Bound State of the Anion: the Doorway Role into Chemical Reactions"		
11:30-12:00	**Lecture & EPJD Sponsorship**	Sylwia Ptasinska	University of Notre Dame, USA
	“Advances in Instrumentation for Product Detection and Understanding Molecular Dissociation Dynamics Triggered by Electrons”		
12:00-12:15	**Lightning Talk**	Charlotte Titeca	KU Leuven, Belgium
	“Theoretical prediction of dissociative electron attachment using electron localization functions and Berlin’s binding function”		
12:15-12:30	**Open Discussion**	Nigel Mason	University of Kent, UK
	“Whitepapers on Sustaining and Advancing Foundational Sciences”		
12:30-14:00	**Lunch**		

Wednesday – Day 1 – Afternoon Sessions – 19.06.2024

Session 3	***Surface Insights: Exploring the Effect of Electrons***		**Chair: Oddur Ingólfsson**
14:00-14:20	**Lecture**	Lionel Amiaud	Université Paris-Saclay, France
	"Non-thermal desorption from molecular ices: Quantifying the contribution of electrons and photons"		
14:20-14:40	**Lecture**	Petra Swiderek	University of Bremen, Germany
	"Beyond DEA: Mechanisms of Electron-Induced Syntheses in Molecular Ices"		
14:40-14:55	**Lightning Talk**	Katja Höflich	Leibniz-Institut für Höchstfrequenztechnik, Berlin
	“Area Selective Chemical Vapor Deposition of Gold by Electron Beam Seeding”		

Session 4	***DEA Club Awards***		**Chair: Nigel Mason**
15:00-15:20	**Lecture “DEA Club Award”**	Pamir Nag	J. Heyrovsky Institute of Physical Chemistry, Czechia
	“Electron-induced processes in liquid micro-jets”		
15:20-15:50	**Lecture “DEA Club Lifetime Award”**	Ilya Fabrikant	University of Nebraska, Lincoln, Nebraska, United States
	"Electron and positronium attachment to molecules"		
15:50-16:10	**Coffee Break**		

Session 5	***Plasmonic-mediated processes***		**Chair: Ilko Bald**
16:10-16:30	**Lecture**	Andrei Stefancu	Ludwig Maximilian University of Munich, Germany
	"Charge and energy transfer at the plasmonic metal – molecule interface"		
16:30-16:50	**Lecture**	Anushree Dutra	University of Potsdam, Germany
	“Unlocking Chemical Reactivity in Plasmonic Systems: Role of Dissociative Electron Attachment”		
16:50-17:10	**Lecture**	Janina Kopyra	Sieldce University, Poland
	"Electron driven fragmentation of analogues of nucleobases"		
17:10-17:30	**Lecture**	Sérgio Kogikoski Jr.	University of Potsdam, Germany
	“Low-Energy Electron-Induced Decomposition of DNA Nucleobase Derivatives by Dissociative Electron Attachment Processes”		

17:30-19:00 ***Poster session***

Thursday – Day 2 – Morning Sessions – 20.06.2024

Session 6	***Electron Dynamics: From Interstellar Clouds to Materials***		**Chair: Mónica Mendes**
09:00-09:30	**Keynote Lecture**	Ann Orel	University of California Davis, USA
	"DEA as a Possible Source for CN- in Interstellar Clouds"		
09:30-09:50	**Lecture**	Kate Nixon	The Open University, UK
	“Electron momentum spectroscopy of benzonitrile*”*		
09:50-10:10	**Lecture**	Daly Davis	Somaiya Vidyavihar University, Mumbai, India
	“Low Energy Electron-Induced Chemistry: Insights into Astrochemistry”		
10:10-10:30	**Lecture**	Simone Taioli	European Centre for Theoretical Studies in Nuclear Physics and Related Areas (ECT), Fondazione Bruno Kessler - Trento (Italy)
	"Electron collisions: From materials science to astrophysics"		
10:30-11:00	**Coffee Break**		

Session 7	***Exploring Electron Interactions with Gaseous Molecules***		**Chair: Dhananjay Nandi**
11:00-11:30	**Keynote Lecture**	Vaibhav S. Prabhudesai	Tata Institute of Fundamental Research, India
	"Electron attachment to overlapping resonances"		
11:30-11:50	**Lecture**	Jelena Maljkovic	Institute of Physics Belgrade, Serbia
	“Electron interaction with anaesthetic molecules in the gas phase”		
11:50-12:10	**Lecture**	Shanxi Tian	University of Science and Technology of China, China
	“Dissociative electron attachment *of molecular* CO_2 *and clusters”*		
12:10-12:30	**Lecture**	Gustavo García	Consejo Superior de Investigaciones Científicas (CSIC), Spain
	"New insights into the electron attachment to nitric oxide (NO)"		
12:30-14:00	**Lunch**		

Thursday – Day 2 – Afternoon Sessions – 20.06.2024

Session 8	***Electron Dynamics Across Solvation and Bio-molecular Systems***		**Chair: Sylwia Ptasisnka**
14:00-14:30	**Keynote Lecture**	Jan Verlet	University of Durham, UK
	"Electron spectroscopy with photons: Probing effect of solvation on resonances"		
14:30-14:50	**Lecture**	Juraj Fedor	J. Heyrovsky Institute of Physical Chemistry, Czechia
	"What do we learn from the *electron detachment channel?"*		
14:50-15:10	**Lecture**	Daniel S. Slaughter	Lawrence Berkeley National Laboratory, USA
	"Dynamics of electronic Feshbach resonances in small carboxylic acids and amides"		
15:10-15:30	**Lecture**	Stephan Denifl	University of Innsbruck, Austria
	"The dissociation of temporary negative ions formed upon electron attachment to biologically relevant molecules"		
15:30-16:00	**Keynote Lecture Online**	Léon Sanche	Université de Sherbrooke, Canada
	"DEA to condensed-phase biomolecules: From O_2 to plasmid DNA"		
16:00-16:30	**Coffee Break**		

16:30-17:00	***Break***		
17:00-19:00	***Guided City-Tour***		
19:00	***Conference Dinner***		

Friday – Day 3 – 21.06.2024

Session 9	***Advancements in Modeling and Experimental Studies***		**Chair: Jan Verlet**
09:00-09:30	**Keynote Lecture**	Thomas Jagau	KU Leuven, Belgium
	“Modeling dissociative electron attachment using complex-energy methods”		
09:30-09:50	**Lecture**	Greg Armstrong	Quantemol, UK
	“Estimation of dissociative electron attachment cross sections for arbitrary molecules”		
09:50-10:10	**Lecture**	Peter Papp	Cormenius University, Slovakia
	“Ion induced reactions of various thiophenes”		
10:10-10:25	**Lightning Talk**	Marnik Metting van Rijn	ETH Zurich, Switzerland
	“Absolute Attachment Cross Sections in Hydrofluorocarbons”		
10:25-10:45	**Lecture**	Dragana Maric	University of Belgrade, Serbia
	“Breakdown in fluorocarbon gases”		
10:45-11:10	**Coffee Break**		

Session 10	***Innovative Approaches to investigate DEA***		**Chair: Petra Swiderek**
11:10-11:30	**Lecture**	Dhananjay Nandi	Indian Institute of Science Education and Research Kolkata, India
	"Novel experimental approaches to study dissociative electron attachment and ion pair dissociation"		
11:30-11:50	**Lecture**	Stefan Matejcik	Cormenius University, Slovakia
	"Electron induced fluorescence studies to O2 and N2"		
11:50-12:10	**Perspective Lecture**	Nigel Mason	University of Kent, UK
	“Electron scattering studies - the next ten years. Renaissance or Revolution?"		
12:10-12:30	**Lecture**	Andrew Cassidy	Aarhus University, Denmark
	“Spontaneous electric fields in molecular films”		
12:30-12:50	**Lecture**	Martin Čižek	Charles University, Czechia
	"Vibronic coupling of resonances in electron molecule collisions"		
12:50-13:00	**Closing remarks**		
13:00	**Lunch**		

Poster Session: P01. to P10.

P01.	*“Dissociative electron attachment to 2-chlorobenzonitrile”*	
	Filipe Ferreira da Silva	NOVA University of Lisbon, Portugal
P02.	*“Electron interactions with perfluorophenyl trifluoromethanesulfonate (F-PhTf) EUVL photoresist material”*	
	Filipe Ferreira da Silva	NOVA University of Lisbon, Portugal
P03.	*“Low-energy electron attachment to Diethyl Carbonate”*	
	Giorgi Kharchilava	University of Notre Dame, USA
P04.	*“Real-Time Observation of the Nonvalence-Bound State Mediated Anion Formation”*	
	Sejun An	KAIST, South Korea
P05.	*“Surprising oscillations in DEA cross sections in electron-oxygen collisions”*	
	Václav Alt	Charles University, Czech Republic
P06.	*“Dissociative recombination model for direct processes”*	
	Roman Čurík	Institute of Physical Chemistry, ASCR, Czech Republic
P07.	*“Energy thresholds for electron-induced reactions in solution-processed metal-organic materials”*	
	Petra Swiderek	University of Bremen, Germany
P08.	“Electron-induced deposition using $Fe(CO)_4MA$ and $Fe(CO)_5$ – Effect of MA ligand and process conditions”	
	Petra Swiderek	University of Bremen, Germany
P09.	*“Electron Triggered Processes in Halogenated Carboxylates and Their Clusters”*	
	Barbora Kocábková	J. Heyrovský Institute of Physical Chemistry v.v.i., Czech Academy of Sciences & Institute of Physical Chemistry, University of Chemistry and Technology in Prague, Czech Republic
P10.	*“Hydrated Formic Acid Clusters and their Interaction with Electrons Examined in Molecular Beam Experiment”*	
	Barbora Kocábková	J. Heyrovský Institute of Physical Chemistry v.v.i., Czech Academy of Sciences, Czech Republic

Poster Session: P11. to P19.

P11.	*“Dissociative electron attachment to* $C_5F_{10}O$*”*	
	Mateusz Zawadzki	Gdańsk University of Technology, Poland
P12.	*“Experimental and theoretical study on electron scattering from propionaldehyde (*C_2H_5CHO*) molecule”*	
	Paweł Możejko	Gdańsk University of Technology, Poland
P13.	*“Dissociation of* NH_3 *by electron impact in low-temperature plasma and the isotope effect of the process”*	
	Xianwu Jiang	Wuhan University of Technology, China
P14.	*“Electron Attachment to Isolated and Clustered Methylmethacrylate”*	
	Jaroslav Kočišek	J. Heyrovský Institute of Physical Chemistry of the CAS, Czechia
P15.	*“Gas-phase fragmentation dynamics induced by low-energy electron ionization”*	
	Alexander Butler	University of Oxford, UK
P16.	*“Radiative vs dissociative electron attachment as mechanisms for formation of negative molecular ions in the interstellar medium”*	
	Viatcheslav Kokoouline	University of Central Florida, USA
P17.	*“Contrasting Dynamics in Isoelectronic Anions Formed by Electron Attachment”*	
	Miloš Ranković	J.Heyrovský Institute of Physical Chemistry, The Czech Academy of Sciences, Czech Republic
P18.	*“Temporary anions of the dielectric gas* C_3F_7CN *and their decay channels”*	
	Miloš Ranković	J.Heyrovský Institute of Physical Chemistry, The Czech Academy of Sciences, Czech Republic
P19.	*Distance-dependent resonances in interparticle Coulombic electron capture*	
	Vincent Graves	The Open University, UK

Poster Session: P20. to P24.

P20.	*Probing few-molecule chemical reactions and hot spot dynamics using DNA-origami-assembled nanoparticle dimers*	
	Cristina Beresowski	University of Potsdam, Germany
P21.	*Investigating the incorporation of halogens into DNA: Effects on electron-induced strand breakage using DNA Origami*	
	Ilko Bald	University of Potsdam, Germany
P22.	*“Dissociative electron attachment and dissociative ionisation of the potential FEBID precursor* $CF_3AuCNC(CH_3)_3$ *under single collision conditions and at elevated pressures.”*	
	Oddur Ingólfsson	University of Iceland, Iceland
P23.	*“Dissociative electron attachment, dissociative ionisation and focused electron beam induced deposition of the potential Au(I) precursors* $(CH_3)AuP(CH_3)_3$ *and* $[(CH_3)_2AuCl]_2$*.”*	
	Oddur Ingólfsson	University of Iceland, Iceland
P24.	"Electron collision with molecular hydrogen"	
	Vaibhav S. Prabhudesai	Tata Institute of Fundamental Research, Mumbai, India

Abstracts of Lectures & Lightning Talks

Current trends in negative ion formation from charge transfer experiments

Paulo Limão-Vieira[1,*] and G. García[2]

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The role of electron transfer to different polyatomic molecules has been thoroughly investigated over the last 15 years probing key aspects of the collision dynamics which are responsible for the available anionic channels.[1] In such low-energy collisions, typically from a few eV up to 1 keV, the role of the electron donor has been probed to be pivotal on the intramolecular energy redistribution allowing access to different (fragment) anions which are not attained in dissociative electron attachment (DEA) experiments. Within the collision induced process, such charge transfer experiments may allow access to electronic states of the negative ion with positive electron affinities.[2,3]

We have performed gas-phase experiments with time-of-flight mass detection either in a linear or in a reflectron configuration, the former to obtain additional information on kinetic energy release distributions (KERD),[4] the latter for higher mass resolution. In this presentation I will show some of our most recent achievements on key selected molecular targets where electron transfer processes can be prevalent (e.g. in industrial, technological and even biological applications).

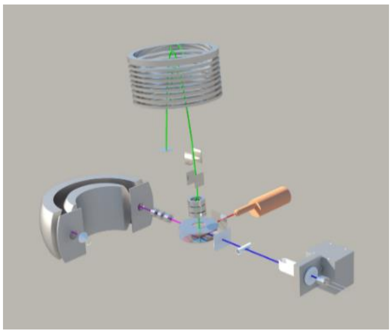

Figure 1. Time-of-flight mass spectrometer and energy loss analyser electron transfer experiment schematics installed in the Lisbon laboratory.

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[1] Charge transfer processes in key selected biological systems in Radiation in Bioanalysis - Spectroscopic Techniques and Theoretical Methods, Springer-Nature, Ed. Alice S Pereira, Pedro Tavares, Paulo Limão-Vieira (2019) 329–348.

[2] Regeta, K., et al. (2020), Combined experimental and theoretical studies on electron-transfer in potassium collisions with CCl_4, *J. Phys. Chem. A*, 124, 3220-3227. DOI: 10.1021/acs.jpca.0c02076.

[3] Kumar, S., et al. (2022), Anionic states of C_6Cl_6 probed in electron transfer experiments, *Phys. Chem. Chem. Phys.*, 24, 366-374. DOI: 10.1039/D1CP04500H.

[4] Kumar, S., et al. (2021), Cl^- kinetic-energy release distributions from chlorobenzene and related molecules in electron transfer experiments, *Eur. Phys. J. D*, 75, 294. DOI: 10.1140/epjd/s10053-021-00307-0.

Electron induced gas phase fragmentation and deposit formation from Au(I) FEBID precursors. Role of secondary and tertiary reactions in electron beam induced deposition.

Oddur Ingólfsson[1*], Ali Kamali[1], Elif Bilgilisoy[2], Alexander Wolfram [2], Gerd Ballmann[2], Sjoerd Harder[2], Thomas Xaver Gentner[2], Hans-Peter Steinrück[2], Hubertus Marbach[2,3] Will G. Carden[4], Jodie V. Johnson[4], Lisa McElwee-White[4]

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It is well recognised that secondary electrons play a determining role in focused electron beam induced deposition (FEBID). These electrons have a wide energy distribution and may cause dissociation by as different processes as dissociative electron attachment (DEA), dissociative ionization (DI), and neutral and dipolar dissociation (ND and DD, respectively)[1] It is thus important in the design of high performance FEBID precursors to understand these processes and their reflection in the respective deposits.

In the current presentation, gas phase DEA and DI studies on three different gold precursors with different ligand structures, i.e., $(CH_3)AuP(CH_3)_3$[2], $CF_3AuCNC(CH_3)_3$[3] and $[(CH_3)_2AuCl]_2$[4] are discussed and compared to depositions made by FEBID under UHV and HV conditions. The observed fragmentation reactions of the selected gold precursors are discussed in relation to the underlying reactions, the deposits composition, and potential implications for their suitability as FEBID precursors.

While the metal content in deposits from these compounds correlates well with the gas phase processes observed, this is not the case for the deposit's compositions of the remaining ligand elements. We anticipate this to be due to the initial processes leading to immobilized fragments, while the final composition of the deposit results from electron-induced secondary and tertiary reactions induced in in the further exposure of these immobilized deposits. Importantly, this has consequences for both the precursor design and deposition strategies applied, calling for precursors that lead to fragments that maintain high cross sections for further electron-induced fragmentation and desorption of the respective secondary ligand fragments.

-This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722149.

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[1] Ingólfsson O. Ed, (2019). Low-Energy Electrons Fundamentals and Applications, Jenny Stanford Publishing, New York.

[2] Kamali A., et al. (2023). Eur. Phys. J. D 77, 157; https://doi.org/10.1140/epjd/s10053-023-00721-6

[3] Kamali A., et al. (2022). Nanomaterials, 12(15), 2727; https://doi.org/10.3390/nano12152727

[4] Bilgilisoy E., et al (2023). Beilstein J Nanotechnol, 6 (14),1178. https://doi.org/10.3762/bjnano.14.98.

Electron-induced chemistry in EUVL photoresist materials: study on perfluorophenyl trifluoromethanesulfonate

Mónica Mendes[1,*], Pedro Guerra[1], Fabian Holzmeier[2], Oddur Ingólfsson[3], Filipe Ferreira da Silva[1]
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Extreme ultraviolet lithography (EUVL) represents the latest generation lithographic technology with important applications on nanofabrication techniques for the semiconductor industry[1]. EUVL with 13.5 nm light is the advanced cost-effective lithography method yielding a significant improvement in resolution, which scales with the wavelength, compared to deep UV lithography at 193 nm[2]. However, this means a transition from the non-ionizing to ionizing radiation where the production of photoelectrons and secondary electrons plays an important role in the photoresist materials. These electrons can act mainly through dissociative electron attachment (DEA), dissociative ionization (DI) and neutral and dipolar dissociation (ND and DD, respectively) upon electronic excitation[1,3]. Currently, aryl sulfonates, like perfluorophenyl trifluoromethanesulfonate (F-PhTf, $C_7F_8O_3S$), are used as potential photoacid generators (PAGs) in chemically amplified photoresists used in EUVL. Therefore, understanding the EUV-induced chemistry triggered by low energy electrons, which are generated in a thin film in neutral PAGs at a fundamental level helps to formulate novel performant photoresist materials.

Considering this, we carried out DEA and DI experiments in F-PhTf by using a trochoidal electron monochromator coupled with an orthogonal reflectron time-of-flight mass spectrometer. From the electron ionization study, ionization energy of neutral F-PhTf was found to be 10.57 eV. Several cationic fragments resulted from the dissociation of F-PhTf were also observed, notably $C_6F_5O^+$ (m/z 183), $C_5F_5^+$ (m/z 155) and CF_3^+ (m/z 69). The appearance energies for the observed ions have been determined experimentally. We have also observed that electron attachment to F-PhTf leads to a rich fragmentation pattern with many anions formed at different energies between 0 and 15 eV.

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[1] Tafrishi, R., Torres-Diaz, D., Amiaud, L., Lafosse, A., Ingólfsson, O. (2023). Low-energy electron interaction with 2-(trifluoromethyl)acrylic acid, a potential component for EUVL resist material. *Phys. Chem. Chem. Phys.*, *25*, 17987-17998. DOI: 10.1039/d3cp01860a.

[2] Wang, X., *et al.* (2023). Trends in photoresist materials for extreme ultraviolet lithography: A review. *Materials Today, 67*, 299-319. DOI: 10.1016/j.mattod.2023.05.027.

[3] Ho, G., *et al.* (2010). Photochemistry of photoresists and underlayer materials upon irradiation at 13.5 nm. *Journal of Photochemistry and Photobiology A: Chemistry, 211*, 78-87. DOI:10.1016/j.jphotochem.2010.02.008

Electron-Induced Chemistry of π-Facial Ligand Complexes: From Cp to Methyl Acrylate

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The most important class of FEBID materials are the nanostructures deposited from organometallic precursors. We have been using mechanism-based precursor design to map out a set of privileged ligands that can be used in FEBID without causing low metal content due to contamination derived from the organic ligands.[1-2] [1-2] Our prior results have identified privileged ligands, such as CO, while ruling out other ligands such as the anionic polyhapto moieties allyl and cyclopentadienyl (Cp). We are currently determining the structure-reactivity relationship for η^2-olefins, neutral π-facial ligands with bonding similar to CO (Figure 1). Electron-induced reactions of the η^2-olefin complex $Fe(CO)_4MA$ (MA = methyl acrylate) in the gas phase[33] and on a surface in ultrahigh vacuum[44] will be discussed in the context of use of olefin ligands in FEBID.

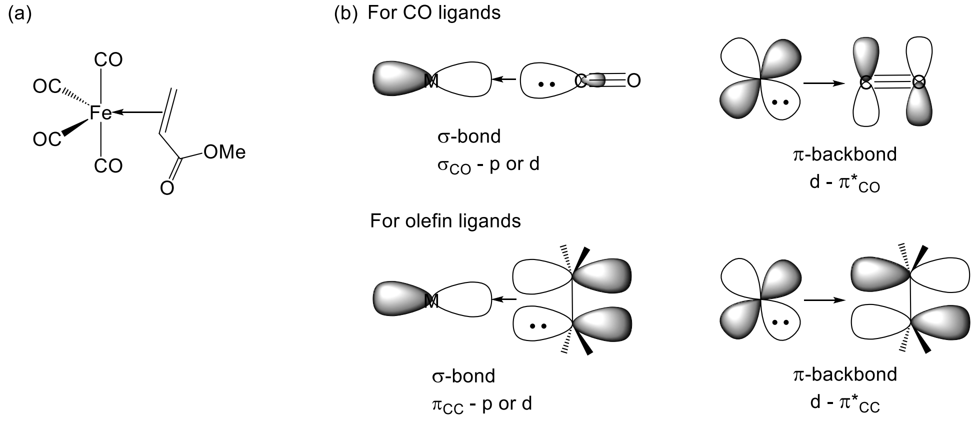

Figure 1. (a) Structure of $Fe(CO)_4MA$. (b) Bonding of CO and olefin ligands to transition metals.

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[1] Carden, W. G.; Lu, H.; Spencer, J. A.; Fairbrother, D. H.; McElwee-White, L., Mechanism-Based Design of Precursors for Focused Electron Beam-Induced Deposition. *MRS Commun.* **2018,** *8* (2), 343-357.

[2] Yu, J.-C.; Abdel-Rahman, M. K.; Fairbrother, D. H.; McElwee-White, L., Charged Particle-Induced Surface Reactions of Organometallic Complexes as a Guide to Precursor Design for Electron- and Ion-Induced Deposition of Nanostructures. *ACS Appl. Mater. Interfaces* **2021,** *13* (41), 48333-48348.

[3] Lyshchuk, H.; Chaudhary, A.; Luxford, T. F. M.; Ranković, M.; Kočišek, J.; Fedor, J.; McElwee-White, L.; Nag, P., Electron-induced ligand loss from iron tetracarbonyl methyl acrylate. *Beilstein J. Nanotech.* **2024**, submitted for publication.

[4] Boeckers, H.; Chaudhary, A.; Martinović, P.; Walker, A. V.; McElwee-White, L.; Swiderek, P., Electron-induced deposition using $Fe(CO)_4MA$ and $Fe(CO)_5$ – effect of MA ligand and process conditions. *Beilstein J. Nanotech.* **2024**, accepted for publication.

Dynamics of the Nonvalence Bound State of the Anion: the Doorway Role into Chemical Reactions

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State-specific chemical dynamics of the nonvalence-bound state (NBS) using the picosecond time-resolved pump-probe spectroscopy on the cryogenically cooled anions using the velocity-map electron imaging technique has been employed to unravel the nature of the mode-dependent dynamic behavior of the NBS in terms of the autodetachment and/or concomitant fragmentation reactions. The autodetachment rate of the NBS has been precisely measured in a state-specific way for various chemical systems of the phenoxide, 4-cyanophenoxide, or *o*- (*m*- or *p*-) halogen substituted phenoxides. Though the Fermi's golden rule is conceptually right, the much more sophisticated theoretical model was required for the more quantitative analysis as the quantum electron correlation effect should also be taken into account. For (*ortho*-, *meta*-, or *para*-) iodophenoxides, the C-I chemical bond rupture (giving the I^- fragment at the asymptotic limit) has been found to be mediated by multiple Feshbach resonances of the NBS, providing the foremost evidence for the dynamic 'doorway' role of the NBS in the anion chemistry and physics. Autodetachment and the NBS-VBS (valence bound state) nonadiabatic transition processes are kinetically competitive, promising the quantum mechanical control of the anionic reaction.

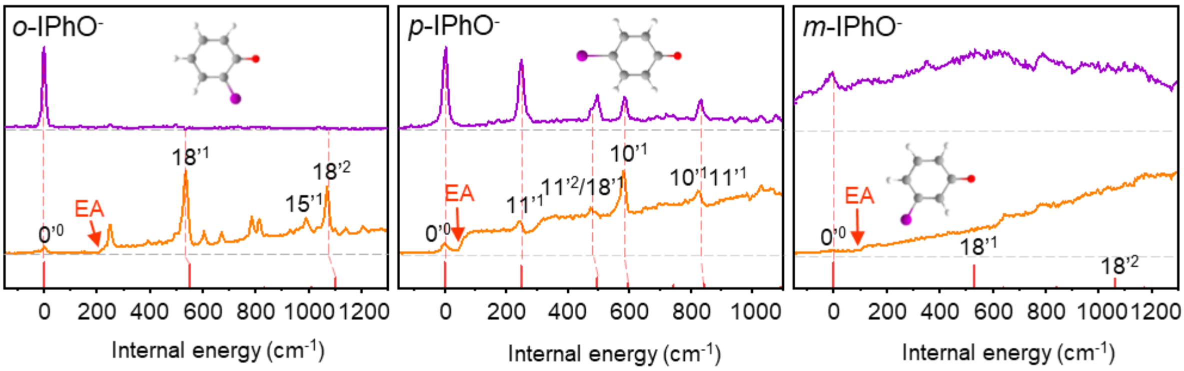

Figure 1. Photoelectron (violet) and photofragment (iodide anion) action spectra taken as a function of the internal energy of the NBS of ortho-, para-, or meta-phenoxide anion [Refs. 2 and 30].

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Advances in Instrumentation for Product Detection and Understanding Molecular Dissociation Dynamics Triggered by Electrons

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Understanding electron-molecule interactions leading to dissociation involves the identification of resultant products and determining their cross-sections. These aspects are crucial for characterizing scattering processes and have applications in radiation, cluster, and plasma sciences. While considerable attention has been paid to detecting charged species using mass spectrometry, neutral fragments resulting from electron collision-induced dissociation present challenges due to technical limitations.

Recent developments in our laboratory have yielded enhanced methodologies for neutral detection, particularly in dissociative electron attachment (DEA) processes. By employing a modified mass spectrometric setup, we successfully detected neutral products from DEA to carbon tetrachloride at near 0 eV electron impact, providing deeper insights into fragment radical formation. Through varying electron energies, we also determined the ionization energy of produced radicals.

Further technological advancements, notably in ion imaging techniques, have enabled simultaneous imaging and facilitated energy- and angle-resolved measurements. Consequently, we constructed a velocity map imaging spectrometer and utilized it to analyze the kinetic energy and angular distributions of molecular fragments resulting from DEA to a diverse array of molecules.

Thus, through ongoing innovation and the integration of diverse detection techniques, our goal is to reveal the complexities of dissociative processes, paving the way for breakthroughs in various scientific fields reliant on electron scattering phenomena.

Theoretical prediction of dissociative electron attachment using electron localization functions and Berlin's binding function

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Computational study of electronic resonances is still a very challenging topic, with the phenomenon of dissociative electron attachment (DEA)[1] being one of the multiple features worth investigating. As conventional Hermitian quantum mechanics is only able to describe bound electrons, the description of the unbound electrons present in these resonances is beyond the reach of these methods.[2] One possible solution for anionic resonances comprises stabilization by adding an artificial potential to the Hamiltonian, enabling a bound-state treatment. The stabilization is achieved upon scaling the nuclear charges. By extrapolation, estimates for the negative electron affinities are obtained.[3]

For the first time, we extend this method to the study of nuclear forces, electronic Fukui functions[4] and electron localization functions (ELF)[5], to get insight into the influence of the unbound electron on the molecular bonds. This is applied to resonance states of various substituted ethene compounds. Additionally, we combine the obtained ELFs with Berlin's binding functions[6,7] of the neutral compounds. This promising methodology allows for accurate predictions of when and where DEA will happen in the molecules studied and provides more insight into the process.[8,9]

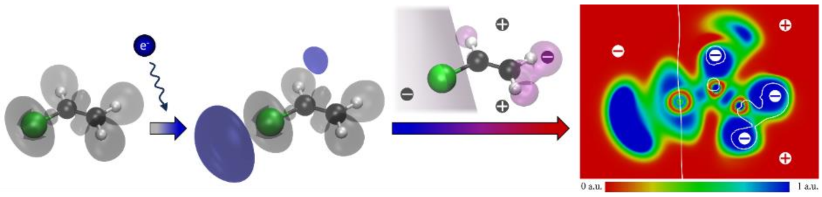

Figure 1. The combination of electron localization function and Berlin's binding function allows for prediction of DEA

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Quantifying Non-Thermal Desorption from NH3 Ices: A Comparative Study of Photon and Electron Irradiation in low energy range

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The relative abundances of gaseous and solid nitrogen in the interstellar medium remain controversial[1] [2]. Besides the difficulty in observing N and N_2, the quantities of nitrogen returning to the gas phase by photo-processing of the ice mantles are not well constrained. In star-forming regions, NH_3 containing ices are exposed to UV and X-Ray photons (*e.g.*[3]). This leads to non-thermal photodesorption induced by the primary radiation or by exothermic photochemistry.

In order to quantify the non-thermal desorption of N containing molecules, we have conducted comparative measurements of photon- and electron-induced desorption (PSD and ESD) from condensed NH_3. The desorption of neutral species is measured by mass spectrometry. Thermal desorption experiments (TPD) were used for calibration and analysis. The photo irradiation was conducted in SOLEIL synchrotron beamline DESIRS (6-12 eV). The twin electron irradiation experiments were performed in ISMO.

Desorption yields are compared either as a function of the incident energy or as a function of the cumulated dose. NH_3 and N_2 are the major desorbing species, with an apparent energy threshold at ~6 eV, showing that both direct and indirect desorption occurs (e.g N_2 production[4]). Different mechanisms at play will be discussed.

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Beyond DEA: Mechanisms of Electron-Induced Syntheses in Molecular Ices

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Electron-induced chemistry is relevant to many processes that occur when ionizing radiation interacts with matter. This includes radiation damage, curing of polymers, and nanofabrication processes but also the formation of complex molecules in molecular ices grown on dust particles in space. High-energy radiation liberates from such materials an abundance of secondary electrons of which most have energies below 20 eV. These electrons efficiently trigger reactions when they attach to molecules or induce electronic excitation or ionization. The dependence of product yields on the electron energy helps to resolve how larger molecules are synthesized when smaller reactants are irradiated with electrons. We identify products of electron-induced reactions in molecular ices and quantify their amounts as function of electron energy using post-irradiation thermal desorption spectrometry (TDS) experiments performed in ultrahigh vacuum (UHV).[1] Based on the results, reaction mechanisms leading to specific products are proposed. This contribution reviews our experimental approach and highlights some results including, in particular, the synthesis of formaldehyde (H_2CO), formic acid (HCOOH), and CO_2 in mixed ices of CO and H_2O.[2]

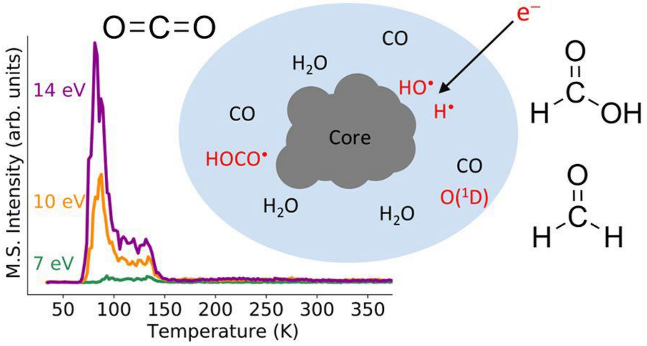

Figure 1. Products of electron-induced reactions in mixed molecular ices of CO and H2O as monitored by post-irradiation thermal desorption spectrometry.[2]

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Area Selective Chemical Vapor Deposition of Gold by Electron Beam Seeding

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This work presents a novel maskless patterning technique that enables area selective CVD of gold[1]. A focused electron beam is used to decompose the metal-organic precursor Au(acac)Me_2 locally[2], thereby creating an autocatalytically active seed layer for subsequent CVD with the same precursor. The procedure can be included in the same CVD cycle without the need for cleanroom lithographic processing. Moreover, it operates at low temperatures of 80 °C, over 200 K lower than standard CVD temperatures for this precursor, reducing thermal load on the specimen.

Given that electron beam seeding operates on any even moderately conductive surface, the process does not constrain device design. This is demonstrated by the example of vertical nanostructures with high aspect ratios of around 40:1 and more. Written using a focused electron beam and the same precursor, these nanopillars exhibit catalytically active nuclei on their surface. Furthermore, they allow for the first time the precise determination of the local temperature increase caused by the writing of nanostructures with an electron beam.

To summarise, this work presents a new, technologically powerful and easy to implement approach to area selective gold deposition. The low temperature neccessary makes it highly suitable for processing innovative flexible devices that rely on heat-sensitive polymers, including flexible electronics and flexible solar cells. In addition, the maskless direct write seeding is possible on 3D architectures, which provides the potential to fabricate nanostructures or localized electric contacts on intricate 3D devices.

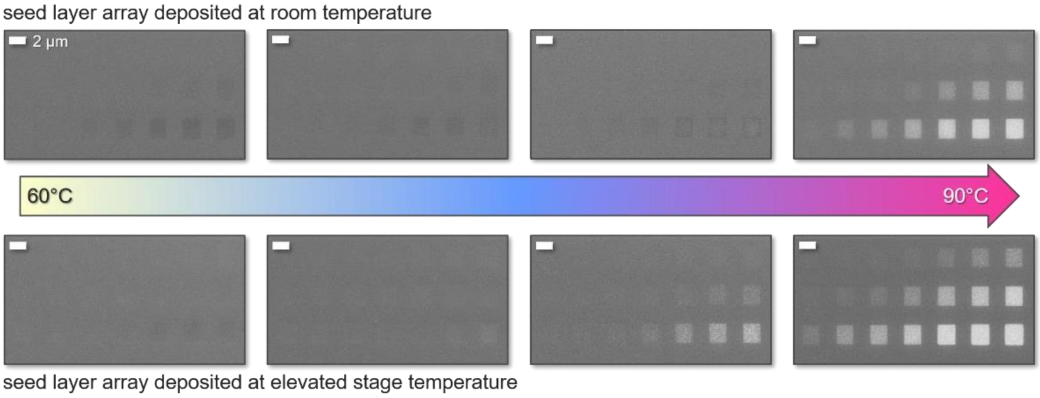

Figure 1: Temperature dependence of area selective autocatalytic film growth.

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Electron-induced processes in liquid micro-jets

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We recently developed a new experimental setup to study electron beam induced processes in liquid- and solvated-phased molecules. One of the motivations for this work is to understand the radiation induced damage to living cells and biologically important molecules in their natural environment – i.e. in aqueous solvated form. The experimental results will also enable us to understand the effect of liquid environment in electron-induced reactions. The experimental setup is equipped with a high-vacuum compatible recyclable liquid micro-jet source and an electron gun producing an electron beam with tuneable energy in between 60 to 800 eV.[1] For electron-induced fluorescence measurements we also attached an optical spectrometer to the setup.

We used the setup to study electron-beam induced reactivity in water solvated TRIS (2-Amino-2-(hydroxymethyl) propane-1,3-diol) molecule. Around 19.3 mM aqueous solution of TRIS was irradiated with 300 eV electron beam, and the irradiated solution was collected and analysed using UV-VIS spectroscopy. We also used the setup to study electron beam induced fluorescence to 1-propanol and few other laser dyes. The incoming electron beam can also lead to OH radical formation in aqueous medium. We used coumarin-3-carboxylic acid as chemical dosimeter to detect the OH radicals and analysing the irradiated samples using spectrofluorometer.

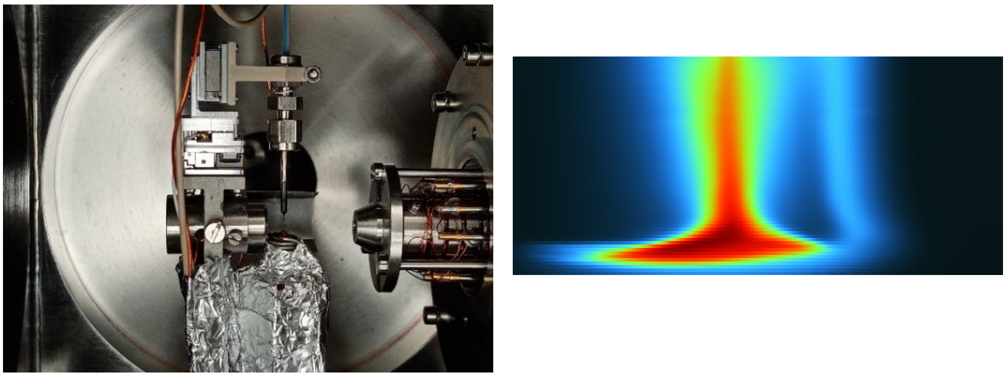

Figure *1*. (a) The experimental setup (b) the scattered electron beam profile from the liquid jet

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Electron and positronium attachment to molecules

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Recent developments of the theory of dissociative electron attachment (DEA) include extension of the nonlocal theory to targets with several vibrational modes and incorporation of cluster environment in the description of the DEA processes. We will discuss two important examples. The first deals with DEA to the CF_3Cl molecule. Inclusion of several vibrational degrees of freedom in the nonlocal theory allows us to explain the experimentally observed low-electron-energy peak at higher gas temperatures. Another important example is the process of electron-induced bond breaking in DNA bases which can be strongly influenced by surrounding water molecules. We have found two effects in the N-H bond breaking in thymine due to electron impact, one leading to the enhancement of the DEA cross section due to the increased lifetime of the intermediate negative-ion state[1], and the other leading to the decrease of the yield of the anionic fragments due to the hydrogen bonding between the nucleobase and the solvent[2] confirming observations of the Heyrovsky Institute group[3].

Another interesting development is the extension of the resonance theory to collisions involving positronium (Ps). The similarity between electron and Ps scattering, found for several molecular targets[4,5] extends to resonance scattering. Resonances have been found experimentally and confirmed theoretically in Ps-N_2 and Ps-CO_2 elastic collisions[6,7]. This raises the question if these resonances can lead to the processes of dissociative Ps attachment. An indirect evidence for this process exists in experiments on ortho-Ps (o-Ps) annihilation in collisions with gas molecules[8]. If the molecule is not in a singlet state, o-Ps may be spin-converted into para-Ps and vice versa via electron exchange. This process explains anomalously large annihilation rates of Ps in O_2 and NO gases. However, extremely large o-Ps annihilation rates in NO_2, Br_2 and I_2, whose ground states are singlet, remain unexplained. This might be an indication of formation of a resonance state of Ps with these targets followed by the dissociative Ps attachment.

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Charge and energy transfer at the plasmonic metal – molecule interface

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Nanostructured surfaces and colloids with designed optical functionalities - such as plasmonic & photonic nano and metamaterials - allow efficient harvesting of light at the nanoscale. Exploiting light-driven matter excitations in these artificial materials opens up a new dimension in the conversion and management of energy at the nanoscale[1][2]. One example are plasmonic and photonic catalysts, that can indeed confine solar energy into molecular regions. In this talk, I will present our recent efforts in order to understand the light-matter interaction in plasmonic nanoparticles and metamaterials for photocatalysis.

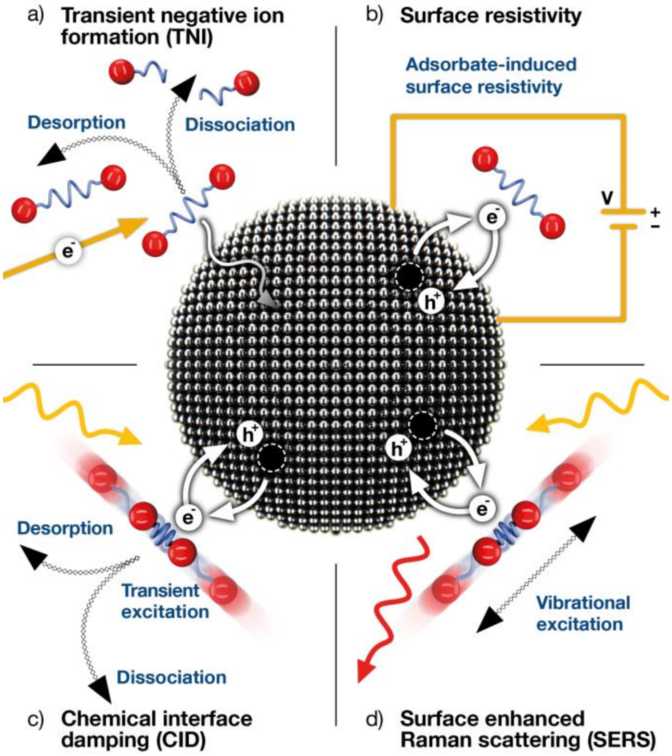

Figure 1. Four phenomena that can be used to monitor charge and energy transfer at the plasmonic – molecule interface.

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Unlocking Chemical Reactivity in Plasmonic Systems: Role of Dissociative Electron Attachment

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It is important to understand the fundamental aspects of the interaction of energetic electrons with molecules and the factors controlling and driving their reaction rate in a heterogeneous system. Dissociative electron attachment is one of the key processes in plasmonic chemistry, enabling the activation and breaking of chemical bonds through the use of hot electrons generated at the plasmonic interface.[1] The probability of such surface plasmon-induced reactions depends on several factors: the feasibility of hot electron transfer and availability of low-lying molecular orbitals of the adsorbate, nature of plasmonic substrate, photon density, excitation energy, etc.[2] This study demonstrated the reactivity of biomolecules, namely secondary amides and brominated nucleosides at the plasmonic interface of gold and silver nanoparticle aggregates supported by dissociative electron attachment studies in the gas phase. An insight into the dependence of the reactivity of such molecules on different reaction conditions has been demonstrated. Surface-enhanced Raman scattering is used as a two-in-one in-situ spectroscopic tool to monitor the molecular reaction and simultaneously monitor and analyze the reaction product supported by computational studies.

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Electron driven fragmentation of analogues of nucleobases

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Reactions initiated by electron capture to gas phase molecules, among them those that result in molecular dissociation, are responsible for the performance of many important processes in diverse areas such as material science, (nano)technology, chemical engineering, astrochemistry, radiation physics, and radiation therapy[1].

In recent decades, we have experienced a marvellous increase in research activities related to low-energy electron interactions with molecules of biological importance. In particular, a large number of experimental and theoretical studies have been devoted to complex biomacromolecules (e.g., DNA) as well as their subunits[2,3,4] to unravel the molecular mechanism by which low energy electrons damage macromolecules.

More recently, much research has been devoted to compounds that can sensitize tumour tissues to ionizing radiation, known as radiosensitizers. Potential radiosensitizers can be exemplified as, *e.g.*, modified nucleobases by the introduction of halogen atom(s) and/or other electrophilic groups into the molecular structure. Some of these compounds exhibit a supraadditive cytotoxic effect when combined with radiation, that is, the reduction of tumour tissues is more efficient in combination than the sum of individual effects from chemotherapy and radiation therapy.

During my presentation, I will show experimental gas phase studies on electron capture by compounds consisting of a six-membered ring substituted with two or three heteroatoms and fused carbocyclic derivatives, such as 5-carboxy-2-thiouracil, 6-azauracil, and 6-aza-2-thiothymine. Particular attention will be given to the description of the formation of transient negative ions and to the comparison of the fragmentation patterns for a set of nucleobase derivatives. Such compounds are often used to mimic the behaviour of (aza)pyrimidine nucleobases under reductive conditions and may be considered potential radiosensitizers.

Acknowledgements: This work was supported by the Polish Ministry of Science and Higher Education.

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Low-Energy Electron-Induced Decomposition of DNA Nucleobases Derivatives by Dissociative Electron Attachment Processes

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One of the most interesting and promising uses of plasmonic nanoparticles is the possibility to induce chemical reactions at their interface giving rise to the emerging field of plasmon chemistry. The reactions are driven by different processes occurring at the interface between the plasmonic nanoparticle and the molecules, such as the generation of hot-carriers and also the thermalization of these carriers into heat. Even though it is very difficult to distinguish the contribution of the two mechanisms, both are suggested to affect the reaction pathways. Our group recently has shown that brominated nucleobases can undergo a plasmon induced reduction when adsorbed onto gold or silver nanoparticles, and that the reaction can be tracked using SERS. The hot-electrons generated on the nanoparticles are transferred to the brominated nucleobase which is followed by cleavage of the C-Br bond in a procedure that only requires one electron and one proton *via* a dissociative electron attachment (DEA) mechanism.[1] Here we study this reaction with the brominated nucleobase incorporated in double stranded DNA. The nanoparticle ensemble design allowed us to provide electromagnetic enhancement enough to track the reduction of the brominated nucleotide by SERS in a single-point modification scale. Also, due to the addressability offered by DNA, it was possible to insert the modified base at precise positions, allowing us to check the possibility of transferring hot-electrons through DNA. The reaction was observed using SERS, where both the starting bromoadenosine (8BrdA) and the adenosine (dA) peaks can be observed while carrying the reaction. The decrease in intensity was used to fit the kinetics of the hydrodehalogenation reaction for all the 8BrdA insertion positions. One possible way to check thermal and electronic energy's role is to perform the plasmon-induced reaction with different incident light intensities, and it was tested.[2] To conclude, we demonstrate that DNA can transfer hot electrons far from the nanoparticle surface. Further understanding of the DNA-nanoparticle interaction at the interface and charge injection into DNA needs to be gained in future experiments.

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DEA as a Possible Source for CN^- in Interstellar Clouds

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The mechanism for the formation of CN^- in circumstellar envelopes such as IRC +10216 is unclear[1]. Previous studies have explored processes such as radiative attachment but found that the rate coeffcients to be too small to produce the anion. It was proposed that dissociative electron attachment to MgCN or MgNC could be involved in CN^- production[2]. The energetics for this process looked promising, but calculations including the dynamics showed that there was an energy threshold that precluded an efficient production in circumstellar envelopes[3]. However other systems may have more favorable energetics.

We will present our results on several possible candidate molecules. We carry out electron scattering calculations using the Complex Kohn Variational Method as a function of the internal degrees of freedom to obtain the resonance energy surfaces and autoionization widths. We use this data as input to form the Hamiltonian relevant to the nuclear dynamics and solve the time-dependent Schrodinger equation. We compute the DEA cross sections and discuss the implications for CN^- in circumstellar envelopes.

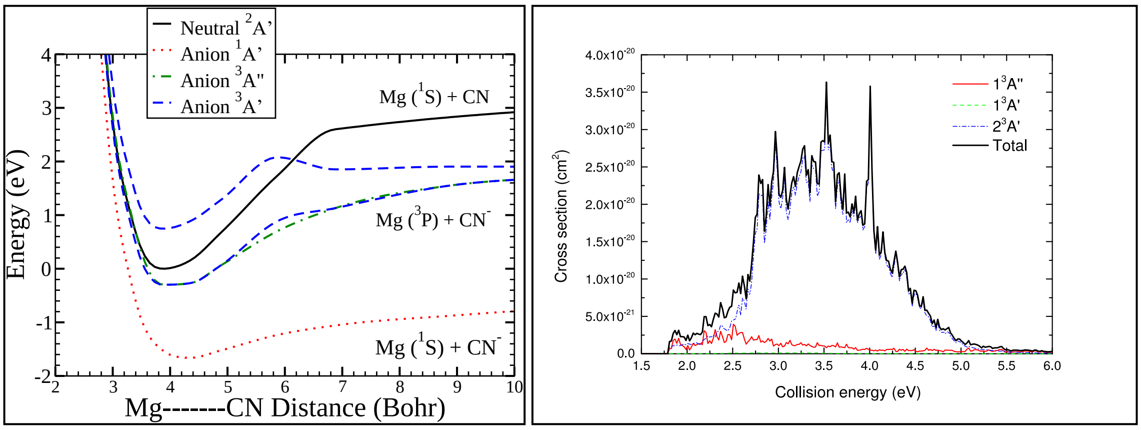

Figure 1. (Left) A one-dimensional slice of the potential energy surface of MgCN, where the CN bond distance is fixed at 2.26 Bohr and the bond angle fixed to one degree, showing the neutral and anion states relative to resonance dissociative attachment. (Right) The dissociative electron attachment cross section for the system MgCN.

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Electron Momentum Spectroscopy of Benzonitrile

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Electron momentum spectroscopy (EMS) is a powerful technique to probe the electronic structure of molecules. EMS uses high energy, kinematically complete, electron impact ionization collisions where the measured cross section is proportional to the square modulus of the wavefunction of the ionized molecular orbital in momentum space, $|\varphi(p)|^2$, referred to as the momentum distribution[1]. The experimental data has been measured using coplanar asymmetric kinematics (see Figure 1). Detection of the incident, scattered electron is fixed to be $\theta_1 = 20°$. Different target momenta are accessed by collecting the ionized, ejected electrons between $\theta_2 = 30 – 110°$.

The outermost 13 orbitals of benzonitrile, C_6H_5CN, has been measured. Benzonitrile, was recently discovered in the interstellar medium from observed transitions in emission bands within a molecular cloud[2]. It makes an interesting target due to the C≡N group.

Experimental data can be compared to theoretical predictions. Here, single point energy calculations were performed at the optimised geometry, using the ωB97X-D and have been calculated using the ωB97X-D and B3LYP density functionals with an aug-cc-pVTZ basis. The theoretical momentum profiles were then calculated within the target-Kohn-Sham approximation using the HEMS program[3].

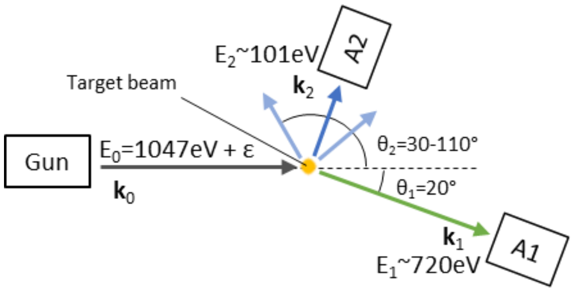

Figure 1: Kinematics of the coplanar symmetric spectrometer at the Open University

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Low Energy Electron-Induced Chemistry: Insights into Astrochemistry

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The interaction between low-energy electrons (LEE) and matter is ubiquitous in both the interstellar medium (ISM) and biological systems. Through interactions between LEE and matter, the efficient initiation of several chemical reactions can be achieved. The prime intermediate that triggers LEE-induced chemical reactions is an electron-molecule compound state known as the negative ion resonance state (NIR). These states, which is formed by the resonant capture of the LEE by reactant molecules, once created can lead to chemical reactions through different channels such as dissociative electron attachment (DEA)[1], and associative electron attachment[2b]. In addition to these well-known channels, NIR can induce highly controlled chemical reactions through catalytic electron channels. Laboratory experiments can be used to simulate the ISM environment and study astro-chemically relevant reactions at ultra-high vacuum and very low temperatures. This talk will focus on astro-chemically relevant LEE induced chemical reactions in the condensed phase that we have studied in our laboratories [4,5] with a focus on the catalytic electron channel. Theoretical calculations on LEE induced reactivity of astrochemically relevant systems [2(a),6] and LEE induced DNA repair shall also be discussed [7]. LEE-induced polymerization reactions, which could play a role in the formation of PAH in the ISM, will be briefly discussed. Controlling the crosslinking of polymers is possible through LEE induced polymerization reactions in the polymer industry.

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Electron collisions: From materials science to astrophysics

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Estimating the electronic excitation spectra induced by electron collisions is essential for understanding charge transport in solids[1]. These studies have a wide range of applications, from the charging of test masses by cosmic rays in the upcoming Laser Interferometer Gravitational-Wave Observatory[2] to the development of materials to improve the effectiveness of hadron therapy in cancer treatment[3], to imaging techniques in electron microscopy and surface spectroscopy for chemical analysis[4].

In this presentation, we introduce a unified theoretical and computational framework that combines ab initio (AI) and Monte Carlo (MC) methods for calculating the electronic, optical and transport properties of condensed phase materials[4]. Our approach involves solving the Dirac equation for elastic scattering processes and using Ritchie's dielectric theory to model inelastic scattering events, including single and collective electron excitation, ionisation and Auger emission. We show that the macroscopic dielectric response function, which is directly related to the collisional energy loss, can be obtained by high-precision linear-response time-dependent density functional theory calculations. Furthermore, our method accounts for the generation of secondary electrons upon ionisation of the sample atomic constituents and can track the trajectories of the resulting electron cascade. The excellent agreement of our simulations with experimental spectra of elastic, Auger, energy-loss and secondary electron processes for different projectiles as well as with total electron yields on a variety of atoms, molecules and solids, such as metals[5], insulators, semiconductors[6,7] and materials of biological interest[3] demonstrates the versatility of our AI/MC approach. Finally, we will also discuss the extension of our technique to the beta decays of isotopes in astrophysical scenarios[8].

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Electron attachment to overlapping resonances

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Electron attachment to molecules can result in the coherent superposition of multiple resonances. This has been demonstrated in dissociative electron attachment (DEA) to H_2, where such a coherent superposition results in quantum interference in two dissociation channels[1]. This interference shows up as the forward-backward asymmetry in the DEA differential cross-section, unexpected for the inversion-symmetric system.

It is interesting to understand how such a coherent superposition of two resonances with two distinct lifetimes decay. In earlier reports on the overlapping resonances in photoabsorption, the decay of such a superposition has been shown to be non-exponential, with the superposition surviving longer than the short-lived resonance lifetime[2,]. How will this affect the DEA process in overlapping resonances accessed by electron attachment?

In our recent systematic momentum imaging measurements on DEA to aliphatic alcohols and thiols, as well as acetaldehyde and trimethyl acetaldehyde, we have observed features in the H- channel that correspond to the site-selective nature of DEA. However, we are unable to explain these features based on earlier reports on DEA and electron scattering from these molecules. Are we seeing the effect of overlapping resonances in DEA? These cases will be discussed in detail.

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Absolute differential cross sections for elastic electron scattering by desflurane - a case of anesthetic molecule in gas phase

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Motivation for this research has become by the significant impact of aneasthetic molecules in global warming[1]. Relative differential cross sections (DCSs) were obtained and normalized on an absolute scale by using the relative flow technique, with argon as the reference gas. Independent Atom Model and the Screening Corrected Additivity Rule with incorporated Interference effects (IAM-SCAR+I) was used to calculate the theoretical differential cross sections. Measurements have been carried out for anesthetics molecules, such as isoflurane[1], sevoflurane[2] and desflurane.

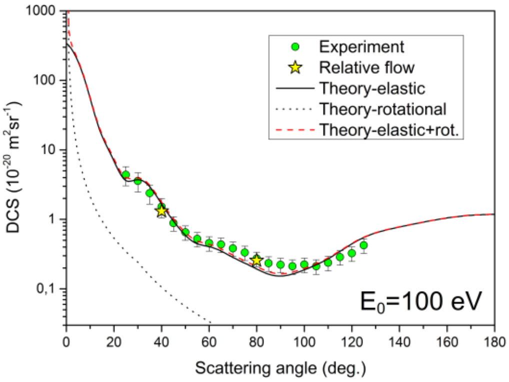

Figure 1 Angular dependence of the DCSs for elastic electron scattering from desfluran at 100 eV. Circles represent absolute experimental differential cross sections; stars represent absolute values obtained by relative flow method and lines represent calculations.

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Dissociative electron attachment of molecular CO_2 and clusters

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Recently we have more insights into molecular dissociative electron attachment (DEA), which is largely attributed to the application of velocity map imaging (VMI) technique in the anionic yield measurements. Dynamics details about electron attachment and fragmentation in resonant states can be retrieved by the analyses of the kinetic energy and angular distributions of anionic yield.

Here I will briefly review our over-one-decade studies on the DEA dynamics of molecular CO_2 and clusters $(CO_2)_n$ and highlight some results about the clusters.[1-6] With the high-resolution VMI measurements and the theoretical simulations, we find the competition between $(CO_2)_mO^-$ and metastable $(CO_2)_{m+1}^-$ (m =1, 2, 3) products from the larger clusters and, for the first time, CO_4^- at the higher electron attachment energies. These findings are helpful to understand the electron-induced or driven processes in CO_2-rich atmospheres and interstellar space.

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New insights into the electron attachment to nitric oxide (NO)

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Nitric oxide (NO) is a very reactive molecule which frequently interacts in biological and environmental media inducing relevant processes for life and climate conditions. This motivated numerous experimental and theoretical electron scattering from NO studies which have been recently compiled and discussed by Song et al.[1]

Dissociative electron attachment (DEA) experiments identified the O^- formation as the most probable dissociation channel and related DEA cross sections have been determined by different authors (see Ref.1 for details). Non dissociative electron attachment resonant processes have been analyzed at very low energy (below 2 eV) by Alle et al.[2] by measuring the total electron scattering cross sections (TCS). However, probably due to a lack of energy resolution, no resonances (apart from the aforementioned DEA processes) have been reported at higher energies (above 2 eV). In the present study we used a "state of the art" magnetically confined electron transmission apparatus to determine the total electron scattering cross sections from NO, with a total uncertainty limit of about 5%, for impact energies from1 to 15 eV. New resonant features have been found in the 3-10 eV energy range. We also have carried out electronic structure calculations, using the equation-of-motion coupled-cluster with single and double excitations approach for the neutral and anionic NO species, to estimate the temporary anion energy levels involved in these resonances. These results will be discussed in the presentation.

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Electron spectroscopy with photons: Probing effect of solvation on resonances

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While the natural approach to probe electron impact processes is to use electron spectroscopy, this has limitations in its application to probing the effect of solvation in a systematic manner and to probing chemical dynamics in real-time. Using light to access the resonances from a corresponding (stable) anion offers a route to overcome these limitations. Here, we will demonstrate the use of two-dimensional photoelectron spectroscopy to probe the effect of hydration[1] and use it to determine the location of resonances for the nucleobase uracil. We show that incremental addition of water molecules increases the electron affinity, but not the excitation energy (from the anion). From the perspective of electron-scattering, the resonances decrease in energy. We are able to extrapolate to the bulk limit and develop a Marcus picture of the energies (assuming linear response). We find that the two lowest energy shape resonances are bound. The third lies around 1 eV above the neutral, but can be readily stabilised by dynamic solvation of the surrounding water.[2] We also probe the intrinsic reorganisation energy associated with the electron attachment to isolated uracil and consider whether a valence-bound uracil is bound or unbound.

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What do we learn from the electron detachment channel?

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A resonance formed in an electron-molecule collision has two major decay possibilities: (i) electron detachment and (ii) dissociation (DEA). While a lot of attention has been paid to the latter channel in recent years, the information on the former is rather scarce. In my talk, I will show how the combination of the two brings insight into the DEA dynamics.

To monitor the electron detachment channel, we utilize electron energy loss spectroscopy (EELS) in which the energies of scattered electrons are recorded. To monitor the DEA channel, we combine measurements of absolute cross sections with velocity map imaging technique (DEA-VMI).

I will present several examples where the electron detachment leads to the target molecule in vibrationally excited states. One them is pyrrole, in which the formation of a $\pi_1^*(b_1)$ resonance leads to a strong excitation of bending modes. We show that this bending leads to coupling with the dissociative (non-resonant) σ^* mechanism and thus opens a pathway to N-H bond cleavage via DEA.[1]

There is also a possibility that the electron leave the target molecule in an electronically excited state. I will demonstrate how the electron energy loss spectra enable us to identify parent states of core-excited resonances. This allowed us to explain very different dissociation dynamics of two isoelectronic molecules HC_3N and NCCN[2].

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Dynamics of electronic Feshbach resonances in small carboxylic acids and amides

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Feshbach resonances occur when the potential energy of the resonance is lower than the corresponding excited neutral molecule. This energetically forbids the resonance from decaying by single-electron autodetachment, thus enabling nuclear motion to proceed on femtosecond timescales, which in turn can permit dissociation to occur.

Electron attachment resonance symmetries and dissociation dynamics are revealed by measuring the momentum of anion fragments produced by breaking specific bonds. In this work we focus on the dissociative electron attachment reactions breaking the hydroxyl and methyl bonds in formic acid[1,2] and acetic acid[3], and the carbonyl and model peptide C-N bond in formamide[4]. We make direct comparisons between the series of Feshbach resonances in the carboxylic acids to understand the dynamics underlying the production of anions and radicals in these reactions.

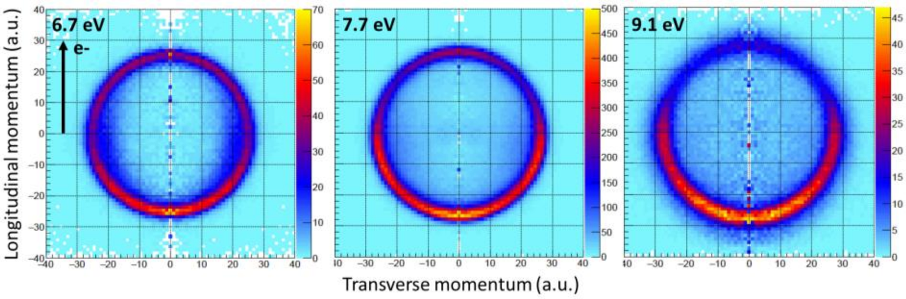

Figure 1. D^- fragment momentum distributions for acetic acid partially deuterated at the hydroxyl site, CH_3COOD, following attachment by electrons with energies at 6.7 eV (left panel), 7.7 eV (center panel), and 9.1 eV (right panel). The incident electron direction is in the longitudinal direction, as indicated by the vertical arrow. The color scale indicates the D^- yield in arbitrary units.

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The dissociation of temporary negative ions formed upon electron attachment to biologically relevant molecules

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The knowledge about the action of low energy electrons (LEEs) is crucial for the description of radiation damage in DNA. Ionizing radiation releases a large number of LEEs in cells. Pioneering studies by Sanche and co-workers demonstrated that LEEs with kinetic energies up to 20 eV can induce single and double strand breaks in a film of dry plasmid DNA[1]. They concluded from the damage yields as function of electron energy that at low electron energies, dissociative electron attachment (DEA) plays a significant role in the formation of strand breaks. Simons modelled the formation of a single strand break at electron energies near 1 eV and predicted in his computational studies that first the excess electron is captured in a π* orbital of the base and subsequently the electron is transferred to the C-O σ* orbital leading to the respective bond cleavage[2]. To also exploit the action of LEEs for the treatment of tumor cells with ionizing radiation, radiosensitizer molecules may be used, which create radical species upon electron attachment.

In this talk I will present recent results on biologically relevant molecules like modified cytidine nucleotides in the gas phase[3], which support the strand break model of Simons. The second emphasis of the talk will be placed on our recent DEA studies with various radiosensitizers. I will discuss the possibly electron attachment induced action of nitroimidazole radiosensitizers. In addition, we propose fundamental electron induced processes in radiosensitizers like bidirectional intersystem crossing and roaming[4].

This work was supported by the FWF, Vienna (I 5390).

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DEA to condensed-phase biomolecules: From O_2 to plasmid DNA

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The decay of transient anions into the DEA channel has been investigated on surfaces and in molecular solids during four decades.[1] Numerous experiments have been conducted on this process, which has been applied to various fields. Two major techniques were developed to investigate DEA in the condensed phase. They consist of measuring the incident low energy electron (LEE) energy dependence of 1) mass-analyzed anions desorbing from a surface covered with simple molecules or more complex biomolecules and 2) negative charges trapped near a dielectric surface. The latter method provides a direct measurement of absolute DEA or resonance stabilization cross sections, if no anion is allowed to escape the surface.[2] Furthermore, when combining measurements of molecular damage yields with those of DEA, it becomes possible to investigate the different LEE mechanisms that can modify complex molecules, e.g., how DEA to basic constituents of DNA combines with electron transfer, within and between nucleotides, to induce different types of lesions, including strand breaks, base damages, crosslinks and cluster damages.[3] These techniques will be explained during the presentation with emphasis on changes of resonance parameters from gas to condensed phase.[4] Results obtained with simple biomolecules (i.e., O_2 and H_2O) and DNA constituents up to plasmid DNA will be shown. An application to targeted chemoradiation therapy will be mentioned taking as an example vectorization of the [^{64}Cu]-NOTA-Terpyridine Platinum Conjugate into the quadruplex structure of genomic DNA in cancer cells.[5]

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Modeling dissociative electron attachment using complex energy methods

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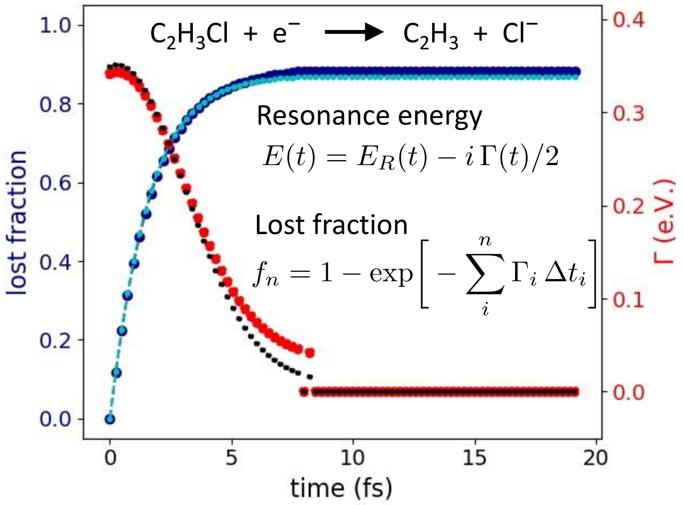
Dissociative electron attachment (DEA) to polyatomic molecules remains very difficult to model with standard quantum-chemical methods because the involved temporary anions are not bound but subject to autodetachment. This challenge can be tackled using non-Hermitian quantum mechanics where temporary anions are described in terms of complex-valued energies.[1]

I will present a new computational development for simulating the dynamics of such anions on complex-valued potential energy surfaces.[2] The imaginary part of these surfaces describes electron loss, whereas the gradient of the real part represents the force on the nuclei, which are described classically. In our method, the forces are computed analytically based on Hartree-Fock theory with a complex absorbing potential.

We performed *ab initio* molecular dynamics simulations for several temporary anions, which show qualitative agreement with experiment and offer mechanistic insights into DEA. The results demonstrate how our method evenhandedly deals with molecules that may undergo dissociation upon electron attachment and those which only undergo autodetachment.



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Estimation of dissociative electron attachment cross sections for arbitrary molecules

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We estimate the dissociative electron attachment cross section for polyatomic molecules using the Quantemol Electron Collisions (QEC) code[1]. QEC interfaces with the Molpro and UKRmol+ suite of molecular R-matrix codes[2,3]. The DEA cross section over the energy range 0-15 eV is estimated using an approximate resonance plus survival method[4] that is applicable to general, polyatomic molecules. Comparison is made between the cross sections calculated using QEC and experimental data where available. Results are also presented in cases where the cross section has not been measured, or where the complexity of the target molecule prevents calculation of the cross section using more detailed methods. The nature of the calculated resonances is analysed using a variety of scattering models.

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Ion induced reactions of various thiophenes

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Sulfur containing hydrocarbons are being studied both experimentally and theoretically. Electron and ion induced processes are of main interest, represented by ionization reactions, electron attachment, as well as charge transfer reactions. In industry, the sulfur containing compounds (thiophenes) in crude oil are among the most abundant constituents, considered as contaminants. In some cases, the content of sulfur in crude oil can be as high as 10%[1]. On the other hand, sulfur is the tenth most abundant element in the universe and is known to play a significant role in biological systems[2], investigation of sulfur containing astrochemical molecules is therefore of high interest. In both cases, sulfur considered as industrial contaminant and in contrast to that as highly important astrochemical constituent, among all possible chemicals five- or six-member rings containing sulfur atom are of interest as well. In this work Atmospheric Pressure Chemical Ionization of thiophen, its methyl-, dimethyl- and benzo- derivatives are studied with Ion Mobility Spectrometry (IMS) combined with Mass Spectrometry (IMS-MS)[3]. Quantum chemistry is used to model the thermochemical properties, ionization energies, electron affinities, bond energies in ions, proton affinities and reactions leading to formation of clusters of the studied analytes with reactant ions in IMS, produced with corona discharge source in ambient air.

This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-19-0386, APVV-22-0133 and the Slovak Grant Agency for Science (contract no. VEGA 1/0553/22). This work was supported in part through the Comenius University in Bratislava CLARA@UNIBA.SK high-performance computing facilities, services and staff expertise of Centre for Information Technology (https://uniba.sk/en/HPC-Clara).

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Absolute Attachment Cross Sections in Hydrofluorocarbons

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The greenhouse gas SF_6 widely used in high-voltage applications is expected to be substituted by more environmentally friendly mixtures containing hydrofluorocarbons. Simulating electron transport phenomena of novel mixtures requires the electron molecule scattering cross sections of the hydrofluorocarbons. Crucial for predicting the electric-breakdown strength are the attachment cross sections, which often cannot be inferred from numerical calculations due to large molecular size. The attachment cross sections are thus experimentally measured using specialized electron scattering devices[1].

Cross sections serve as input for Boltzmann Equation solvers[2] or Monte-Carlo simulations[3], which enable calculating the electron transport coefficients. These coefficients can further be experimentally attained using the Pulsed Townsend apparatus[4] situated at ETH Zurich. Comparing simulated electron transport coefficients with the measurements verifies the cross sections acquired from electron scattering.

This contribution elaborates on how dissociative electron attachment cross sections are deduced in presence as well as in absence[5] of electron scattering data. It is shown that electron scattering measurements are particularly expedient when resonances occur, and how the experimental data is included in the cross-section fitting procedures. The effects of modifying the attachment cross sections on the electron transport coefficients are illustrated for an exemplary hydrofluorocarbon.

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Breakdown in fluorocarbon gases

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Fluorocarbon gases underpin various modern technologies, including plasma etching for microchip fabrication, plasma-based nanotechnologies, particle detection, refrigeration, and gas insulation. In response to growing environmental issues with this class of gases, significant attention in the field is directed towards finding eco-friendly solutions – gases with low global warming potential (GWP) and low ozone depletion potential (ODP) that would sustain or improve the efficiency of applications.

Many applications operate at moderate and high electrical fields, making it crucial to gather data for those conditions. Our work is focused on studies of elementary processes, based on breakdown data and emission properties of gases relevant to medium and high-voltage technologies. DC breakdown curves represent a sensitive balance between processes of gain and loss of charged particles in the gas phase and on surfaces, while spatial emission profiles reveal the kinetics of charged particles and fast neutrals[1,2].

Our measurements were made in the low-current steady-state Townsend's regime of discharge, under swarm conditions. Thus, in addition to breakdown voltages and spatially and spectrally resolved emission profiles, we were also able to determine effective ionization coefficients and secondary electron yields. The emphasis of this study was on newer generation low GWP gas – hydrofluoroolefin $C_3H_2F_4$ (CH2=CFCF3)[3], in comparison with fluorocarbons that have been phased out or banned recently, such as $CHClF_2$ (R22), $C_2H_2F_4$ (R134a).

Acknowledgements This research was supported by MSTD the Science Fund of the Republic of Serbia, Grant No. 7749560, project EGWIn. Zoran Lj. Petrović is grateful to the SASA project F155.

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Novel experimental approaches to study dissociative electron attachment and ion pair dissociation

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Our understanding on dissociative electron attachment (DEA) and ion pair dissociation (IPD) have been improved dramatically due to the development of novel experimental techniques. The state-of-the-art velocity slice imaging (VSI) technique having extremely high sensitivity has revolutionized the electron molecule collision studies in the last few decades. Furthermore, the implementation of wedge slice technique for detailed analysis of the experimental data enrich the results by improving resolution. At IISER Kolkata, we have developed two experimental techniques for the study of electron molecule collisions, particularly, dissociative electron attachment and ion pair dissociation. The time-of-flight (ToF) mass spectrometer in total ion collection mode has been used to measure the absolute cross sections for the formation of negative ions. On the other hand, complete fragmentation dynamics for both the DEA and IPD processes has been probed using velocity slice imaging technique.

In this meeting, we will present our recent measurements on absolute cross section for the formation of various negative ions in the low energy electron collisions with ethanol[1], the kinematically complete fragmentation dynamics in the DEA to OCS molecule[2], and the electron induced ion pair dissociation dynamics to oxygen molecule[3].

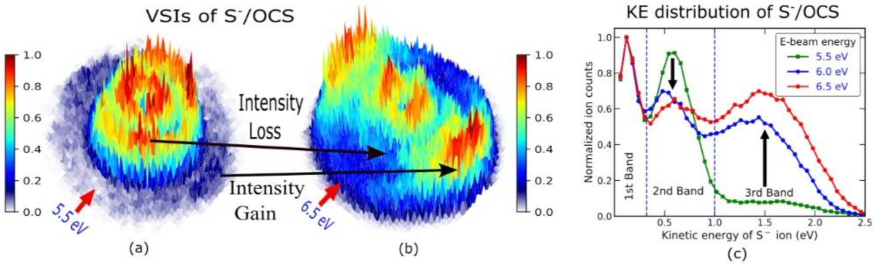

Figure 1. (a, b) Velocity (wedge) slice images of S^-/OCS at 5.5 eV and 6.5 eV electron energy, respectively. (c) The kinetic energy of the S^-/OCS extracted from sliced images taken at the indicated electron energies.

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Electron induced fluorescence studies to O_2 and N_2.

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The inelastic interactions of electrons with atoms and molecules pose significant experimental challenges, particularly regarding processes involving dissociation into neutral fragments. One such technique used to investigate these interactions is Electron Induced Fluorescence (EIF), where dissociative excitation processes are major channels in polyatomic molecules.

In two atomic molecules, such as O_2 and N_2, dissociative excitation process is present, however, in these molecules the emission from the molecular excited states and from the excited states of molecular ions are prominent in the emission spectra of molecules in UV-VIS range.

In the presentation, we will show recent experimental findings from the Department of Experimental Physics at Comenius University in Bratislava. For N_2, we will present a 2D spectral map covering electronic emission spectra ranging from 300 to 1100 nm and electron excitation energies from 5 to 100 eV[1]. These data offer a comprehensive understanding of the excitation-emission processes initiated by electron collisions.

In the case of O_2 we will present recent data for the excitation of the first ($b^4\Sigma^-_g$ - $a^4\Pi_u$) and the second ($A^2\Pi_u$ – X $^2\Pi g$) O_2^+ negative band of systems of O_2, as well as emission from O I and O II fragments in the rage 200 – 650 nm and relevant cross section.

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Electron Scattering Studies - The Next Ten Years: Renaissance or Revolution?

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The study of electron interactions with atomic and molecular targets has been at the forefront of both our understanding of quantum phenomena and the foundation of many modern technologies. Only through a quantum approach to scattering can we explain such effects as the Ramsauer-Townsend minimum and ‘resonances’ - the decay of which leads to the Dissociative Electron Attachment (DEA) process, the core topic of this meeting. Understanding electron collisions has allowed us to study natural phenomena such as the aurora (on Earth and now other planets) and both physical and chemical effects of radiation, indeed the discovery of the role of DEA in radiation induced DNA damage has been a major breakthrough in our development of new radiotherapies. However, perhaps the major advantage of understanding electron collisions has been the development of technologies that uses such knowledge of which the plasma industry is an exemplar. The ability to design and control plasmas is the basis of many of the key modern technologies such as the semiconductor industry whilst (cold, atmospheric) plasmas are used for a wide range of materials processing and (hot) plasmas for fusion energy. Electron collisions are also the basis of many analytical tools, most notably mass spectrometry.

Given the importance of electron collisions across such a range of modern science and technology the continued need to study such processes may appear obvious. However, the research community in this important field is declining across the world with resultant risks. In this presentation, we will highlight not only the need for such studies but also show that, by exploiting new instrumentation and computational developments, we may address new challenges and provide new insights into physical, chemical, and biological processes that have the potential to herald a new era in the field as transformative as that of the last century. In our study of electron collisions, the ‘best may be yet to come.’

Spontaneous electric fields in molecular films

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When a dipolar molecular species is condensed to form a thin film, the molecular dipoles associated with each individual molecule can orient such that the ice-film spontaneously polarises. This manifests as a polarisation charge at the film-vacuum interface, relative to the substrate-film interface, meaning films harbour electric fields of up 10^8 Vm^{-1}, with no free change present in the material.[1]

We first detected this phenomenon while irradiating molecular films with very low currents (10 fA) of low energy electrons (<10 meV) and reported a deflection of the electron beam by the polarisation charge at the film surface. We subsequently demonstrated that the spontaneously generated electric fields, resulting from dipole orientation, produce temperature-dependent Stark shifts in absorption peaks in the VUV spectra of these films. Taking advantage of the ASTRID2 storage ring at Aarhus University, we have used spectroscopy, in the vacuum-ultraviolet range, to characterise this phenomenon in ice-films prepared via condensation at cryo-temperatures with a particular focus on molecular ices of relevance to astrochemistry. The results demonstrate that both amorphous and crystalline ice films, of species such as ammonia and water, harbour electric and our observations will be discussed in the context of water ice as the reservoir from which chemical complexity is derived in the interstellar medium.

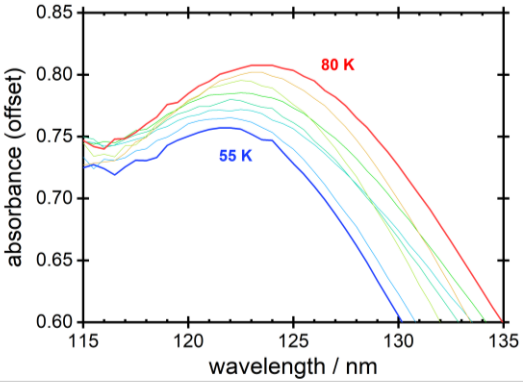

Figure 1. The vacuum ultra-violet spectrum of solid ammonia is Stark-shifted to the red as the film is condensed at increasingly higher temperatures, indicating a temperature dependent electric field.

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Vibronic coupling of resonances in electron molecule collisions

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I will review recent activities in our group considering the role of vibronic coupling of metastable states in the low energy collisions of electrons with molecules. In our work we generalize the previous treatment of diatomic molecules using the nonlocal discrete-state-in-continuum approach also for polyatomic molecules. Our approach builds on ideas of Estrada, Cederbam, Domcke[1,] including the conical intersections of resonance states. I will discuss the specific properties of conical intersections of metastable states extending the work of Feuerbacher et al.[2] Then I will briefly introduce our method for the numerical treatment of the vibronic dynamics of the electron-molecule collision[3] and discuss its application to electron energy loss spectroscopy of CO_2 molecule[4]. I demonstrate the potential of the theory to discuss complicated spectra in terms of symmetry and time dependence that are not accessible to the experiment. I will also show some theoretical results for the dissociative attachment in gas phase[5] and molecular junctions[6].

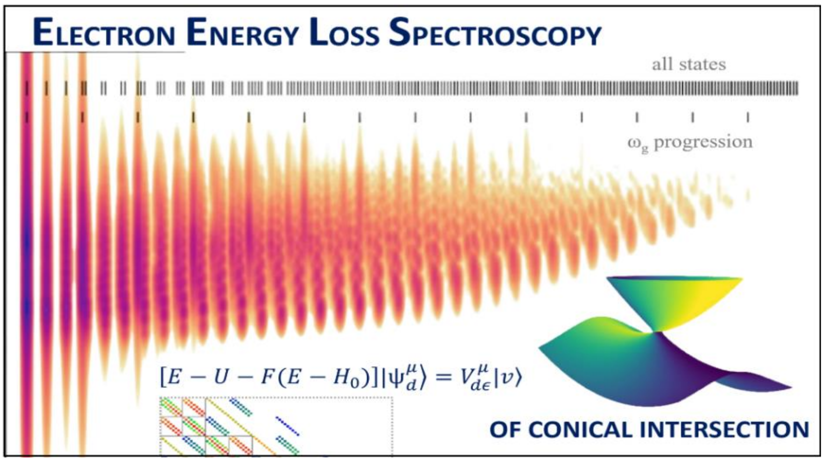

Figure: Illustrative example of 2D electron energy loss spectrum of model molecule with conical intersection (reprinted from graphical abstract of Cosic et al.[3]).

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Abstracts of Poster Presentations

Dissociative electron attachment to 2-chlorobenzonitrile

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Since Benzonitrile's identification in the interstellar medium (ISM) in 2018[1], and the proposed formation pathway through Benzene, some studies about electron interactions with this molecule have surfaced, mainly about dissociative ionization (DI) and dissociative electron attachment (DEA). The past identification of Chlorobenzene in dust grains in meteorites samples and in Mars craters[2,3], has originated interest in the possibility of halogenation of a precursor aromatic ring, namely, by chlorination and how these changes effect expected interactions of low energy electrons (LEEs) within the ISM.

The anionic species resulting from electron interactions with 2-chlorobenzonitrile (2-ClC_4H_6CN) through DEA are reported. The beam energy ranges from 0 up to 13 eV. For energies below 1 eV the most intense signal is attributed to Cl^- at ~0.5 eV electron energy, followed up by the parent anion M^- at 0 eV, where a second resonance is observed at ~0.3 eV. The observation of the parent anion at 0 eV is consistent with the relatively large electron affinity (0.54 eV), which is about ~0.3 eV higher than for benzonitrile. For electron energies above 1 eV, up until 10 eV, two resonances are observed for the formation of CN^-, while its counterpart $[M\text{-}CN]^-$ is only observed at ~6.5 eV. Within these last range, the most intense signal is attributed to $[M\text{-}Cl]^-$ at ~6 eV, formed by three individual resonance peaks.

The experiments were carried out in a crossed electron-molecular beam set-up, composed by a trochoidal electron monochromator coupled with orthogonal reflectron time of flight mass spectrometer[4].

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Electron interactions with perfluorophenyl trifluoromethanesulfonate (F-PhTf) EUVL photoresist material

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Extreme ultra violet lithography (EUVL) is a powerful technique introduced to enable more advanced technology nodes in the electronic chips fabrication not feasible with conventional deep ultraviolet lithography (DUVL). The EUVL uses 13.5 nm light instead of 248 or 193 nm currently used in DUVL, to induce chemistry in the photoresist materials achieving the required patterning[1]. The energy of photons with wavelength of 13.5 nm is ~92 eV, generating photoelectrons in organic resist materials with an energy range from 60 to 85 eV. The generated electrons, will have an energy distribution tailing from ~0 eV to the binding energy of the valence band, due to the sequential ionization events. It is well know that in this energy regime several resonant and non-resonant process can take place, namely dissociative electron attachment (DEA) and dissociative ionization (DI) leading to the molecular fragmentation.[2]

In the present contribution DEA and DI studies of perfluorophenyl trifluoromethanesulfonate (F-PhTf) are described. Th DI channels lead to the formation of 13 fragments with intensity above 2% besides the parent cation, that is formed at 10.6 eV (EI). The most intense formed cation is CF_3^+ m/z 60 due the cleavage of S-CF3 bond. DEA shows the three most intense fragments m/z 182 m/z 148 m/z 132, formed through the electron attachment in five different orbitals.

The experiments were carried out in a crossed electron-molecular beam set-up, composed by a trochoidal electron monochromator coupled with orthogonal reflectron time of flight mass spectrometer.[3]

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[3] Pereira da Silva, J., et al. (2021) Electron driven reactions in tetrafluoroethane: positive and negative ions formation. *J. Am. Soc. Mass Spectrom.*, 32, 6, 1459–1468. DOI:10.1021/jasms.1c00057

Low-energy electron attachment to Diethyl Carbonate

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Diethyl carbonate (DEC) is an organic linear symmetric carbonate with extensive industrial applications. It is most commonly used in the anode of Lithium Ion Batteries (LIBs) and as a potential fuel additive. DEC has high polarity, low toxicity, is biodegradable, and is associated with high oxygen content and decreased particulate emissions as a fuel additive[1]. Because of its symmetric structure, DEC is used in the production of globally-used polycarbonates. DEC is an excellent solvent, widely utilized in pharmaceutical products, fertilizers, pesticides, and dyes. However, DEC is also listed as a volatile organic compound (VOC), and potential photo-pollutant[2]. Because of its large and varied use in industry, a DEA study of diethyl carbonate can establish the safety of DEC and the larger polycarbonate systems it produces. Furthermore, degradation of DEC and various other carbonates is a chief cause of LIB degradation; our DEA study of DEC hopes to illuminate the pathways of decay that can occur at the LIB anode. Our analysis of this simple carbonate also expands the database on the dissociation of organic compounds with a carbonate functional group. Our preliminary studies involved an apparatus with a quadrupole mass spectrometer to study DEA to gas-phase DEC[3]. Our analyses of ion yields found 4 anionic fragments from DEC, each of which emerges from dissociation of the central carbonate. These are the O- (16 amu), CH_2CHO- (43 amu), HCOO- (45 amu), and $C_2H_5CO_3$- (89 amu). Notably, the three multi-atomic anions are stabilized by charge delocalization activated by the dissociation of the carbonate group and the ease of hydrogen shifts within the system. Making use of the B3LYP functional and the aug-cc-pVTZ basis set, we provide a density functional theory analysis on the fragment anions and molecules to determine plausible fragmentation channels associated with each ion peak. With subsequent theoretical analyses of electronic state transitions, we combine our various experimental and theoretical findings to better understand the fragmentation of this practically and synthetically important molecule.

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Real-Time Observation of the Nonvalence-Bound State Mediated Anion Formation

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Using energy- and time-resolved photofragment spectroscopy, the electronic structure of the multiple nonvalence-bound states (NBS) of the nitromethane anion and its dissociation dynamics were elucidated. Due to low electron affinities, most radical anions have been challenging to conduct using conventional pump-probe experiments, leaving their dynamics unexplored. The time-resolved spectroscopy introduced in this study enables observation of the energetic flow along the potential energy surface as dissociation unfolds over time. This research demonstrates that the NBS can function as a doorway state for anion formation. Moreover, it was revealed that solvent molecules can effectively act as vibrational energy dissipaters, preventing the disintegration of anions.

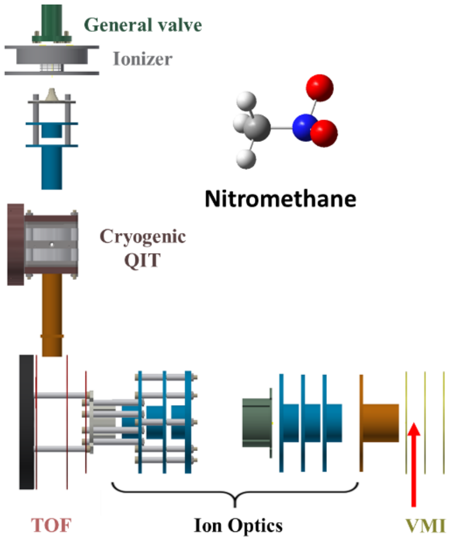

Figure 1. A schematic figure of the radical anion photoelectron and photofragment spectrometer

Surprising oscillations in DEA cross sections in electron-oxygen collisions

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In their paper, Laporta *et al.*[1] present DEA cross sections in electron-oxygen collisions calculated within the Local Complex Potential (LCP) approximation. These cross sections show unusual oscillations in energy dependence seen in Fig. 1. We managed to reproduce these oscillations both in our LCP and Nonlocal Resonance Model (NRM) calculations[2] and proposed an explanation of their origin.

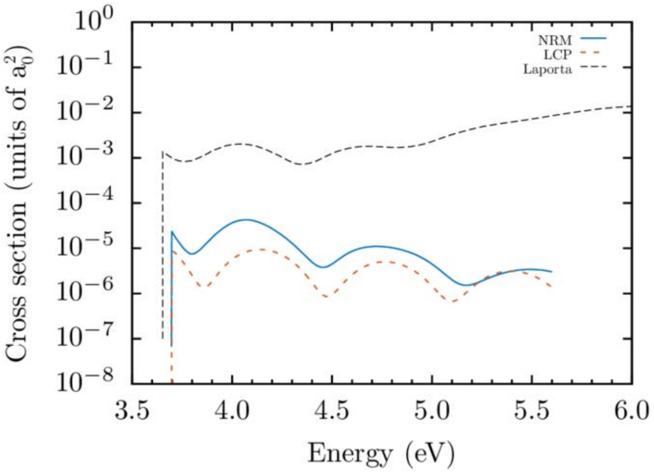

Figure 1. DEA cross sections in electron-oxygen collisions, showing unusual oscillations. Results by Laporta compared to our results from a nonlocal resonance model (NRM) and LCP approximation^s.

The specific configuration of the potential energy curves in oxygen allows the nuclei to move either directly away from each other, or first towards each other, then reflect and continue outwards. The oscillations then arise from the interference of these two waves.

In our contribution, we present a simple LCP toy model exhibiting the same oscillatory behavior and use it to probe the fragile conditions needed for the oscillations to occur. It is interesting to see how even slight changes in the configurations cause the oscillatory structure to quickly vanish.

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Dissociative recombination model for direct processes

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Dissociative recombination (DR) is a process is which a free electron with a positive kinetic energy is captured by a molecular ion while breaking one or several chemical bonds,

$$e^- + \mathrm{H}_2^+ \rightarrow \mathrm{H} + \mathrm{H}(n)\,.$$

This is a very efficient chemical process, but is rarely described in chemical textbooks. It is considered to be the most complex of gas-phase reactions leading to the production of neutral atoms and molecules[1].

A numerically solvable two-dimensional (2D) model, employed by the authors to study the dissociative recombination of H_2^+ in the ungerade symmetry[2,3], is extended to describe the collision process in the gerade symmetry of H_2. In this symmetry, the ionization and dissociation processes are driven primarily by the direct, curve-crossing mechanism. The model is represented by a set of three coupled electronic channels in 2D, in the space of s, p, d partial waves of the colliding electron. We demonstrate that the Born-Oppenheimer properties of the H_2 molecule in the relevant range of internuclear distances can be described by such a model. The molecular rotational degrees of freedom are accounted for by the rotational frame transformation. The numerical solution of the model is discussed, and the resulting rovibrationally inelastic and dissociative recombination cross sections are compared with the available data.

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Energy thresholds for electron-induced reactions in solution-processed metal-organic materials

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Irradiation of metal-organic precursors plays an important role in nanofabrication processes. While the most versatile approach is to deliver these precursors via the gas phase to the focus point of an impinging electron or ion beam, non-volatile compounds may also be processed from solution. For instance, thin spin-coated films of palladium acetate were recently used for irradiation by a focused Ga^+ beam, resulting in palladium nanostructures.[1] However, to fully use the potential of such processes, the underlying chemistry must be understood at a fundamental level.

To gain insight into the electron-induced fragmentation mechanisms of metal carboxylate compounds, the surface-grown copper-based metal-organic coordination polymer copper(II) oxalate was previously studied.[2] It was proposed that the reaction proceeds via electron ionization leading to release of the stable product CO_2. However, the energies used to identify the reaction products were well above the ionization threshold and loss of CO_2 via ligand-to-metal charge-transfer electronic excitation has been observed for iron(III) oxalate upon irradiation with photons at lower energies.[3] This raises questions if such neutral dissociation also contributes to the electron-induced decomposition of copper(II) oxalate and related materials. Therefore, we have studied the electron-stimulated desorption of CO_2 from copper(II) oxalate and from spin-coated layers of copper(II) acetate at electron energies from 2-10 eV. This contribution describes our experimental approach and preliminary results suggesting that the energy thresholds are as low as 4 eV for copper(II) oxalate and around 5-6 eV for copper(II) acetate.

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Electron-induced deposition using $Fe(CO)_4MA$ and $Fe(CO)_5$ – Effect of MA ligand and process conditions

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The electron-induced decomposition of $Fe(CO)_4MA$ (MA = methyl acrylate), a potential new heteroleptic precursor for focused electron beam induced deposition (FEBID) was investigated by surface science experiments under UHV conditions and compared to the established FEBID precursor $Fe(CO)_5$.[1] Experiments that mimic FEBID and cryo-FEBID processes (Figure 1) were performed to reveal the effect of the modified ligand architecture. As a key finding, the deposits obtained from $Fe(CO)_4MA$ and $Fe(CO)_5$ were surprisingly similar. The relative amount of carbon in deposits prepared from $Fe(CO)_4MA$ was considerably less than the amount of carbon in MA showing that electron irradiation efficiently cleaves the neutral MA ligand from the precursor. In addition to deposit formation by electron irradiation, the thermal decomposition of $Fe(CO)_4MA$ and $Fe(CO)_5$ on an Fe seed layer prepared by EBID was compared. While $Fe(CO)_5$ sustains autocatalytic growth of the deposit, the MA ligand of $Fe(CO)_4MA$ hinders the thermal decomposition. $Fe(CO)_4MA$ thus offers the possibility to suppress contributions of thermal reactions which can compromise control over deposit shapes in FEBID processes.

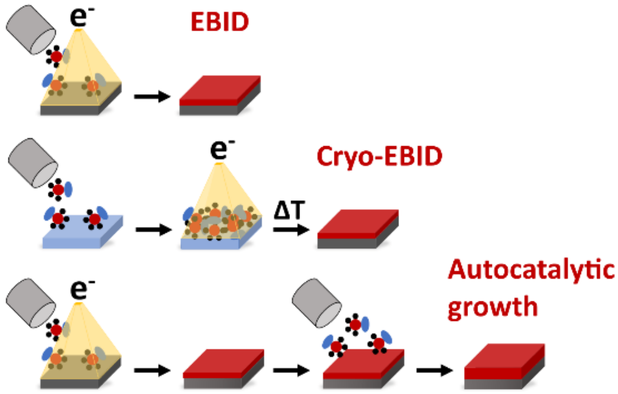

Figure 1. Schematic of UHV experiments that mimic EBID, cryo-EBID, and autocatalytic growth processes.

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Electron Triggered Processes in Halogenated Carboxylates and Their Clusters

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It is a well-known fact that an environment can change completely the pathways of the DEA processes. It is best illustrated when comparing the DEA of individual isolated molecules with the same molecules in clusters. Here we demonstrate this for the case atmospherically relevant halogenated carboxylates molecules.

Even though the use of hydrochlorofluorocarbons (HCFCs) is being abandoned, residues of those compounds will be present in the environment due to their chemical resilience. The degradation products are often halogenated carboxylic acids and their halo-derivates. In this work we investigate interactions of trichloroacetic acid (CCl_3COOH) and acetyl chloride (CH_3COCl) molecules and clusters with low energy electrons, particularly the electron attachment, and compare the results with trifluoroacetyl chloride (CF_3COCl) from our previous work[1].

The CLUB[2] apparatus was used for the experiment. A particle beam was created via continuous supersonic co-expansion of the sample with a buffer gas (Ar or He) through a conical nozzle. Helium was used to generate a beam of individual molecules, while clusters were formed in argon. After low energy electron attachment, the beam was probed with reflectron time-of-flight mass spectrometer.

The results suggest not only the expected influence of the electron density distribution over the molecule on the dissociation pathways, but also strong effect of the environment, as the fragmentation patterns differ for all three compounds when comparing molecular and cluster mass spectra.

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Hydrated Formic Acid Clusters and their Interaction with Electrons Examined in Molecular Beam Experiment[1]

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Upon other techniques of investigating the aerosol formation, molecular beams can provide us with information about the process dynamics, however the amount of information is conditioned by the knowledge of the neutral cluster distribution, often concealed after fragmenting ionization. A significant portion of the atmospheric aerosol is formed by water nucleated with a precursor such as H_2SO_4, NH_3 or oxidized organics (especially organic acids). In this work, we investigate the ion formation in mixed water/formic acid clusters $FA_M{\cdot}W_N$ upon collision with various energy electrons in order to determine the extent of the cluster fragmentation.

The experiment was done using the CLUB apparatus. The beam of hydrated FA clusters was produced by a continuous supersonic co-expansion of FA/H_2O vapor with helium as a buffer gas through a conical nozzle. Different concentrations of FA were used to influence the hydration extent. The beam was probed using a reflectron time-of-flight mass spectrometer with 70 eV electron ionization (EI) for positive ions and 1.5-15 eV electron attachment (EA) for negative ones.

The main product after EI were protonated $[FA_m+H]^+$ clusters. The EA at lower energies produced mostly intact $[FA_m.W_n]^-$ ions, while higher energy EA led to deprotonated $[FA_m.W_n-H]^-$. The comparison of positive and negative ion spectra suggests that the mass spectra of FA-rich clusters may indicate their actual size and composition. On the other hand, for hydrated clusters, the water evaporation from the clusters depends strongly on the ionization. Thus, for the hydrated clusters, the neutral cluster size can hardly be estimated from the mass spectra.

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Dissociative electron attachment to $C_5F_{10}O$

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Studies on electron attachment are of great importance to the identification and understanding of electron-induced molecular fragmentation. Additionally, theoretical and experimental investigation can shed light on the mechanisms of negative ion formation. Such research is of practical value for a number of systems and applications.

We experimentally probe the main dissociative electron attachment (DEA) channels in a member of the Novec brand family ($C_5F_{10}O$) – see Fig. 1. Novec gases are fluorinated ketones, typically composed of carbon, fluorine, and oxygen atoms. In contrary to SF_6, which is considered one of the most potent greenhouse gases, they have a low global warming potential (GWP) and are non-ozone depleting. These molecules are also very effective in preventing electron arcing in electrical system. Novec 5110 gas, with its high dielectric strength and thermal stability, can act as an effective insulating medium in electrical equipment, such as circuit breakers and switchgear, thereby reducing the risk of electron arcing.

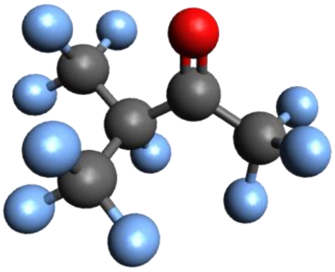

Figure 1. A schematic diagram of a NOVEC 5110 molecule

In our studies the abundance of fragmentation fragments is revealed when the molecule is bombarded with beam of electrons. Most dominant fragments are F^-, $C(O)CF(CF_3)_2^-$, CF_3^-, $C(CF_3)CF_2^-$. This constitutes a segment of the broader endeavor to explore optimal molecular compounds as substitutes for SF_6 dielectric gas in high-voltage insulation[1,2].

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Experimental and theoretical study on electron scattering from propionaldehyde (C_2H_5CHO) molecule

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The desire to understand the processes incorporating simple organic molecules, basic building blocks of life, in extraterrestrial conditions in many cases requires comprehensive knowledge of the electron-molecule interaction[1]. Propionaldehyde, one of the simplest aliphatic aldehydes, is quite abundant in space, as it has been detected on the comet 67P/Churymov-Gerasimenko, Murchison meteorite[2] and in interstellar molecular clouds[3]. Therefore, detailed data related to the interaction of electrons with this molecule may be very valuable.

In the present study we have measured the absolute grand-total cross section (TCS) for low-energy (0-300 eV) electron scattering on propionaldehyde molecule using an electrostatic electron spectrometer[4] operating in the linear transmission configuration. Calculations of the elastic scattering cross section (ECS) have been also carried out using R-matrix method[5] within static-exchange (SE), static-exchange with polarization (SEP) and SEP with applied Born correction[6] approximations. Figure 1 shows a comparison of experimental data and calculation results.

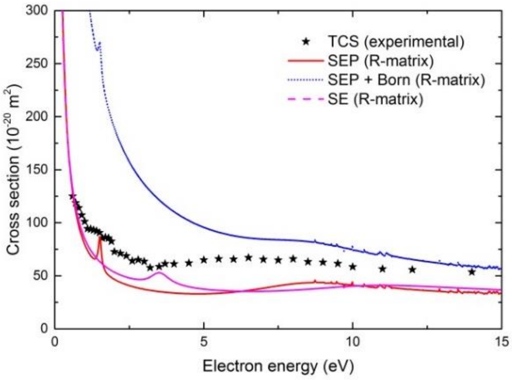

Figure 1. Comparison of measured TCS and calculated ECSes.

Acknowledgments: Financial support of these studies from Gdańsk University of Technology by the DEC-9/1/2023/IDUB/III.1a/Ra grant under the Radium Learning Through Research Programs – "Excellence Initiative - Research University" program is gratefully acknowledged. Numerical calculations have been performed at the Academic Computer Center (TASK) in Gdańsk.

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Dissociation of NH_3 by electron impact in low-temperature plasma and the isotope effect of the process

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Understanding the dissociative electron attachment (DEA) in low-temperature ammonia plasma is crucial for many technological applications, in particular, for alternative energy sources. However, theoretical modeling of this process has been challenging due to the complex interplay of electronic motion and multidimensional nuclear dynamics. The present study presents a theoretical approach to investigate the process, applying it to the breakup of the NH_3 molecule by low-energy electrons. The potential energy surface of the NH_3^- 5.5 eV resonant state is computed to elucidate the mechanism of the dissociative process. The cross section of DEA via the 5.5 eV resonance is then calculated for both NH_3 and ND_3. As seen in Figure 1, the positions of the peaks in both cross sections and the ratio between them are in excellent agreement with previous experiments. Our findings suggest that the developed theoretical model accurately describes the DEA process and could serve as a useful tool for providing DEA cross sections for other molecules to model low-temperature plasma.

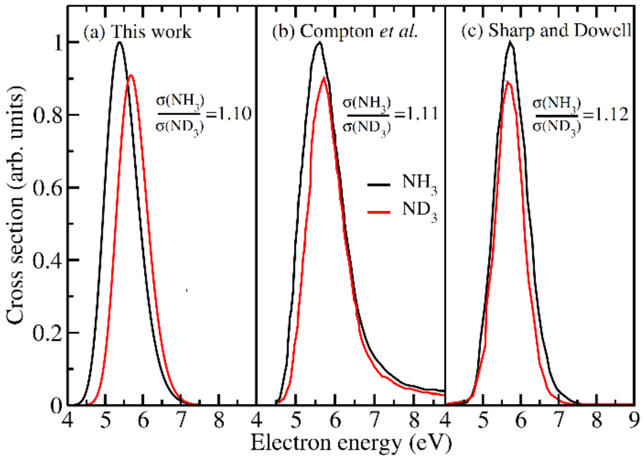

Figure 1. Comparison of the DEA cross sections for the NH_3 and ND_3 isotopologues from the present study (panel a), and two experiments (panels b[1] and c[2]). The NH_3 and ND_3 cross sections in each panel are scaled by a factor such that the NH_3 cross section is 1 at its maximum. The ratio σ(NH_3)/ σ(ND_3) of the peak values of the cross sections are indicated in the panels..

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Electron Attachment to Isolated and Clustered Methylmethacrylate

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Collisions of ballistic electrons with molecular precursors of photoresist polymers represent a way to explore the photoresist chemistry on the fundamental level, particularly for the XUV lithography, where the anion-induced scission and polymerization represent important mechanisms induced by secondary electrons.[1]

Here we explore the attachment of low-energy electrons to methylmethacrylate a precursor of PMMA, one of the most common bases for photopolymers. Except for the dissociation dynamics of the isolated molecule, we explored also the environmental effects on the molecule by studying its homogeneous clusters.[2]

Methylmethacrylate is an efficient electron scavenger redistributing the energy of the incoming electron into molecular vibrations. This effect transfers to the cluster environment, where the intermolecular energy transfer is very efficient in stabilizing the molecular anions. However, in contrast to recently studied butadiene, where the incoming electron is well localized on a single molecular subunit of the cluster, in the present case the self-scavenging and electron transfer processes drive a parent and fragment anion formation in a wide range of the energies of the incoming electron. Except for the fundamental interest from the point of view of the coupling of the electronic excitation and nuclear motion, the results provide an important insight into the behavior of MMA in a dense environment simulating the processes in photoresist.

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Gas-phase fragmentation dynamics induced by low-energy electron ionisation

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Collisions between electrons and molecules are ubiquitous in natural and industrial plasmas. Therefore, understanding electron-induced processes is relevant in fields ranging from atmospheric and interstellar chemistry[1], to mass spectrometry and radiation damage of biomolecules[2].

This work employs velocity-map imaging (VMI) to characterise the dynamics of gas-phase reactions initiated by electron ionisation[3]. Experiments are conducted at electron energies in increasing steps from a molecule's ionisation threshold. This energy range is particularly relevant for studying reactions initiated by secondary electrons, which usually have kinetic energies of up to 20 eV[1]. By stepping over thresholds for accessing different electronic states of a cation, their contribution to the fragmentation dynamics can be resolved. We demonstrate this approach with several simple halocarbon molecules, which have applications including industrial plasma etching[4], and find evidence of an anisotropic effect dependent on molecular orientation relative to the incident electron beam.

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Radiative vs dissociative electron attachment as mechanisms for formation of negative molecular ions in the interstellar medium

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Several negative molecular ions have been detected in the interstellar medium CN^-, C_3N^-, C_5N^-, C_7N^-, C_4H^-,C_6H^-,C_8H^-,$C_{10}H^-$. Since their discovery, for several years, there had been a general consensus in the community of modellers that in the interstellar medium (ISM) the ions are formed by the process of radiative electron attachment (REA). In a series of theoretical studies, we explored the REA process and the process inverse to it, photodetachment using ab initio methods. Cross sections and rate coefficients for formation of these ions by REA to the corresponding neutral radicals are calculated. For completeness of the theoretical approach, three pathways for the process have been considered:

(i) A direct pathway, in which the electron in collision with the molecule spontaneously emits a photon and forms a negative ion in one of the lowest vibrational levels;
(ii) an indirect, or two-step pathway, in which the electron is initially captured through non-Born-Oppenheimer coupling into a vibrationally resonant excited state of the anion, which then stabilizes by radiative decay; and
(iii) a pathway via a weakly-bound dipolar state of the ion.

The contribution of the (ii) and (iii) pathways to the formation of the anions, detected in the space, was found to be negligible in comparison to the direct mechanism. The obtained total rate coefficients of radiative electronic attachment at 30K for the considered ions are ranging in the interval $0.7\text{-}10\times10^{-16}$ cm^3/s. The validity of our calculations is verified by comparing the present theoretical results with data from recent photodetachment experiments performed in Innsbruck.

The second part of the study is devoted to an alternative process of formation of the negative molecular ions in the interstellar medium: by dissociative electron attachment (DEA). Ab initio studies were performed for DEA to H_2CN and HNCCC, leading to formation of CN^- and C_3N^- in the ISM. The results will be presented at the workshop

Contrasting Dynamics in Isoelectronic Anions Formed by Electron Attachment

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In recent years, 2D vibrational electron energy loss spectroscopy was used extensively for providing more detailed insight into the nuclear dynamics on resonances. An important advances have been made in the entire field of molecular dynamics, namely by anion fragment imaging[1], an experimental technique derived from the velocity map imaging (VMI), aided with position- and time-sensitive detectors.

In this work[2], we demonstrate how a combination of VMI with electron energy loss spectroscopy (EELS) in the electronic excitation range can explain a very different behavior of two isoelectronic linear molecules: cyanogen NCCN and cyanoacetylene HC_3N. Among the simplest nitrogen-containing molecules, both have been identified as potential reactants or intermediates in the prebiotic synthesis of the building blocks of life.

The dissociative electron attachment (DEA) to both NCCN and HC_3N leads to formation of CN^- anion. The DEA cross sections have very similar shapes, and both spectra have a dominant band peaking slightly above 5 eV, with an important difference of a factor of 6 larger cross section magnitude in NCCN. Moreover, NCCN fragments have higher kinetic energy release and a highly anisotropic angular distribution. In contrast, the HC_3N has an isotropic angular distribution with maximum intensity in the center, Figure , corresponding to low kinetic energy release.

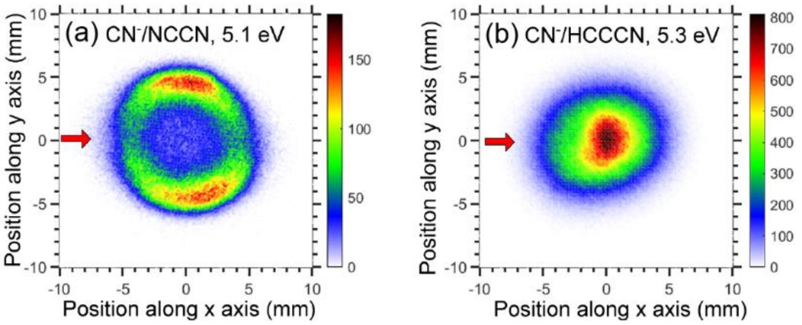

Figure 1. Velocity map images of CN^- anion produced upon DEA from (a) NCCN and (b) HCCCN parent molecules.

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Temporary anions of the dielectric gas C_3F_7CN and their decay channels

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Due to its very high dielectric strength, SF_6 (Sulfur hexafluride) has been used for many decades in power distribution industry as an insulating gas. However, it has an extremely high global warming potential (GWP) of 23k. GWP is a measure of how much heat a gas traps in the atmosphere relative to the same mass of CO_2. Given the raised ecological awareness, this fact makes it no longer suitable for wide commercial use and large efforts are put into finding its replacements. Therefore, an interest in electron collisions with one of possible candidates C_3F_7CN (heptafluoroisobutyronitrile) is motivated by its potential use in high-voltage switchgear and insulation.

In this work[1], we focus on the temporary anions of C_3F_7CN formed under the single collision conditions, when one electron is interacting with maximum one target molecule. Using three complimentary experimental setups located in Prague, we analyze either the scattered electrons, thus obtaining information about the detachment channel, or the formed stable anions, thus obtaining information about the final attachment products. The experiments reveal several phenomena occurring in electron collisions with this gas. A number of resonances are formed in the scattering, which lead to vibrational excitation of the target molecule. Some vibrational excitations corresponding to C-C bond stretch are presented in Figure . Moreover, apart from the direct vibrational excitation, we observe an unspecific vibrational excitation, where the electron is emitted statistically after an internal vibrational distribution on the anion surface. At low incident energies, there is a strong emission of slow electrons with a statistical kinetic energy distribution, which corresponds to the thermionic emission from the hot transient anion.

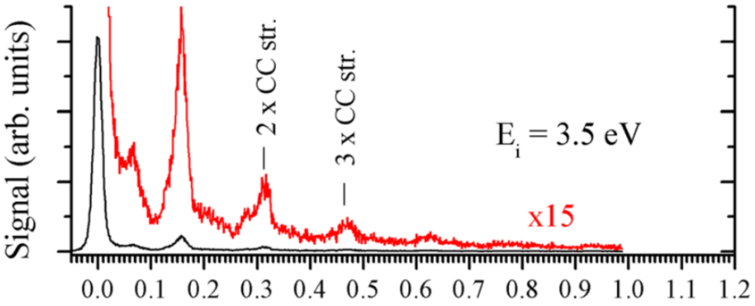

Figure 1. Electron energy loss spectra of C_3F_7CN obtained at 3.5eV incident electron energy.

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Distance-dependent resonances in interparticle Coulombic electron capture

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Interparticle Coulombic electron capture (ICEC)[1] is a novel neighbour-enabled electron scattering process which has seen several publications in recent years[2]. In recent *ab initio* studies, several resonances have been identified[3]. As ICEC is still a new area of study, the impact of these resonances is unknown but they could provide pathways to DEA-like processes. In this work, we present resonances which have a strong dependence on the inter-neighbour distance (*R*) and discuss their nature.

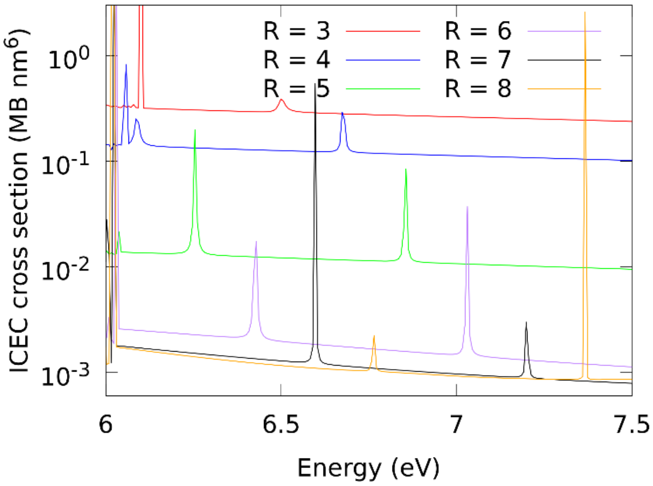

Figure 1. ICEC-W cross section for several inter-neighbour distances, *R* (Å). Two R-dependent resonances are visible.

Two ICEC processes are investigated: $H^+ \cdot H_2O + e^- \rightarrow H \cdot H_2O^+ + e^-$, denoted ICEC-P and $H \cdot H_2O^+ + e^- \rightarrow H^+ \cdot H_2O + e^-$, denoted ICEC-W[4]. The effect of *R* and the position of the $H^{(+)}$ relative to the $H_2O^{(+)}$ is investigated. Two *R*-dependent resonances are identified and shown in Fig.1 for ICEC-W with *R* = 3 to 8 Å. Both resonances appear at the same energy in ICEC-P and ICEC-W, strongly suggesting that they are the same. A logical assumption is that the dependence on *R* comes from a Coulombic interaction and therefore, the formation of an ion-pair. However, the resonance energies do not exhibit the expected ion-pair dependence on 1/*R*. Current analysis of the resonances indicates that their nature is mixed with character similar to ion-pair and Rydberg or shape resonances.

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Probing few-molecule chemical reactions and hot spot dynamics using DNA-origami-assembled nanoparticle dimers

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Due to its versatile characteristics, DNA origami structures demonstrate the capability to precisely position plasmonic metal nanoparticles in close proximity.These resultant dimeric configurations can subsequently serve as valuable tools for investigating plasmon-induced chemical reactions at the level of individual to few molecules. In this study, we employ a DNA origami nanofork as a plasmonic nanoantenna to investigate the dimerization process of 4-nitrothiphenol (NTP) to 4-4’-Dimercaptoazobenzene (DMAB) and also study hot spots dynamics with a heteromeric dimer with unlabeled and labeled 2-nitro-5-thiobenzoate (TNB). The dimerization reaction as well as the hot spot dynamic were monitored using surface-enhanced Raman spectroscopy (SERS). Figure 1 (a-c) illustrates the dimerization of NTP to DMAB on 60 nm silver nanoparticles (AgNp). Specifically, Figure 1a provides a schematic representation of the process, while Figure 1b presents the SERS spectrum of NTP on 60 nm AgNP. The corresponding time series data is shown in Figure 1c. Specific bands for DMAB where found at 1136 cm^{-1}, 1394 cm^{-1} and at 1445 cm^{-1}(grey shaded). However, these changes were transient in nature, which leads us to believe that molecular fluctuations occur at the surface and within the hotspot. To investigate molecular fluctuations in the hotspot, we created heterodimers using unlabeled TNB and ^{15}N-labeled TNB functionalized 60 nm gold nanoparticles (AuNP) dimers, as shown in Figure 1d. These heterodimers exhibited characteristic vibrations for both components and demonstrated peak fluctuations in the SERS spectra (Figure 1e).

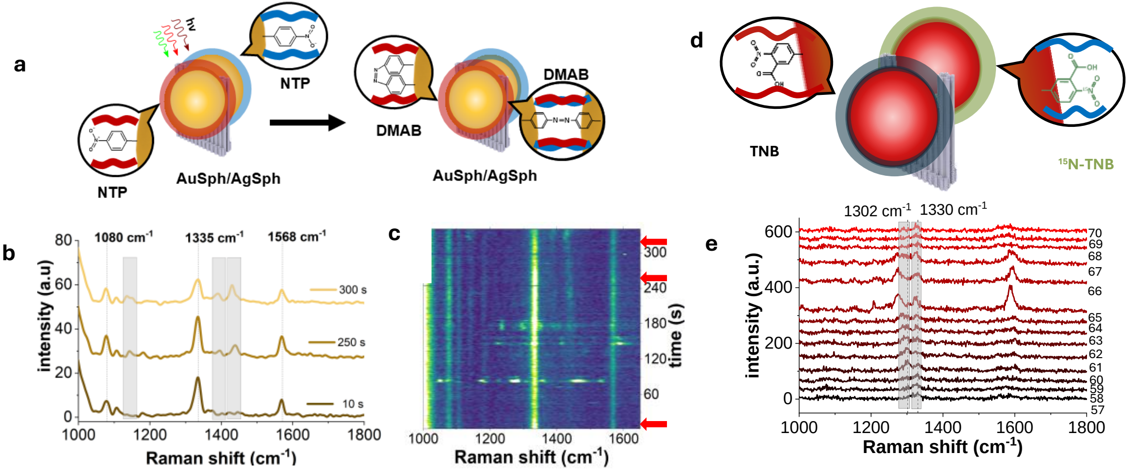

Figure 2.a: schematic process of NTP dimerization of NTP to DMAB on AgNp/AuNp; b-c SERS spectra and corresponding time series of NTP on 60 nm AgNp; d: hetero dimer with unlabeled TNB and ^{15}N labeled TNB; e: SERS time series of hetero Dimer.

Investigating the incorporation of halogens into DNA: Effects on electron-induced strand breakage using DNA Origami

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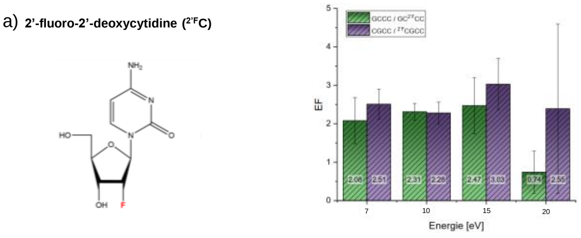
The halogenation of DNA enhances its response to radiation through dissociative electron attachment (DEA) reactions with secondary low-energy electrons, resulting in DNA lesions like single- and double-strand breaks, and crosslinking.[1] Using DNA origami nanotechnology and atomic force microscopy (AFM) analysis[2], we have quantified the effect of incorporating two different halogenated nucleosides, 2'-fluoro-2'-deoxycytidine ($^{2'F}$C) and 5-iodo-4-thio-2-deoxyuridine (ISdU), on electron-induced DNA single-strand breaks at energies of 0.5, 7 and 20 eV.

As shown in figure 1a, the determined enhancement factor (EF) related to the fluorination of DNA at the sugar moiety due to the incorporation of $^{2'F}$C exhibits a clear dependence on both energy and sequence. At 20 eV, the strand break cross section for the strand 5'-2´FCGCC is more than double of that of the DNA strand 5'- GC$^{2'F}$CC, suggesting that ionization processes start contributing to the observed strand-break cross section. Regarding the incorporation of ISdU into DNA, substituing one adenine (A) by ISdU exhibits a clear sensitizing effect, as shown in Figure 1b. At 7 eV, the determined EF is 1.3, while at 0.5 eV there is no indication of enhancement. Our observations are in contrast with the DEA gas-phase study with ISdU[3], reporting dominant anionic fragmentation features at ~ 0 eV, and weaker ion yields up to 5 eV.


a) 2'-fluoro-2'-deoxycytidine ($^{2'F}$C)

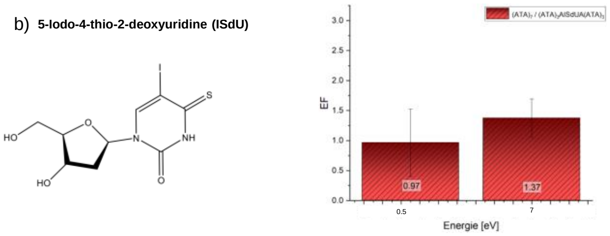

b) 5-Iodo-4-thio-2-deoxyuridine (ISdU)

Figure 3. Panel a: Enhancement factor (EF) at different electron energies – green: GCCC/GC$^{2'F}$CC, purple: CGCC/$^{2'F}$CGCC. Panel b: Enhancement factors (EF) due to ISdU incorporation at the electron energies 0.5 and 7 eV – $(ATA)_7/(ATA)_3AISdU(ATA)_3$.

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Dissociative electron attachment and dissociative ionisation of the potential FEBID precursor $CF_3AuCNC(CH_3)_3$ under single collision conditions and at elevated pressures

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In the attempt to better understand the fundamental fragmentation processes induced by secondary electrons in focused electron beam induced deposition (FEBID), a significant number of gas phase studies on electron induce decomposition of FEBID precursor molecules has been conducted in the past (see e.g. refs[1][2][3] and refs therein). These experiments have mainly been conducted under single collision condition where no energy dissipation is provided, while electron induced deposition takes place at surfaces providing an efficient energy sink. Furthermore, in FEBID the current density is comparatively high and, depending on the deposition rate, secondary and even tertiary electrons-induced reactions of the initially immobilized fragments may be expected.

In the current contribution we present a gas phase dissociative electron attachment and dissociative ionization study of the potential Au(I) FEBID precursor $CF_3AuCNC(CH_3)_3$[4] conducted in a crossed beam experiment under single collision conditions and with direct insertion probe mass spectrometry (DIP MS), where collisional stabilisation is provided. Both dissociative ionization (DI) and dissociative electron attachment (DEA) is studied, and discussed in relation to the underlying reactions, in context to the potential influence of collisional stabilisation, and in context to the deposit compositions found in previous electron induced deposition experiments with this compound.

While there is significant difference between the relative fragment intensities observed in DI under single collision conditions as compared to these observed in DIP MS, under collisional stabilisation, only one and the same channel is observed in DEA with or without collisional stabilisation. We do not find direct correlation of the DI or DEA channels observed in the gas phase with the composition of deposits formed in the electron induced deposition process. Rather, we expect the initial fragmentation processes as observed in the gas phase to determine the first step deposition of immobilized fragments, while the final composition of the deposits is determined by electron induced secondary and tertiary reactions in the immobilised fragments up on further irradiation.

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Dissociative electron attachment, dissociative ionisation and focused electron beam induced deposition of the potential Au(I) precursors $(CH_3)AuP(CH_3)_3$ and $[(CH_3)_2AuCl]_2$

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Due to their distinct dielectric properties and biocompatibility, gold nanostructures have high potential for fabrication of functional nanodevices. Specifically, gold has high potential in the fabrication of plasmonic devices. In such devices, however, the purity, shape and particle distribution is critical. Focused Electron Beam Induced Deposition (FEBID) is a direct writing method that suitable for precision fabrication of nanostructures of as good as any shape, and equally on flat and non-flat surfaces. However, to date no practically applicable FEBID precursors for gold deposition are available that allow for fabrication of high purity gold nanostructures. Accordingly, the design of high performance FEBID gold precursor molecules is highly desirable in this field.

In the current contribution we present a collaborative evaluation of the compounds $(CH_3)AuP(CH_3)_3$[1], and $[(CH_3)_2AuCl]_2$[2].. Specifically, we evaluate the fundamental electron induced dissociation processes of these potential Au(I) precursors, and how these are reflected in the composition and morphology of the respective deposits formed in FEBID. Dissociative ionization and dissociative electron attachment were studied under single collision conditions in the gas phase and quantum chemical threshold calculations were used to aid the interpretation of the observed fragmentation pathways. These are then compared with the composition of deposits that were fabricated with FEBID in an UHV chamber on different surfaces and at different beam currents.

Depending on the conditions, 31-34 and, 45-61 at. % Au was achieved in the deposits formed with $(CH_3)AuP(CH_3)_3$ and $[(CH_3)_2AuCl]_2$ respectively. In both cases this correlates well with the gold content that would be expected if the unaltered DI processes, as they are observed in the gas phase under single collision conditions, were responsible for the deposit composition observed in FEBID. However, with respect to the remaining ligand elements, the deposit compositions differ significantly from what would be expected from the gas phase experiments – an observation that we attribute to electron induced secondary and tertiary reactions with immobilized fragments generated in the initial fragmentation process.

-This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722149.

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Electron collision with molecular hydrogen

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Electron collision with molecular hydrogen is the most extensively studied process, particularly in low-energy regimes. However, there have been many ununderstood issues with various findings. For example, what is the nature of the resonance contributing to DEA at 10 eV? The dissociative electron attachment (DEA) at 10 eV and 14 eV shows a distinct vibrational structure in the cross-section, indicating contribution from the bound anion state via predissociation. Although the nature of the bound state contributing to the 10 eV peak is well understood, there is an ambiguity in the nature of such a bound state contributing at 14 eV. Why are these features absent in D_2, a heavier isotopologue? What is the effect of the permanent electric dipole moment of HD, a heteronuclear isotopologue, on the electron attachment process, and how does it manifest in subsequent dynamics? How does the isotope effect manifest in the dipolar dissociation?

Moreover, we have unravelled many hitherto unseen features in recent measurements, like quantum coherence in the DEA dynamics via the formation of coherent superposition of multiple resonances[1]. We have found that these features are far more prevalent in inelastic collisions and show up in non-resonant interactions, like dipolar dissociation[2]. How do these features change for the homonuclear and heteronuclear isotopologues?

With a series of experiments, we have answered many of these questions[3, 4, 5]. We will present these findings and their analysis in this poster.

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