CHIMIA 2021, Volume 75
ISSN 0009-4293
www.chimia.ch
Supplementa to Issue 7-8/2021

SCS
Swiss Chemical
Society

SCS Fall Meeting 2021 (online conference)
Lecture, Short Talk and Poster Abstracts

Session of Physical Chemistry

September 10, 2021
University of Bern (online conference)
https://fm21.scg.ch

Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

How to Assess Reduced-Risk Products Faster Using a Chemical Reactivity-Directed Non-Targeted Screening Approach

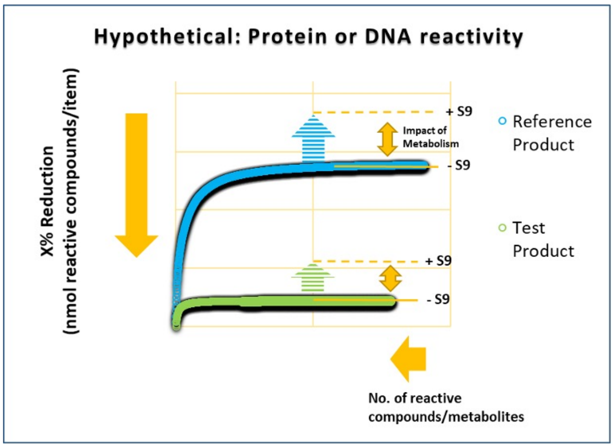
H. Andrade[1,2], A. Knorr[1,3], J. Sabaratnam[1], S. Sendyk[1], C. Goujon Ginglinger[1]

[1]PMI R&D, Philip Morris Products S.A., Quai Jeanrenaud 5, CH-2000 Neuchâtel, Switzerland, [2] Helena.andrade@pmi.com, [3]Arno.knorr@pmi.com

Cigarette smoke is a complex matrix with more than 6000 constituents, and some are harmful and potentially harmful constituents (HPHC). Aerosols of the new reduced-risk products (RRP) developed at Philip Morris International (PMI) have different profiles, which have been already comprehensively characterized [1]. As portfolio extension of RRP is foreseen, methodologies aiming at quickly assessing their risk should be considered. The chemical reactivity-directed non-targeted screening (ChemReact-NTS) approach aims at supporting and speeding up decisions on these processes in the RRP development pipeline. This novel workflow simplifies the comprehensive non-targeted screening (NTS) process for toxicologically relevant compounds by addressing their chemical reactivity towards relevant biological macromolecules such as proteins and DNA.

The underlying mechanism of our approach focuses on the potential of HPHCs (or their metabolites) to react with essential biomolecules and generate adducts — an accepted rationale for initiation of toxicity. Adducts are then identified and semi-quantified in chemico by liquid chromatography coupled to high-resolution accurate-mass spectrometry (LC–HRAM-MS) [2, 3]. Further, ChemReact-NTS addresses potential adduct formation with or without metabolic activation of HPHCs [4].

The ChemReact-NTS workflow will be used to rapidly prescreen the overall effects of accumulation of adduct signals in terms of adduct numbers and represented mass. Later, detailed information on the identity of the reactive chemicals and their relevance can be derived by ranking the reactive chemicals on the basis of their represented levels at a given time (or adduct formation rates). Assuming the proposed methodology proves to be relevant and suitable, the information collected will be used to generate product-specific HPHC lists and to refine and update our risk assessment strategy. This effort will materialize by assay design in the context of safety and toxicity assessment using data that will generate relevant information.



[1] M. C. Bentley, M. Almstetter, D. Arndt, A. Knorr, E. Martin, P. Pospisil, S. Maeder, *Anal Bioanal Chem*, **2020**, *412(11)*, 2675-85.
[2] M. E. Andersen, H. J. Clewell, P. L. Carmichael, K. Boekelheide, *ALTEX*, **2011**, *28 (3)*, 175-82.
[3] S. J. Enoch, M. T. Cronin, *Crit Rev Toxicol*, **2010**, *40 (8)*, 728-48.
[4] J. Ashby, R. W. Tennant, *Mutant Res*, **1988**, *204 (1)*, 17-115.

Red-emitting fluorophores as nanoscopic water sensors

J. Maillard[1,2], A. Fürstenberg[2,1]*

[1]University of Geneva, Department of Physical Chemistry, [2]University of Geneva, Department of Inorganic and Analytical Chemistry

Fluorescence microscopy and spectroscopy are nowadays standard tools to address biological questions. Small organic fluorescent probes are frequently chemically linked to biomolecules of interest to enable their detection in an aqueous environment. Although many fluorophores approved for biological applications are rather insensitive to their environment, i.e they display little solvatochromism and small Stokes shifts, water is nonetheless known to quench their emission. The fluorescence may efficiently be restored in D_2O, which leads to a better contrast and an improved localization precision in single-molecule based super-resolution imaging experiments [1, 2].

In this contribution, we explore the quenching of 40 organic fluorophores by water and alcohols and explain why solvent-assisted quenching is stronger for red-emitting fluorophores. The efficiency of the quenching can indeed be related to the spectral overlap between the emission of fluorophores with the absorption of water in the 700-800 nm region originating from overtone and combination bands of the vibrational modes of OH groups, thus enabling through-space resonant energy transfer [3]. Inspired by those observations, we further selected a handful of red-emitting fluorophores to explore the sensitivity of their fluorescence properties to water more quantitatively. We demonstrate that oxazine fluorophores are particularly well suited to act as nanoscopic water sensors both in homogeneous solvent mixtures and in complex environments such as in reverse micelles, in host-guest complexes, and on protein surfaces [4]. We directly relate the fluorescence lifetime of the probe to the average quantity of water in contact with the fluorophore by defining a residual quenching fraction, which brings us one step closer to our goal of using red-emitting fluorophores to count water molecules.

[1] S. F. Lee, Q. Vérolet, A. Fürstenberg, *Angew. Chem. Int. Ed.* **2013**, *52*, 8948-8951.
[2] K. Klehs, C. Spahn, U. Endesfelder, S. F. Lee, A. Fürstenberg, M. Heilemann,*ChemPhysChem* **2014**, *15*, 637-641.
[3] J. Maillard, K. Klehs, C. Rumble, E. Vauthey, M. Heilemann, A. Fürstenberg, *Chem. Sci.* **2021**, *12*, 1352–1362.
[4] J. Maillard, C. Rumble, A. Fürstenberg, submitted.

Ion-dipole and ion-quadrupole interaction effects in ion-molecule reactions at collisional energies E_{coll} between 0 and $40 \cdot k_B$ K.

V. Zhelyazkova[1], F. B. V. Martins[1], J. A. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]ETH Zürich, Laboratory of Physical Chemistry

Many ion-molecule reactions are barrierless, exothermic reactions which proceed with high rate coefficients even at zero temperatures and are important for the synthesis of molecules in the interstellar medium [1]. These reactions are usually modelled by the classical Langevin model which predicts a temperature- and collisional-energy-independent reaction capture rate coefficients. However, at low collision energies, significant deviations from the Langevin rate coefficients arise resulting from the electrostatic interaction between the charge of the ion and the electric dipole [2-3] and quadrupole [4-5] moments of the neutral molecule.

We present experimental and theoretical studies of ion-molecule reactions involving He^+ and simple neutral molecules. These reactions are studied within the orbit of a Rydberg electron in a merged Rydberg-neutral beams set-up as described in Refs.[2,4,6]. The helium atoms are excited to a low-field-seeking Rydberg-Stark state, and deflected and merged with a supersonic beam of the neutral molecule using a curved surface-electrode Rydberg-Stark decelerator [2]. We monitor the product-ion yield in a time-of-flight mass spectrometer as a function of the Rydberg helium velocity.

The measured total product yields, *I*, display a significant dependence on the collisional energy, E_{coll}, when the molecule has a permanent dipole or quadrupole moments. With decreasing $E_{\text{coll below } 10 \cdot kB\ K}$, we observe (i) a significant increase of *I* in the case of a molecule with a permanent dipole moment (e.g., NH_3, ND_3 and CH_3F), and (ii) a pronounced suppression of *I* in the case of a molecule with a negative Q_{zz} component of the quadrupole moment (e.g., N_2 and CO). We calculate the reaction rate coefficients using a capture model that includes the rotational-state-dependent energy shift of the molecule in the electric field of the He^+ ion and average over the rotational state population distribution in the supersonic source, including nuclear-spin statistics effects. The agreement between the experimental data and the model is very good for a number of molecules: CH_3F [2], NH_3, ND_3, N_2 and CO. The observed significant deviation from the Langevin model is attributed to the locking of the molecular angular momentum at low collisional energies [3].

[1] D. Smith, *Chem. Rev.,* **1992**, 92, 1473.

[2] V. Zhelyazkova, F. B. V. Martins, J. A. Agner, H. Schmutz and F. Merkt, *Phys. Rev. Lett.*, **2020**, 125, 263401.

[3] J. Troe, *Chem. Phys.*, **1987**, 87, 2773.

[4] P. Allmendinger, J. Deiglmayr, K. Höveler, O. Schullian and F. Merkt, *J. Chem. Phys.*, **2016**, 145, 244316.

[5] E. I. Dashevskaya, I. Litvin, E. E. Nikitin and J. Troe, *J. Chem.Phys.*, **2005**, 122, 184311.

[6] K. Höveler, J. Deiglmayr, J. A. Agner, H. Schmutz and F. Merkt, *Phys. Chem. Chem. Phys.*, **2021**, 23, 2676–2683.

Time dependent dynamics of nuclear spin symmetry and parity violation in dichlorodisulfane (ClSSCl) during and after coherent radiative excitation

G. Wichmann[1], G. Seyfang[1], M. Quack[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland

Parity and nuclear spin symmetry are approximate symmetries, which for many primary processes in molecular spectroscopy and kinetics lead to almost exact constants of the motion [1-3]. The violation of these symmetries leads to very slow primary processes such as the time dependence of parity or nuclear spin symmetry, which can be observed, in principle, by the generation of exotic quantum superposition states for instance of two different enantiomers [4], which would also provide access to the measurement of the parity violating energy difference $\Delta_{pv}E$ between the ground states of the enantiomers, predicted to be very small in the sub-eV range, but not yet confirmed experimentally (refs. [1-5] and references cited therein). ClSSCl is chiral and has been investigated in this context predicting a $\Delta_{pv}E$ of about 0.17 feV [6], making it suitable for such experiments.

The symmetric isotopomer $^{35}Cl^{32}S^{32}S^{35}Cl$ is chiral with two enantiomers, each of which has also two nuclear spin isomers (ortho and para). Recent microwave spectroscopy has indicated ‘forbidden’ microwave transition between these nuclear spin isomers [7]. ClSSCl is thus a unique example to study the two time dependent processes of nuclear spin symmetry and parity violation for the first time ever. We report quantum dynamical simulations demonstrating these phenomena in detail. We shall also discuss the general concept of preparing a quantum system in an exotic superposition ’chameleon state’ with a time dependent spectrum but constant energy eigenstate populations [1].

[1] M. Quack, G. Seyfang, G.Wichmann, *Adv. Quant. Chem.,* **2020,** 81, 51-104.
[2] M. Quack, Fundamental Symmetries and Symmetry Violations from High Resolution Spectroscopy, chapter 18 in ‚Handbook of High-Resolution Spectroscopy‘, Vol. 1, pages 659- 722, M. Quack, and F.
Merkt, Eds., Wiley Chichester, **2011**, ISBN-13: 978-0-470-06653-9.
[3] R. Marquardt and M. Quack Eds. Molecular Spectroscopy and Quantum Dynamics, Elsevier, Amsterdam, **2020**, **ISBN:** 9780128172346
[4] M. Quack, *Chem. Phys. Letters.,* **1986**, 132, 147.
[5] M. Quack and G. Seyfang, Tunnelling and Parity Violation in Chiral and Achiral Molecules: Theory and High-resolution Spectroscopy, chapter 6 in ‚Tunnelling in Molecules: Nuclear Quantum Effects from Bio to Physical Chemistry‘, J. Kästner, and S. Kozuch Eds. The Royal Society of Chemistry, Cambridge, **2021**, pages 192-244, ISBN: 978-1-78801-870-8
[6] R. Berger, M. Gottselig, M. Quack and M. Willeke, *Angew. Chem. Int. Ed.*, **2001**, 40, 4195–4198.
[7] H. Kanamori, Z.T. Dehghani, A. Mizoguchi and Y. Endo, *Phys. Rev. Lett.*, **2017**, 119, 173401-1 -173401.-5.

Understanding water dissociation on O-Cu(111)

H. Vejayan[1,2], R. D. Beck[1]*

[1]Institute of Chemical Sciences and Engineering (ISIC) École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland, [2]Harmina.vejayan@epfl.ch

Dissociative adsorption of water is the rate-limiting step in the water-gas shift (WGS) reaction

$$H_2O + CO \rightarrow H_2 + CO_2$$

which is used for large-scale production of hydrogen for fuel cells, ammonia production and methanol synthesis. Due to its industrial importance, the detailed study of this reaction is crucial for optimising the catalytic conditions. Many experimental studies and theoretical predictions have been made for this reaction on different transition metal surfaces.

Here, I will focus on water dissociation on a flat Cu(111) surface, a surface which is well-known for low reactivity for water dissociation due its high activation barrier of 1.17 eV [1]. Although a clean Cu(111) surface is not reactive towards water dissociation, adsorbates such as O reduces the activation barrier to 0.76 eV, hence making the surface much more reactive to the dissociative chemisorption of water [2]. Recently, Zhou et al. showed experimentally that water dissociation on the Cu(111) is enhanced when the surface is covered with O(ads) [3]. They also claimed that the oxygen on the surface reacts with the incoming gaseous water molecule to produce 2OH chemisorbed on the surface,

$$H_2O(g) + O(ads) \rightarrow 2OH(ads).$$

This conclusion was based on their X-ray photoelectron spectroscopy where they observed a change in the binding energy of the O(ads) when water is deposited on the surface, from 530 eV to 530.9 eV [3].

Interestingly, using Reflection Absorption Infrared Spectroscopy (RAIRS), I found contradicting evidence for the O(ads) consumption during water dissociation. In my talk, I will present a RAIRS study of water dissociation using isotopic substitution to elucidate the mechanism of water dissociation on O-Cu(111).

[1] C. T. Campbell and K. A. Daube, *J. Catal*, **1987**, *104*, 109-119.
[2] G. C. Wang, S. X. Tau and X. H. Bu, *J. Catal*, **2006**, *244*, 10-16.
[3] Q. Liu, J. Li, X. Tong and G. Zhou, *J. Phys. Chem. C*, **2017**, 22, 12117-12126.

Observation of optical confinement effects on the reduction of iron in individual aerosol particles

P. Corral Arroyo[1], G. David[1], P. A. Alpert[2], E. A. Parmentier[1], M. Ammann[2], R. Signorell[1]*

[1]Laboratory of Physical Chemistry, Department of Chemistry and and Applied Biosciences, ETH Zurich, [2]Laboratory of Environmental Chemistry, Energy and Environment Research Division, Paul Scherrer Institute

Atmospheric aerosol particles contain a wide variety of chromophores that, by absorbing solar radiation, trigger physical and chemical transformations and contribute to the heating of the atmosphere. Optical confinement effects within particles can lead to enhancement of the overall light intensity and to structuring of the internal optical fields[1], which influence atmospheric photochemistry and radiative forcing.

Here, we study the influence of optical confinement effects on the photolysis of iron (III) citrate (FeCit) in individual particles. FeCit is a chromophore that is photolyzed by UV light, resulting in the reduction of Fe (III) to Fe (II). Experiments were performed at the PolLux beamline of the Swiss Light Source by means of scanning transmission x-ray microscopy coupled to near edge x-ray absorption fine structure spectroscopy (STXM/NEXAFS). Particles containing FeCit were generated, dried, size selected (640 nm in diameter), and deposited on x-ray transparent silicon nitride windows. Samples were placed in the PolLux end station and they were illuminated in vacuo by a monochromatic UV light source (367.7 nm) located orthogonal to the X-ray beam. Composition maps of individual particles were recorded at the iron L-edge (from 700 to 720 eV) with an image resolution of 25x25 nm. Maps of the iron oxidation state were retrieved using the parameterization described in Moffet et al.[2] The Fe (III) / Fe (II) maps show inhomogeneous photochemically-generated patterns within individual particles. To analyse the experimental data, we have constructed a 3D particle model that combines light intensity simulations with DDA (discrete dipole approximation) with a photochemical model. Good agreement with the STXM/NEXAFS experimental results was found.

To obtain a better picture of the influence of optical confinement effects in the atmosphere, we simulated the overall amplification of the Earth actinic radiation for a range of particles with typical sizes and compositions of aerosol particles in the atmosphere. On average, the light intensity inside such particles is enhanced by a factor of about 3, which implies an overall non-negligible acceleration of photochemical reactions in atmospheric particles. This acceleration of photochemical reactions might be more important than previously anticipated and should thus be considered in atmospheric aerosol and cloud models.

[1] Johannes W. Cremer, Klemens M. Thaler, Christoph Haisch, Ruth Signorell, *Nat. Commun.*, **2016**, 7, 10941

[2] Ryan C. Moffet, Hiroshi Furutani, Tobias C. Rödel, Tobias R. Henn, Peter O. Sprau, Alexander Laskin, Mitsuo Uematsu, Mary K. Gilles, *J. Geophys. Res.*, **2012**, 117, D07204

Spin-labeled nanobodies as conformation reporters of membrane proteins in cells

E. Bordignon[1,2], L. Galazzo[2], G. Meier[3], D. Januliene[4], A. Moeller[4], M. A. Seeger[3]

[1]Department of Physical Chemistry, University of Geneva, Switzerland, [2]Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Germany, [3]Institute of Medical Microbiology, University of Zurich, Switzerland, [4]Department of Structural Biology, Osnabrück University, Germany

The biochemical and structural characterization of membrane proteins requires extraction from their native membranes with detergents, often followed by reconstitution into liposomes or nanodiscs to mimic the lipid bilayer. However, to fully understand the biophysical properties of membrane proteins, they should be ideally investigated within living cells. Site-directed spin labeling Electron Paramagnetic Resonance (EPR) spectroscopy is one of the techniques developing tools for in cell applications. Yet, it is limited in terms of sensitivity and fidelity when it comes to membrane proteins in vivo due to the lack of methods to introduce spectroscopic labels at specific positions inside the cell. Here, we generated a spin-labeled nanobody as structural probe to interrogate the conformational cycle of the ABC transporter MsbA in vitro and in cell by Double Electron Electron Resonance (DEER). Surprisingly, in metabolically active cells we identified a wide inward-open conformation of MsbA, which is commonly considered a non-physiological state. A comparative DEER and cryo-EM analysis shed light on the funneling towards a narrow inward-open conformation of MsbA induced by nanodisc reconstitution. This study paves the way towards the use of spin-labeled nanobodies for in-cell EPR applications on membrane proteins[1,2].

[1] L. Galazzo, G. Meier, M.H. Timachi, C.A.J. Hutter, M.A. Seeger, E. Bordignon *PNAS*, **2020**, 117(5):2441-2448.
[2] L. Galazzo, G. Meier et al. in preparation

Molecular light-upconversion: when excited state absorption (ESA) overcomes energy transfer upconversion (ETU) in Cr(III)/Er(III) complexes

I. Taarit[1], B. Golesorkhi[1], C. Piguet[1]*

[1]Université de Genève, Department of Inorganic and Analytical Chemistry

For a long period, metal-based linear light-upconversion, that is the conversion of near-infrared (NIR) light into emitted visible light by successive linear absorption of NIR photons, was limited to the statistical doping of low phonon bulk solids and garnets. The design of closely related upconversion processes operating in nanoparticles allowed to reach the nanoscale.[1] The next miniaturizing step aims at inducing linear light upconversion at the molecular level, which opens challenging perspectives in terms of improved reproducibility, chemical control and optical programming. Achieving this goal requires either the piling up of low-energy near-infrared photons onto a single short-lived lanthanide center via excited state absorption (ESA), or the implementation of the alternative energy transfer upconversion (ETU) mechanism, which combines a short-lived lanthanide activator surrounded with long-lived sensitizers.[2] However, only a very few numbers of sophisticated multicenter devices which exploit the indirect ETU mechanism have been evidenced in molecular complexes and the ESA mechanism in isolated coordination complexes is essentially unknown for isolated coordination complexes except under massive incident excitation powers. The judicious wrapping of three polyaromatic ligand strands around trivalent erbium,[3] in $[\mathrm{Er}(\mathbf{Lk})_3]^{3+}$$[\mathrm{GaErGa}(\mathbf{L1})_3]^{9+}$ or $[\mathrm{CrErCr}(\mathbf{L1})_3]^{9+}$ indeed brought a small revolution with the demonstration that low-power room temperature near-infrared to green light upconversion can be programmed in mononuclear coordination complexes.

In this contribution, the erbium-centered downshifted emission and opposite NIR to visible upconversion and their quantifying in molecular complexes will be discussed as well as their mechanisms. The associated quantum yields measured for ESA appear to be 1–3 orders of magnitude larger than those predicted by the accepted mechanism. An even larger discrepancy by 4–6 orders of magnitude occurs between theoretical models and experimental data for ETU.[4] An unexpected boosted ESA process is proposed for reconciling predictions and measurements.

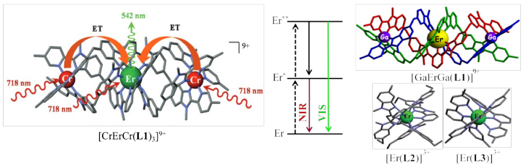


Figure 1. Erbium-based coordination complexes exhibiting linear upconversion processes and associated kinetic model for the single- ion ESA process.

[1] Jing Zhou, Qian Liu, Wei Feng, Yun Sun, Fuyou Li, *Chem. Rev,* **2015**, 115, 395-465.
[2] Yan Suffren, Davood Zare, Svetlana V. Eliseeva, Laure Guénée, Homayoun Nozary, Timothée Lathion, Lilit Aboshyan-Sorgho, Stéphane Petoud, Claude Piguet, *J. Phys. Chem. C,* **2013**, 117, 26957-26963.
[3] Bahman Golesorkhi, Alexandre Fürstenberg, Homayoun Nozary, Claude Piguet, *Chem. Sci,* **2019**, 10, 6876-6685.
[4] Bahman Golesorkhi, Inès Taarit, Hélène Bolvin, Homayoun Nozary, Juan-Ramón Jiménez, Céline Besnard, Laure Guénée, Alexandre Fürstenberg, Claude Piguet, *Dalton Trans*, **2021**, Advance Article.

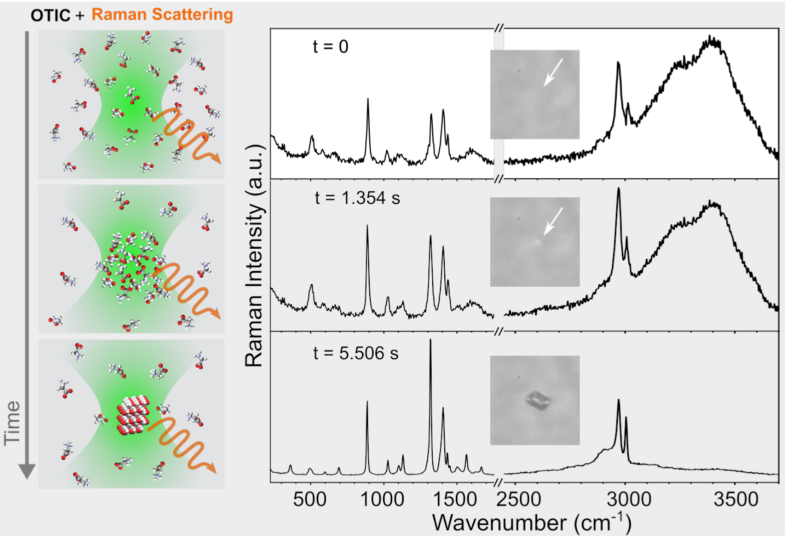
Optical spectroscopy of crystal nucleation one nucleus at a time

O. Urquidi[1], J. Brazard[1], N. LeMessurier[2], L. Simine[2], T. Adachi[1]

[1]Department of Physical Chemistry, Sciences II, University of Geneva, 30, Quai Ernest Ansermet, 1211 Geneva, Switzerland, [2]Department of Chemistry, McGill University, 801 Sherbrooke Street W, Montreal, Quebec H3A 0B8, Canada

Crystallization is an important process in many science and industry disciplines. Despite decades of dedicated research, the fundamental understanding of crystal nucleation at the molecular level is yet to be established. Recent studies agree that the process of crystal nucleation is more complex than what is described by the classical nucleation theory. *In-situ* optical spectroscopy has the potential to gather complex information from nucleation dynamics. The stochastic and heterogenous nature of crystal nucleation, however, has limited its application in the past. While not yet applied in this field, *single molecule spectroscopy* is a powerful and well-established concept to tackle the study of stochastic, complex, and heterogeneous systems. If the location of nucleation is precisely predicted, optical spectroscopy can be used with its full potential by probing *single* nucleation events at a time.

In this work, we present the development of Single Nucleus Spectroscopy (SNS), aimed to perform *in-situ* optical spectroscopy on crystal nucleation. SNS is based on a novel combination of Raman micro-spectroscopy and optical trapping induced crystallization (OTIC). OTIC was first demonstrated by Sugiyama *et al.* in 2007 by focusing a near infrared (NIR) laser in a supersaturated glycine/D_2O solution. In our approach, we apply OTIC to spatially control a single nucleation event at the focused laser spot, while simultaneously measuring the Raman spectral evolution. We achieved the measurement of the Raman spectral evolution of a *single* glycine crystal formation, in aqueous solution and at room temperature, with a time resolution of 46ms. Measurements of Raman spectral evolution during single nucleation events, analyzed by a non-supervised spectral decomposition technique, showed that the nucleation occurs in a non-classical mechanism and led us to uncover the Raman spectrum of pre-nucleation aggregates. The agreement between the simulated and experimentally extracted spectra of pre-nucleation aggregates, allowed us to assign loosely-bound linear chains of glycine, as likely precursors of crystal formation. These results not only provide us more details about the early stages of glycine nucleation, but they also highlight the power of SNS as a platform to study crystallization problems by means of optical spectroscopy.



First *in situ* THz measurements on organic electrochemical transistors: New perspectives from the microscale

G. Rebetez[1], O. Bardagot[1], J. Réhault[1], N. Banerji[2]*

[1]University Bern, [2]Department of Chemistry, University of Bern

Organic electrochemical transistors (OECTs) are highly sensitive sensors used in increasingly challenging biologic applications such as wearable textiles with integrated biosensors and *in vivo* recording of brain activity.[1,2] They can be described as an ionic circuit embedded with an electronic circuit. Upon a voltage bias, ions penetrate and modifiy the doping level of the organic channel thereby changing its conductivity at both macro- and micro-scales.

One of today's challenge to further develop this promising technology lies in the fundamental understanding of the interplay between doping level and conductivity. [3] Previous investigations have been addressing this question *via* macroscopic approaches which are inherently sensible to devices geometries and morphological features. [3-4] In this work, we propose an innovative *in situ* bottom-up approach that correlates the channel doping level (neutral, polaron and bipolaron populations) with its microscopic conductivity (hundred of nanometers).

We use UV-vis-NIR absorption spectroelectrochemistry combined with a multivariance curve resolution (MCR) analysis [4] to extract neutral, polaron and bipolaron populations. The microscopic conductivity is probed *via in situ* THz spectroscopy [5], which represents the first measurement of this kind on OECTs. Overall, this new versatile approach provides two promising perspectives:

1. Disentangle underlying mechanisms limiting long-range charge transport such as device geometries and morphological features
2. Accessing fondamental properties to push further microscale modelling

Results on the archetypal PEDOT:PSS-based OECTs will be discussed along with the promising perspectives of this new approach on the development of OECTs in general.

[1] I. Gualandi, M. Marzocchi, A. Achilli *et al., Sci Rep,* **2016**, 6, 33637.

[2] D. Khodagholy, T. Doublet, P. Quilichini *et al., Nat Commun,* **2013**, 4, 1575.

[3] R. Colucci, H. F. de Paula Barbosa, F. Günther et al., *Flexible and Printed Electronics*, **2020**, 5, 013001

[4] J. Rivnay, S. Inal, A. Salleo *et al.*, *Nat Rev Mater,* **2018**, 3, 17086

[5] A dę Juan, J. Jaumot, R. Tauler, Anal. *Methodes*, **2014**, 6, 4964-4976

[6] T. Unuma, N. Yamada, A. Nakamura *et al., Appl Phys Lett, **2013**,* 103, 053303

Ultrafast process(es) in strongly confined perovskite nanocrystals

E. Socie[1,2], J. Moser[1,2]*

[1]Photochemical Dynamics Group, Institute of Chemical Sciences & Engineering, [2]Lausanne Centre for Ultrafast Science (LACUS)

Lead halide perovskite nanocrystals (NCs) are of great promise for light-emitting devices owing to their high photoluminescence (PL) quantum yields. However, due to the instability of chloride compounds, perovskite devices have limited performances in the blue spectral range. To overcome this issue, some group focused their attention on strongly confined NC systems, such as nanoplatelets (NPls). Due to the quantum confinement of the perovskite structure, NPls exhibit different photophysical behaviors than traditional perovskite NCs. Notably, the charge carrier interactions are enhanced, leading to stable excitons and short fluorescence lifetimes. Nonetheless, because of the increased number of surface trap states, perovskite NPls display PLQY barely up to 50%.[1] Today there is an urge to fully understand the physical and structural limitations of these materials and optimize the NPl-based devices. Here, we combine transient absorption spectroscopy (TAS) and fluorescence upconversion spectroscopy (FLUPS), two ultrafast spectroscopic techniques, to probe the ultrafast exciton and multiexciton dynamics in $CsPbBr_3$ NPls. We first observe spectral signatures of biexciton states with a binding energy of 74 meV.[2] By isolating the biexciton signal, the biexciton lifetime is estimated to 10 ps due to biexciton-Auger recombination. Secondly, we highlight that the band edge exciton dynamics greatly differ from TAS to FLUPS at early timescales.[3] The PL exhibits a fast decay, within a few ps, which does not follow the trend observed by TAS. We propose a simplified model by including shallow trap states lying close to the band edge. The reversible trapping of band edge excitons possibly explains the observed delayed fluorescence in perovskite NCs.

[1] B. J. Bohn, Y. Tong, M. Gramlich, M. L. Lai, M. Döblinger, K. Wang, R. L. Z. Hoye, P. Müller-Buschbaum, S. D. Stranks, A. S. Urban, L. Polavarapu, J. Feldmann, *Nano Lett.,* **2018,** 18, 5231-5238
[2] B. R. C. Vale, E. Socie, A. Burgos-Caminal, J. Bettini, M. A. Schiavon, J.-E. Moser, *J. Phys. Chem. Lett,* **2019**, *11*(2), 387-394.
[3] E. Socie, B. R. C. Vale, A. Burgos-Caminal, J.-E. Moser, *Adv. Opt. Mat.*, **2021**, 9(1), 2001308.

Directed evolution of nanosensors for the detection of mycotoxins

B. P. Lambert[1], A. Taheri[2], S. Wu[1], A. J. Gillen[3], A. A. Boghossian[1]*

[1]Institute of Chemical Sciences and Engineering (ISIC), École Polytechnique Fédérale de Lausanne (EPFL), [2]Department of Food Process Engineering, Faculty of Food Science and Technology, Gorgan University of Agricultural Sciences and Natural Resources, [3]Materials Science Division, Lawrence Livermore National Laboratory (LLNL)

Single-walled carbon nanotubes (SWCNTs) demonstrate distinctive fluorescence properties that have motivated their use as optical sensors. Their fluorescence properties, such as quantum yield and optical responsivity and specificity towards analytes, are controlled by the non-covalent wrapping that is used to solubilize the SWCNTs in aqueous media. Single-stranded DNA is among the most common SWCNT wrappings, whereby sensor properties such as specificity can be modulated by altering the DNA sequence. However, the relationship between the DNA sequence and its effects on the sensors are unknown, hindering the ability to engineer these sensors in a predictive manner. The state-of-the-art for developing these sensors is therefore limited to empirical approaches that yield sensors with sub-optimal performances.

Inspired by strategies in protein engineering, we have developed a bioengineering approach based on directed evolution that allows us to modulate the DNA-SWCNT optoelectronic behavior in a more controlled and directed manner. We apply this approach to develop optical nanosensors for the detection of the mycotoxins aflatoxin and fumonisin, toxic metabolites found in various foodstocks. Through directed evolution, we demonstrate a guided approach to orthogonally tuning the sensor properties, including specificity, sensitivity, brightness, and even chirality-dependent responsivity towards each of these analytes. We further explore the underlying mechanisms of the evolved sensors and demonstrate the use of these sensors in a multi-modal platform that allows us to detect multiple toxins at different wavelengths of light. Bioengineering therefore provides us an unconventional means for overcoming conventional challenges in nanotube optoelectronics.

Mapping Techniques in Nonadiabatic Quantum Dynamics

G. Amati[1], J. O. Richardson[1]*

[1]Laboratory of Physical Chemistry, ETH Zürich

In the poster I introduce my postdoctoral project, involving the development and test of novel mapping approaches to study quantum nonadiabatic dynamics. Recasting hard quantum-mechanical problems onto quasi-classical systems allows us to reduce the complexity of the dynamics, which can be calculated with a favorable scaling with time and system size.

I discuss a novel 'spin-mapping' technique recently developed in our group, suited to the calculation of correlation functions for nonadiabatic systems in thermal equilibrium. The accuracy of our method is assessed by comparing our mapping results with numerically exact benchmarks for a wide range of systems. Also, I analyze how the long-time relaxation of out-of-equilibrium nonadiabatic models can be improved by coupling mapping approaches with the Nakajima-Mori-Zwanzig formalism. Within this framework, I show that a non-Markovian generalized quantum master equation allows to increase the accuracy of mapping predictions, restoring the correct mixing limit of correlation functions at long times.

An outlook on future challenges and perspectives concludes the presentation.

Cold ion chemistry within a Rydberg-electron orbit: Test of the spectator role of the Rydberg electron in the He(n) + CO → C(n') + O + He reaction

F. B. V. Martins[1], V. Zhelyazkova[1], C. Seiler[1], F. Merkt[1]*

[1]ETH Zürich, Laboratory of Physical Chemistry

Ion-molecule reactions are usually challenging to study at low temperatures because ions are heated up by stray fields. To overcome this limitation, we study the ion-molecule reaction within the orbit of a highly excited Rydberg electron, making it possible to reach collision energies as low as ~k_B.100 mK [1-3]. We present experimental studies of the reaction between CO molecules and helium atoms excited to Rydberg-Stark states [He(n)] in a merged-beam apparatus. The supersonic beams of CO and of He(n) with principal quantum number n in the range 27–45 are merged using a surface-electrode deflector [4,5]. The reaction between a Rydberg atom and a molecule is expected to correspond closely to the ion-molecule reaction [6-8]. In the He(n) + CO reaction, long-lived atomic C(n') atoms are formed. This reaction system thus offers the possibility to study n-changing processes taking place before and during the reaction and to test the spectator role of the Rydberg electron.

We study the Rydberg-Stark-state distribution of the He(n) atoms and of the C(n') products experimentally by pulsed-field ionization and theoretically. The integrated signal from pulsed-field ionized He(n) and C(n') recorded with different electric field values is compared to the predicted diabatic ionization for a distribution of Rydberg-Stark states. The He sample initially excited to a specific n state is redistributed among a number of states prior to the reaction via fluorescence and blackbody-radiation-induced transitions during the 85-µs time between excitation and detection. We calculate the rates of these radiative processes and include them in Monte Carlo simulations to model the evolution of the He(n) population and its n-distribution. The agreement between the modeled ionization and the measured ionized He(n) signal confirms that a range of Rydberg-Stark states of He is populated. Discrepancies between experimental and modeled ionization of C(n') can be explained by the different ionization dynamics of C(n'). This finding indicates the validity of the Rydberg-electron-spectator model.

[1] P. Allmendinger, J. Deiglmayr, O. Schullian, K. Höveler, J. A. Agner, H. Schmutz, and F. Merkt, Chem. Phys. Chem., **2016**, 17, 3596.
[2] V. Zhelyazkova, F. B. V. Martins, J. A. Agner, H. Schmutz, and F. Merkt, Phys. Rev. Lett., **2020**, 125, 263401.
[3] K. Höveler, J. Deiglmayr, J. A. Agner, H. Schmutz, and F. Merkt, Phys. Chem. Chem. Phys., **2021**, 23, 2676.
[4] P. Allmendinger, J. Deiglmayr, J. A. Agner, H. Schmutz, and F. Merkt, Phys. Rev. A, **2014**, 90, 043403.
[5] V. Zhelyazkova, M. Žeško, H. Schmutz, J. A. Agner, and F. Merkt, Mol. Phys., **2019**, 117, 2980.
[6] S. T. Pratt, J. L. Dehmer, P. M. Dehmer, and W. A. Chupka, J. Chem. Phys., **1994**, 101, 882.
[7] E. Wrede, L. Schnieder, K. Seekamp-Schnieder, B. Niederjohann, and K. H. Welge, Phys. Chem. Chem. Phys., **2005**, 7, 1577.
[8] M. Matsuzawa, Phys. Rev. A, **2010**, 82, 054701.

Size- and time-resolved electron solvation following below band gap photoexcitation of neutral water clusters

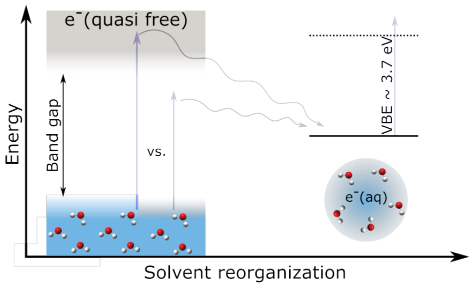
L. Ban[1], C. W. West[1], E. Chasovskikh[1], T. E. Gartmann[1], B. L. Yoder[1], R. Signorell[1]*

[1]Laboratory of Physical Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich

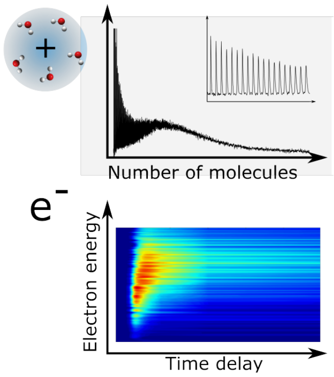
Recent time-resolved photoelectron studies on electron solvation upon direct photoexcitation of water allowed for a direct comparison between neutral water clusters[1,2,3] and water liquid jet[4]. Observed relaxation timescales are essentially independent of the aqueous environment (clusters vs. bulk) and the excitation energy[1]. However, some questions regarding the formation mechanism and dynamics remain open.

In this contribution, we build upon the abovementioned studies and present an experiment to further investigate electron solvation following below band gap excitation. The hydrated electron is formed by photoexcitation of neutral water clusters ($(H_2O)_n$ with n < 200 molecules) with femtosecond laser pulses of 7.8 eV photon energy from high-harmonic generation. The subsequent relaxation dynamics are probed with laser pulses of 4.7 eV by means of pump-probe mass spectrometry. In this way, we obtain time-dependent yields of ions which originate from photoionization of the hydrated electron. From this we infer size-resolved information on hydrated electron formation and relaxation dynamics. Combining these results with the time-dependent photoelectron study[1], we will discuss the current understanding of electron solvation following below band gap excitation of water.

Photoionization of neutral clusters



Photoelectron and ion detection



[1] Loren Ban, *et al.*, *J. Phys. Chem. A*, **2020**, 124, 7959.

[2] Thomas E. Gartmann, Loren Ban, *et al.*, *J. Phys. Chem. Lett.*, **2019**, 10, 4777.

[3] Vit Svoboda, *et al.*, *Sci. Adv.*, **2020**, 6, eaaz0385.

[4] Yo-ichi Yamamoto, T. Suzuki, *J. Phys. Chem. Lett.*, **2020**, 11, 5510.

Super-resolution microscopy with cucurbituril-encapsulated fluorophores.

L. Briant[1,2], A. Fürstenberg[1,2]*

[1]University of Geneva, Department of Inorganic and Analytical Chemistry, [2]University of Geneva, Department of Physical Chemistry

The development of super-resolution microscopy has been one of the most important advances in order to image tissue structure or cellular dynamics below the diffraction limit. In single-molecule localization microscopy, super-resolution is achieved by detecting and localizing individual fluorophores, and the precision with which these can be localized is inversely proportional to the square root of the number of emitted photons: the more photons can be collected from a single fluorophore, the more accurately it can be localized, which is a key requirement for a good resolution. Because of the biological targets, super-resolution experiments are typically performed in aqueous solution. However, water is known to be a fluorescence quencher of organic dyes and the replacement of H_2O by D_2O can drastically increase the fluorescence quantum yield and the localization precision[1-2]. Recently, the quenching of 40 dyes was investigated leading to the conclusion of a FRET mechanism between red-emitting fluorophores and vibrational overtones and combination bands of OH groups of the solvent in direct contact with the dyes[3]. Since fluorophores in biological samples are mostly surrounded by water, one way to prevent quenching from occurring would be to isolate them from the solvent using macrocyclic cavities such as cyclodextrins[4] and cucurbiturils.

The aim of this study was to investigate a possible encapsulation and isolation of common red-emitting dyes from water by cucurbiturils. After a successful synthesis of the macrocyclic hosts, host-guest complexes between cucurbiturils and red-emitting fluorophores were studied using absorption, fluorescence and time-resolved fluorescence spectroscopies leading to the determination of their binding affinities. Furthermore, the suitability of encapsulated fluorophores for single-molecule and super-resolution experiments was successfully evaluated by studying their photophysics at the single-molecule level and by achieving super-resolution imaging on cells in the absence and in the presence of cucurbiturils.

[1] S. F. Lee, Q. Vérolet, and A. Fürstenberg, *Angew. Chem. Int. Ed.* **2013**, 52, 8948-8951.

[2] K. Klehs, C. Spahn, U. Endesfelder, S. F. Lee, A. Fürstenberg, and M. Heilemann, *ChemPhysChem* **2014**, 15, 637-641.

[3] J. Maillard, K. Klehs, C. Rumble, E. Vauthey, M. Heilemann, and A. Fürstenberg, *Chem. Sci.* **2021**, 12, 1352-1362.

[4] J. Maillard, C. Rumble, and A. Fürstenberg, submitted.

Excited-state dynamics of organic molecules at liquid-phospholipid-liquid interfaces

D. S. Budkina[1], J. Sissaoui[1], E. Vauthey[1]*

[1]Physical Chemistry Department, University of Geneva, Geneva, Switzerland

Monolayers of phospholipids at an oil-water interface can be considered as simple models of biological membranes. To better understand the interactions between water-soluble molecules and biological membranes, we investigate the orientation and excited-state dynamics of environment-sensitive dyes at dodecane-phospholipid-water interfaces using polarised as well as time-resolved surface-second-harmonic generation. Results obtained with amphiphilic hemocyanin dyes reveal a strong dependence of the orientation of these dyes at the interface as well as of their excited-state lifetime on the nature of the phospholipids. This information allows drawing a picture at the molecular level of how organic molecules interact with the surface of biological membranes.

Ionization energy of the metastable 2 $^1S_0$ state of ^{4}He from Rydberg-series extrapolation

G. Clausen[1], P. Jansen[1], S. Scheidegger[1], J. A. Agner[1], H. Schmutz[1], F. Merkt[2]*

[1]Laboratory of Physical Chemistry, ETH Zurich, [2]Laboratory of Physical Chemistry

In a very recent breakthrough in first-principles calculations of two-electron systems, Patkóš, Yerokhin and Pachucki (PRA **103**, 042809 (2021)) have performed the first complete calculation of the Lamb shift of the helium 2 $^3S_1$ and 2 ^3P_J triplet states up to the term in α^7m. Whereas their theoretical result of the frequency of the 2 ^{3}P ←2 ^{3}S transition perfectly agrees with the experimental value, a more than 10σ discrepancy was identified for the 3 ^{3}D ← 2 ^{3}S and 3^{3}D ← 2^{3}P transitions, which hinders the determination of the He^{2+} charge radius from atomic spectroscopy that is necessary to complement the recent α-particle charge radius determination using muonic helium (J. Krauth *et al.*, Nature **589**, 527531 (2021)).

We report on the determination of the ionization energy of the metastable 2 $^1S_0$ state of helium (960'332'040.491(32) MHz) by Rydberg-series extrapolation based on the frequencies of 21 transitions from the 2 $^1S_0$ state to *n*p Rydberg states with principal quantum number *n* in the range between 24 and 102, yielding a relative uncertainty of 3×10^{-11}. A one-photon (~312 nm) excitation scheme is used for Rydberg-state excitation of metastable He atoms in a doubly skimmed supersonic beam.

The absolute frequency calibration is achieved using a frequency comb referenced to a GPS-disciplined Rb clock. This absolute measurement is used in combination with the 2 $^3S_1$ ← 2 $^1S_0$ interval measured by van Rooij *et al.* (Science **333**, 196 (2011)) and the 2 ^{3}P ← 2 $^3S_1$ interval measured by Zheng *et al.* (PRL **119**, 263002 (2017)) and Cancio Pastor *et al.* (PRL **92**, 023001 (2004)) to derive experimental ionization energies of the 2 $^3S_1$ state 1'152'842'742.637(32) MHz) and the 2 ^{3}P centroid energy (876'106'247.017(32) MHz). These values reveal disagreements with the α^7m Lamb shift prediction by 6.5σ and 11σ, respectively, and support the suggestion by Patkóš *et al.* of an unknown theoretical contribution to the Lamb shifts of the 2 ^{3}S and 2 ^{3}P states of He.

Femtosecond broadband fluorescence upconversion spectroscopy to study the planarization dynamics of 9,10 -bis(phenylethynyl)anthracene

I. Fureraj[1], E. Vauthey[1]*

[1]Department of Physical Chemistry, University of Geneva

Most arylethynyl-based chromophores are characterised by a non-mirror image relationship of their absorption and emission spectra. Their broad absorption spectrum results from torsional disorder in the electronic ground state, whereas their structured emission spectrum arises from a planar and relatively rigid excited state. Therefore, significant structural relaxation involving planarisation takes place upon photoexcitation of these molecules.

To better understand this process, we are investigating the planarisation dynamics of 9,10-bis(phenylethynyl) anthracene, a highly emissive aromatic hydrocarbon, well-known for its applications in optics and electronics.[1] For this, we use femtosecond broadband fluorescence up-conversion spectroscopy[2] with sub 100 fs resolution and tunable excitation. The latter allows for a photoselection of molecules with different ground-state geometries. Measurements are performed in solvents of varying viscosity to better understand the effect of friction and to distinguish the relaxation of high-frequency modes from that of low-frequency mode associated with large-amplitude motion.

[1] Masaaki Mitsui, Yuya Kawano, Ryoya Takahashi, Hiroki Fukui, *RSC Advances* **2012**, 2 (26), 9921.

[2] Mario Gerecke, Genaro Bierhance, Micheal Gutmann, Nikolaus P. Ernsting, Arnulf Rosspeintner, *Review of Scientific Instruments* **2016**, 87 (5), 053115.

Electric Field Gradient calculation within Frozen-Density Embedding Theory

Y. Gimbal-Zofka[1], T. A. Wesolowski[1]*

[1]Department of Physical Chemistry, University of Geneva, Switzerland

Frozen-Density Embedding Theory[1],[2] (FDET) provides a system-independent formal framework for multi-level computational methods allowing to describe the effect of a frozen electron density of the environment on the chromophore. Within this framework, it is possible to treat either explicitly or implicitly the effect of the embedding species on the electron distribution in the environment in numerical simulations. In the pre-polarization protocol[3], the response of the environment to the electronic structure of the chromophore can be taken into account in the process of generating . In practice, due to some approximations made for the FDET potential ranging from the approximate nature of the DFT (bi)functionals to the neglect of Pauli repulsion in the prepolarisation procedure, this treatment is not exact.

The Electric Field Gradient (EFG) beeing a sensitive parameter, it has been shown that the commonly used Sternheimer approximation does not hold [4],[5]. In this work, we used the FDET-based with and without polarization methods to evaluate the EFG of H-bonded systems and coordinated alkaline metals[6]. This study shows that FDET allows for an accurate description of the EFG, demonstrating the importance of the contribution of the Pauli repulsion term in the embedding potential, which is missing in the commonly used point-charge embedding approach.

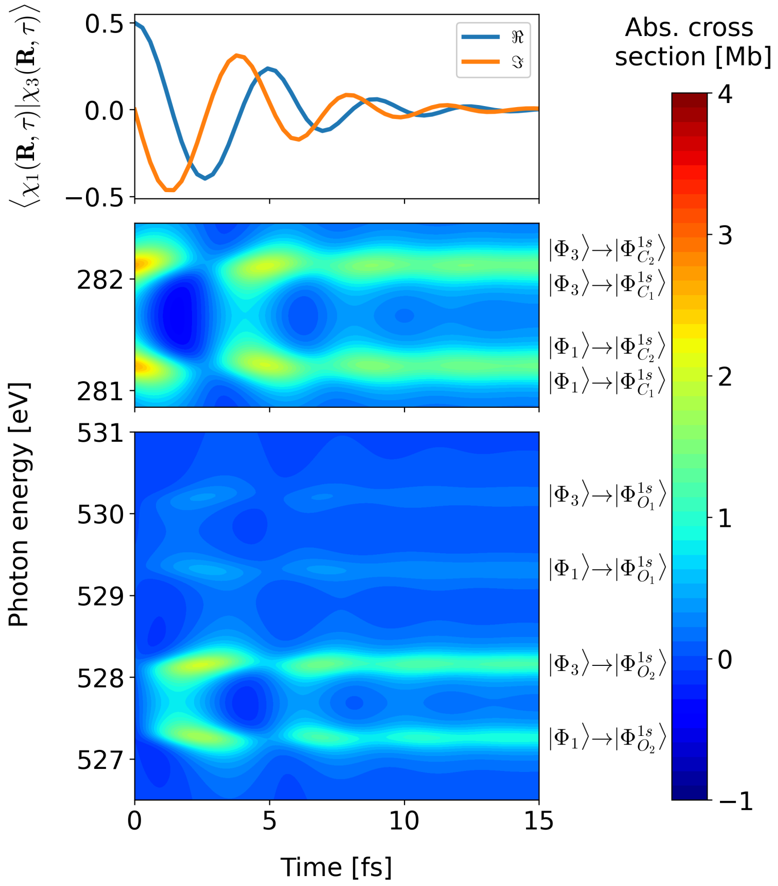
[1] Tomasz Wesolowski, Arieh Warshel, *J. Phys. Chem.*, **1993**, 97, 8050
[2] Tomasz Wesolowski, *Phys. Rev. A*, **2008**, 77, 012504
[3] Niccolò Ricardi, Alexander Zech, Yann Gimbal-Zofka, Tomasz A. Wesolowski, *Phys. Chem. Chem. Phys.*, **2018**, 20, 26053-26062
[4] Kestutis Aidas, Hans Agren, Jacob Kongsted, Aatto Laaksonen, and Francesca Mocci. Phys. Chem. Chem. Phys., 15:162-1631, 2013.
[5] Antoine Carof, Mathieu Salanne, Thibault Charpentier, and Benjamin Rotenberg. The Journal of Physical Chemistry B, 118(46):13252-13257, 2014.
PMID: 25340813.
[6] Yann Gimbal-Zofka, Tomasz Wesolowski, To be published

Core-valence attosecond transient absorption spectroscopy of polyatomic molecules

N. V. Golubev[1], J. Vaníček[1], A. I. Kuleff[2,3]

[1]Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingenierie Chimiques, Ecole Polytechnique Federale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, [2]Theoretische Chemie, Universitat Heidelberg, Im Neuenheimer Feld 229, D-69120 Heidelberg, Germany, [3]ELI-ALPS, Wolfgang Sandner utca 3, H-6728 Szeged, Hungary

Tracing ultrafast processes induced by interaction of light with matter is often very challenging. In molecular systems, the initially created electronic coherence becomes damped by the slow nuclear rearrangement on a femtosecond timescale which makes real-time observations of electron dynamics in molecules particularly difficult. In this work, we demonstrate theoretically that the attosecond transient absorption spectroscopy (ATAS) can be a very useful technique to trace such ultrafast processes in molecules. We report an extension of the theory underlying ATAS for the case of molecules, including a full account for the coupled electron-nuclear dynamics in the initially created wave packet, and apply it to probe the oscillations of the positive charge created after outer-valence ionization of the propiolic acid molecule. By taking advantage of element-specific core-to-valence transitions induced by X-ray radiation, we show that the resolution of ATAS makes it possible to trace the dynamics of electron density with atomic spatial resolution.



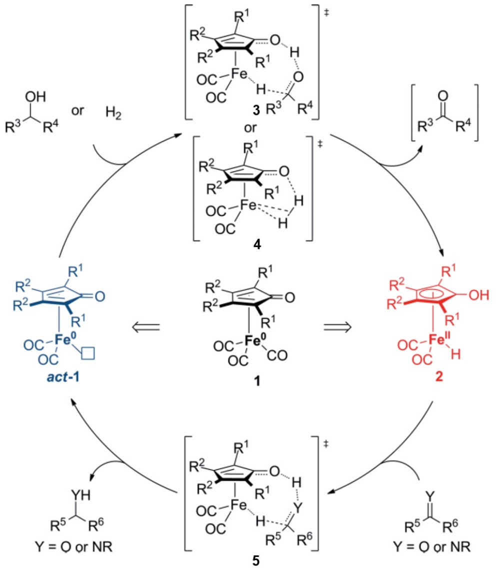
[1] N. V. Golubev, J. Vaníček, and A. I. Kuleff; arXiv:2010.15051

Investigation of Hydrogen Transfer Catalytic Cycle of (Cyclopentadienone)iron Complexes by Cryogenic Ion Vibrational Predissociation (CIVP) Spectroscopy

V. Gorbachev[1], A. Bütikofer[1], P. Chen[1]*

[1]Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland

(Cyclopentadienone)iron complexes have great potential in homogeneous iron catalysis due to their easy preparation and robustness. The non-innocent, tunable ligand can exist in two forms: the cyclopentadienone and the hydroxycyclopentadienyl; thus, the ligand induces iron to engage in hydrogen heterolytic cleavage and transfer. Despite many efforts to adjust the properties of the iron's ligands or isolate intermediates, the mechanism[1] of the hydrogen transfer is poorly understood. There is limited experimental data - only complexes **1** and **2** were characterized to the best of our knowledge.



To elucidate the catalytic cycle, we tagged compounds of interest by differently charge moieties and perform an Operando MS/NMR study (for details, see André Butikofer's virtual poster) as well as Cryogenic Ion Vibrational Predissociation (CIVP) spectroscopic [2,3] investigation (this work). In this way, we transfer the catalytic cycle in the gas phase by electrospray ionization, mass-select specific ions, and cool them to cryogenic temperatures in a liquid He-cooled Fourier-transform ion cyclotron resonance (FT-ICR) cell. Thus, our work will shed light on the putative Fe(0)/Fe(II) catalytic cycle of hydrogen transfer reaction.

[1] Luca Pignataro, Cesare Gennari, *EurJOC*, **2020**, 22, 3192-3205.
[2] Lukas Fritsche, Andreas Bach, Larisa Miloglyadova, Alexandra Tsybizova, Peter Chen, *Rev. Sci. Instrum*, **2018**, 89, 063119.
[3] Vladimir Gorbachev, Larisa Miloglyadova, Alexandra Tsybizova, Peter Chen, *Rev. Sci. Instrum*, in preparation.

Low-energy reactive collisions of all stable molecular hydrogen isotopologues: branching ratios, deviation from Langevin behavior and kinetic energy analysis of the products.

R. Hahn[1], K. Höveler[1], J. Deiglmayr[2], J. A. Agner[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, ETH-Zürich, [2]Department of Physics, University of Leipzig

The study of low-temperature collisions between small molecules, molecular hydrogen in particular, is crucial to understand the chemistry of interstellar clouds, characterized by temperatures typically in the 3 K to 60 K range. These studies can also be used to test theoretical predictions about the reaction rates, and the product branching ratios and kinetic-energy distributions [1]. The ion-molecule capture rates are well described by the semi-classical Langevin theory at high to moderate energy, but deviations at low energies are predicted, and experimentally observed [1,2,3].

We report on experimental studies of low-energy ion-molecule reactions between the neutral molecules H_2, HD, and D_2 and the molecular ions H_2^+, HD^+, D_2^+. These studies allow the determination of the branching ratios between different reaction channels: electron transfer, H/D-atom transfer or H^+/D^+ transfer [1]. Differences resulting from nuclear-spin symmetry can also be investigated by exchanging natural H_2 with para-H_2.

Low-energy collisions of molecules with ions are difficult to study directly because stray fields heat the ions up. This difficulty is circumvented by replacing the ions with the corresponding parent neutral molecule in highly excited Rydberg states. The Rydberg electron, very far from the core and loosely bound, shields the ion core from external fields while having negligible impact on its reactions with neutral molecules located within the Rydberg-electron orbit [3,4]. To reach low collision energies, velocity-tunable supersonic beams of the reactants are merged.

The Rydberg states are produced in one of the two beams by photoexcitation in the presence of an electric field and subsequently velocity selected and deflected using a curved chip-based surface-electrode deflector [5]. This deflector allows us to merge the Rydberg molecular beam with a supersonic beam of the ground-state neutral molecules. The relative and absolute axial velocity of the reactants can also be varied by adjusting the velocity selected by the deflector, by adjusting the delays between the openings of the valves, and by changing their temperatures. The fact that the longitudinal velocity spread of the molecular beams rapidly evolve into a spatial dispersion enables a high collision-energy resolution and studies at collision energies below 1 K, where the reaction rates are enhanced relative to the Langevin capture rate for a pure ion-induced dipole interaction [1,2].

[1] K. Höveler , J. Deiglmayr, J. A. Agner, H. Schmutz, and F. Merkt,*Phys. Chem. Chem. Phys*., **2021**, 23, 2676

[2] E.I. Dashevskaya, I. Litvin, E.E. Nikitin and J. Troe, *J. Chem. Phys.,* **2016***,* 145, 244315

[3] P. Allmendinger, J. Deiglmayr, K. Höveler, O. Schullian and F. Merkt, *J. Chem. Phys.,* **2016***,* 145, 244316

[4] S.T. Pratt, J.L. Dehmer, P.M. Dehmer and W.A. Chupka, *J. Chem. Phys.,* **1994***,* 101, 882

[5] P. Allmendinger, J. Deiglmayr, J. A. Agner, H. Schmutz, and F. Merkt, *Phys. Rev. A,* **2014***,* 90, 043403

High-Resolution Spectroscopy in Argon using a Long-Pulse Fourier-Transform Limited Laser System

H. Herburger[1], U. Hollenstein[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich

We demonstrate a laser system providing user-designed laser pulses with durations tunable from 10 ns to 1 µs and pulse energies up to 680 mJ per pulse at a repetition rate of 25 Hz and at a wavelength of 1064 nm. This radiation is frequency doubled in an LBO crystal yielding 532 nm radiation with pulse energies of 90 mJ per pulse. The frequency-doubled laser is used as a pump source for a dye amplification line seeded by the output of a commercial continuous-wave ring dye laser. This system enables us to generate 10 ns to 120 ns long pulses with a Gaussian temporal profile in the visible range of the electromagnetic spectrum with output energies of up to 5 mJ per pulse. We also generate long pulses of UV radiation (pulse energies up to 500 µJ, pulse length up to 85 ns) by frequency doubling in a BBO crystal.

The properties of the laser system are illustrated in measurements of the one- and two-photon Rydberg spectrum of atomic argon in the $3p^5 4s[3/2]_2\ ^3P_2$ and $3p^5 4s'[1/2]_0\ ^3P_0$ metastable states. Metastable argon is generated in a supersonic beam using a dielectric barrier discharge. We have recorded spectra of Rydberg series of Ar below the $^2P_{3/2}$ and $^2P_{1/2}$ ionization thresholds. We use the long lifetimes of the former series to characterize the bandwith of the laser system and determine the autoionization linewidth and line shapes of the later series for comparison with earlier work [1].

[1] Victor L. Sukhorukov, I. D. Petrov, Martin Schäfer, Frédéric Merkt, Matthias W. Ruf, and Hartmut Hotop, *Journal of Physics B: Atomic, Molecular and Optical Physics,* **2012**, 45, 092001 and references therein.

Polymer GUVs for Studying Compartmentalized Biological Systems

L. Heuberger[1], E. dos Santos[1], R. Wehr[1], D. Hürlimann[1], C. Palivan[1]*, W. Meier[1]*

[1]Department of Chemistry, University of Basel

Biological systems use compartmentalization strategies to generate microenvironments with controlled biochemical compositions. They serve as a protective method from undesired influences from outside of the compartment and to keep diffusing elements in close proximity. [1] Giant unilamellar vesicles (GUVs) are micrometer-sized vesicles that are used in this context based on their size similarity to cells. [2] Amphiphilic block copolymers can be synthesized with a wide range of compositions, block ratios, and functionalization and serve as excellent alternatives to lipids for vesicle formation. [2] With double emulsion microfluidics, monodisperse GUVs with controllable inner, membrane, and outer composition can be produced at high throughput. [3] By adjusting the inner composition, whole enzymatic cascades, smaller vesicles, and living organisms can be encapsulated within GUVs.

In the presented work, we generate impermeable GUVs using the block copolymer PDMS-PMOXA. By inserting outer membrane porin F (ompF) [3] or the pore-forming peptide melittin into the synthetic membrane, the GUVs can be permeabilized. A subcompartmentalized system was created by encapsulating nanometer-sized polymersomes into GUVs. Furthermore, *Bacillus subtilis*, a model organism for studying biofilms, was encapsulated within GUVs and bacteria growth and biofilm formation inside the GUV could be explored. This approach shows the versatility of double emulsion templated polymer GUVs for studying compartmentalized systems.

[1] Renée Roodbeen, Jan C.M. Van Hest, *BioEssays,* **2009***,* 31(12): 1299–1308.
[2] Elena C. dos Santos, et al., *Advanced Materials,* **2020,** 32(48): 2004804.
[3] Elena C. dos Santos, et al., *Chemistry,* **2020**, 2(2): 470–89.

High-Resolution Spectroscopy in Supersonic Beams using a QCL Dual-Comb Spectrometer

U. Hollenstein[1], J. A. Agner[1], P. Allmendinger[2], A. Hugi[2], K. Keppler[1], M. Mangold[2], F. Merkt[1], M. Quack[1]

[1]Laboratorium für Physikalische Chemie, ETH Zürich, Zürich, Switzerland, [2]IRsweep AG, Stäfa, Switzerland

Optical frequency comb spectroscopy has proven a very useful tool for high resolution molecular spectroscopy. Frequency combs based on quantum cascade lasers (QCL) offer the possibility to easily explore the mid-infrared spectral range (4 µm to 12 µm), but suffer from very large repetition frequencies (~ 10 GHz) which make them seemingly unsuitable for high resolution spectroscopy.

Here, we present techniques to overcome this limitation. We have employed the combined advantages of high temporal (< 4 µs) and high spectral resolution to measure the IR spectra of CF_4 and $CHCl_2F$ in pulsed, skimmed supersonic beams. The low rotational temperature of the beams and the narrow expansion cone after the skimmer enabled the recording of spectra of cold samples with high resolution. The spectra cover the range from 1200 cm^{-1} to 1290 cm^{-1} and the narrowest lines have a full width at half maximum of 15 MHz, limited by the Doppler effect. The results demonstrate the potential of QCL dual-comb spectroscopy for broadband (> 60 cm^{-1}) acquisition of spectra at high resolution (< 15 MHz) and high sensitivity in the mid-infrared range. The power of the new technology is demonstrated by comparison with previous results on these molecules obtained by FTIR and diode laser spectroscopy of seeded cw and pulsed supersonic jets. [1-3]

[1] M. Snels and M. Quack, «High resolution Fourier-transform infrared spectroscopy of $CHCl_2F$ in supersonic jets: Analysis of ν_3, ν_7, and ν_8», *J. Chem. Phys.* **95**, 6355 (1991); doi:10.1063/1.461556.

[2] M. Snels, V. Horká-Zelenková, H. Hollenstein and M. Quack, «High-resolution FTIR and Diode Laser Spectroscopy of Supersonic Jets», in Handbook of High-Resolution Spectroscopy, Eds.; M. Quack and F.Merkt , Vol. 2, pp. 1021-1067, Wiley, Chichester, 2011; doi:10.1002/9780470749593.hrs044.

[3] M. Caviezel, V. Horká-Zelenková, Z. Guennoun , G. Seyfang, M. Quack, unpublished manuscript (in preparation for Mol Phys.)

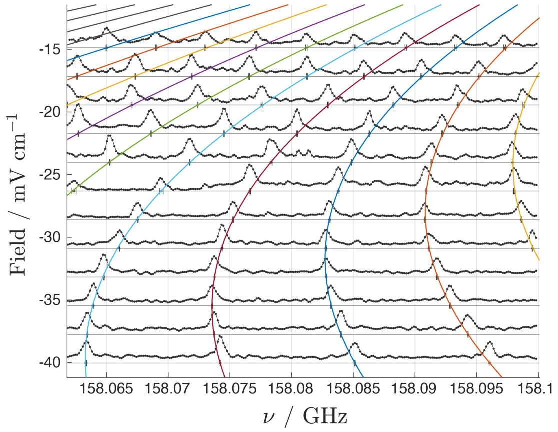
Ionization Energies of Para-H_2 from Zero-Quantum-Defects Positions

N. Hölsch[1], I. Doran[1], F. Merkt[1]*

[1]ETH Zürich, Laboratory of Physical Chemistry

From the precise measurement of the ionization energy of H_2 its dissociation energy can be determined [1], which serves as a benchmark quantity for QED calculations [2]. Additionally, measurements of ionization energies corresponding to higher rovibrational levels of the ion enable the determination of rovibrational intervals in H_2^+ [3]. These intervals can be calculated extremely precisely for one-electron systems, offering the prospect of improving the value of fundamental constants or particle properties such as the proton-to-electron mass ratio [4].

Until now, the most precise determinations of the ionization energies of molecular hydrogen have relied on the extrapolation of Rydberg series using multichannel quantum-defect theory (MQDT) [5]. These extrapolations are typically accurate to less than 500 kHz, currently representing the dominant source of uncertainty in the determinations of ionization energies. Additionally, autoionization lifetimes restrict mmW measurements to states below the lowest ionization threshold which renders accurate extrapolations to higher rovibrational levels of the ion difficult.



We present here a method to determine the binding energies of Rydberg states without having to resort to a Rydberg-series extrapolation. We carry out precision measurements of the linear Stark manifolds associated with near-degenerate high-*l* states by mmW spectroscopy in the presence of intentionally applied electric fields. Extrapolating the linear Stark manifold to zero field yields accurate values of the zero-quantum-defect positions, given by $-R_{H2}/n^2$ relative to the ionization thresholds. This circumvents the current bottlenecks and opens a route for order-of-magnitude improvements of the ionization energies in molecular hydrogen.

[1] N. Hölsch, et al., *Phys. Rev. Lett.*, **2019**, 122(10), 103003

[2] M. Puchalski, et al., *Phys. Rev. Lett.*, **2019**, 122(10), 103003

[3] C. Haase, et al., *J. Chem. Phys.*, **2015**, 142(6), 064310

[4] I.V. Kortunov, et al., *Nat. Phys.*, **2021**, 1-5

[5] D. Sprecher, et al., *J. Chem. Phys.*, **2014**, 140, 104303:1-18

In-operando morphological changes of P3HT studied by vibrational spectroscopy in organic electrochemical transistors

I. Holzer[1], P. Cavassin[1], N. Banerji[1]*

[1]Department of Chemistry, University of Bern

The demand for organic electronic devices increases, because they combine advantageous properties such as versatile processing and synthetic tunability; therefore, they possess a large range of application. An attractive type of electronic device is the OECT (organic electrochemical transistor), which can be used as a highly sensitive biomedical sensor. Its functioning is based on mixed ionic-electronic conduction, whereby ions penetrate the organic film due to a gate bias and lead to doping, which modifies the electronic conductivity. A model material for OECTs is P3HT, which was already characterized by multiple different research groups.[1] Much focus was so far on the device fabrication and on the different material options. Hence there is still a need for a more in-depth understanding of the ionic transport and the morphological effects on the OECTs performance.[2] To obtain information about the local morphology and conformation of P3HT, vibrational spectroscopy like Raman spectroscopy can be used, as it detects the polarizable π-electrons, which are dominant in organic materials.[3] In this work, we have characterized P3HT using in-operando electrochemical resonant Raman spectroscopy and in-situ time-resolved VIS-NIR spectroscopy. We are able to assign different bands in the Raman spectra to the different kinds of species present during the doping process (neutral segments, polarons, bipolarons). Furthermore, with the help of Multivariate Curve Resolution (MCR), the evolution of the species as a function of gate bias could be determined, which is in accordance with the concentration of the species at different doping stages.

[1] Dion Khodagholy, Jonathan Rivnay, Michele Sessolo, Moshe Gurfinkel, Pierr Leleux, Leslie H. Jimison, Eleni Stavrinidou, Thierry Herve, Sébastien Sanaur, Róisín M. Owens, George G. Malliaras, *Nature Communications,* **2013**, 48, 2133.

[2] Jaeyub Chung, , Aditi Khot, Brett M. Savoie, Bryan W. Boudouris, *ACS Macro Letters,* **2020**, 9, 646-655.

[3] James Nightingale, Jessica Wade, Davide Moia, Jenny Nelson, Ji-Seon Kim, *The Journal of Physical Chemistry*, **2018**, 122, 29129-29140.

High Resolution Infrared Spectroscopy of Aziridine-2-Carbonitrile ($C_3H_4N_2$)

K. Keppler[1], S. Albert[1], C. Manca Tanner[1], J. Stohner[2], M. Quack[1]*

[1]ETH Zurich, Laboratory for Physical Chemistry, CH-8093 Zürich, Switzerland, [2]ZHAW Zürich, Institute for Chemistry & Biotechnology, CH-8820 Wädenswil, Switzerland

Molecular parity violation has been critically discussed in relation to homochirality and early biochemical evolution [1]. In this context molecules of potential importance for prebiotic chemistry are of interest [2]. The small chiral heterocyclic molecule aziridine-2-carbonitrile ($CH(CN)CH_2NH$, cyano-aziridine) has been previously examined [3] and the parity violating energy difference between the enantiomers in their ground state has been calculated [4]. Molecular parameters for the ground state of this molecule are available from earlier microwave studies [5], and its conformations have been examined by ab initio theory [6]. Here we report initial results of a high resolution spectroscopic study of cyano-aziridine. The spectrum has been measured at room temperature using the Bruker IFS125 Zurich Prototype (ZP2001) Fourier transform spectrometer [7,8] with a resolution of 0.0011 cm^{-1}. Transitions associated with the ν_{15} and ν_{16} bands in the 800−1000 cm^{-1} region have been assigned, and molecular parameters have been determined using the Watson Hamiltonian. Simulations performed using these parameters reproduce the observed spectra well. The results are discussed in relation to astrophysical spectroscopy and recent efforts on parity violation in chiral molecules [9].

[1] M. Quack, *Angew. Chem. Intl. Ed. (Engl.)*, **2002**, 41(24), 4618.

[2] A. Eschenmoser and E. Loewenthal, *Chem. Soc. Rev*., **1992,** 21(1), 1.

[3] S. Drenkard, J. Ferris, and A. Eschenmoser, *Helv. Chim. Acta*, **1990**, 73, 1373.

[4] R. Berger, M. Quack and G. S. Tschumper, *Helv. Chim. Acta*, **2000**, 83(8), 1919.

[5] R. D. Brown, P. D. Godfrey, and A. L. Ottrey, *J. Mol. Spectrosc.*, **1980**, 82, 73.

[6] G. S. Tschumper, *J. Chem. Phys*., **2001**, 114(1), 225.

[7] S. Albert, K. Albert and M. Quack, *Trends in Optics and Photonics*, **2003**, 84, 177.

[8] S. Albert, K. Keppler Albert, M. Quack, Ch. 26, Handbook of High-resolution Spectroscopy, Vol. 2, p. 965-1019, M. Quack and F. Merkt, Eds.,Wiley, Chichester (2011).

[9] M. Quack and G. Seyfang,“Tunnelling and Parity Violation in Chiral and Achiral Molecules,” Chapter 6, Tunnelling in Molecules: Nuclear Quantum Effects from Bio to Physical Chemistry, p.192−244, J. Kästner, S. Kozuch Eds., RSC, Cambridge (2020). ISBN: 978-1-78801-870-8.

Spectroscopic Studies of Ion-Pair States of Polyatomic Molecules

C. Kreis[1], U. Hollenstein[1], F. Merkt[1]*

[1]ETH, Laboratory of Physical Chemistry

We present the results of spectroscopic investigations of ion-pair states of small polyatomic molecules. Ion-pair states of diatomic molecules are well characterized [1,2].

However, only few studies of ion-pair states of polyatomic molecules have been conducted [3,4] and many of their characteristics are not well understood.

Accurate threshold energies give access to thermochemical properties like the bond energy. We are currently investigating triatomic systems in particular H_2S and its isotopomers.

The molecule of interest in its gas phase is cooled down in a supersonic expansion. The cold gas cloud passes a skimmer before it is excited via a one-photon transition with narrow-band VUV laser radiation and extracted in a photoion/photoelectron time-of-flight spectrometer.

The threshold of the formation of ion-pair states is determined and spectra of vibrational ion-pair states presented.

[1] W.A. Chupka, P.M. Dehmer, W.T. Jivery, *The Journal of Chemical Physics*, **1975,** 63, 3929.

[2] J.D.D. Martin, J.W. Hepburn, *Physical Review Letters*, **1997,** 79, 3154.

[3] R. C. Shiell, X. K. Hu, Q. J. Hu, J. W. Hepburn, *The Journal of Physical Chemistry*, **2000**, 104, 19.

[4] Q. J. Hu, Q. Zhang, J.W. Hepburn, *The Journal of Chemical Physics,* **2006**, 123, 074310.

Mechanism of Material Transfer from Ion Sensing Component-Loaded Nanoemulsions: An Electrochemical Quartz Crystal Microbalance and Thin Film Coulometry Study

C. Mao[1], Y. Soda[1], K. J. Robinson[1], T. Forrest[1], E. Bakker[1]

[1]University of Geneva, Department of Inorganic and Analytical Chemistry,

Recent work has shown that ion-selective materials can be transferred from nanoemulsions (NEs) to endow polymeric membranes with ion-selective sensing properties [1]. This approach has also been used at nanopipette electrodes to achieve single entity electrochemistry, sensing the ion-selective response of single adhered nanospheres [2]. Unfortunately, the exact mechanism and rate of component transfer are not yet clear. We study here the transfer of lipophilic ionic compounds from nanoemulsions into thin plasticized poly(vinyl chloride) (PVC/DOS) films by chronoamperometry and quartz crystal microbalance. Thin-layer coulometric measurements allow one to monitor the uptake of lipophilic species into blank PVC/DOS membranes. Ionophores and ion-exchangers are shown to transfer into the membrane at rates that do not linearly correlate with their lipophilicity, suggesting that a coupled transfer through bulk partitioning into the aqueous phase can be excluded. On the other hand, QCM data suggest that the transfer of polymer and plasticizer is insignificant, ruling out simple coalescence of the nanoemulsions with the membrane film. By rotating disk electrode, which keeps the diffusion layer thickness constant, a linear relationship between diffusion layer thickness and the current was observed, which agrees with Fick’s first law of diffusion. The data suggest a hopping/tunneling mechanism of transfer. The results help to better understand and quantify the interaction between nanoemulsions and ion-selective membranes.

[1] Y. Soda, W. Gao, J. Bosset, E. Bakker, Emulsion Doping of Ionophores and Ion-Exchangers into Ion-Selective Electrode Membranes, Anal. Chem., **2020**, 92, 14319–14324.
[2] S.G. Sabaragamuwe, D. Conti, S.R. Puri, I. Andreu, J. Kim, Single-Entity Electrochemistry of Nanoemulsion: The Nanostructural Effect on Its Electrochemical Behavior, Anal. Chem., **2019**, 91, 9599–9607.

Implementation of a novel transporter system into artificial membranes

M. Muthwill[1], A. Krywko-Cendrowska[1], S. Yorulmaz Avsar[1], R. Wehr[1], D. Sokolova[1], K. Tiefenbacher[1]*, C. Palivan[1]*

[1]Department of Chemistry, University of Basel

Polymer membranes are efficient models for the study of biochemical processes when combined with biomolecules, such as membrane proteins or enzymes. Different assembly types or morphologies of polymer membranes can be exploited for these studies, based on the specific needs and the required complexity of the system. For example, planar membranes are a suitable model to study the physico-chemical aspects of the insertion of membrane proteins and pores[1] or the reaction kinetics when combined with enzymes[2], whereas giant unilamellar vesicles (GUVs) allow for mimicking basic cellular processes.[3, 4] Compared to protein transporter systems, synthetic macromolecular hexameric capsules that self-assemble from resorcinarenes[5] have major advantages, such as specific encapsulation of certain guest molecules and chemical adaptability to the membrane environment. In this joint project, we aim for the generation of hybrid membranes with selective transport function by insertion of resorcinarene-based capsules into artificial polymer membranes. We show physical characterization data of the hybrid membranes as well as different approaches for investigation of the capsule assembly and their transport ability.

[1] X. Zhang, et al., *Scientific Reports*, **2013**, 3, 2196.
[2] S. Di Leone, et al., *J Phys Chem B*, **2020**, 124, 4454-4465.
[3] Santos, E.C., et al., *Adv Mater*, **2020**, 32, 2004804.
[4] Thamboo, S., et al., *Adv Funct Mater*, **2019**, 29.
[5] Némethová, et al., *Chimia (Aarau)*, **2020**, 74, 561-568.

On the absolute photoionization cross section of the fulvenone ketene

Z. Pan[1,2], J. A. van Bokhoven[2]*, P. Hemberger[1]*

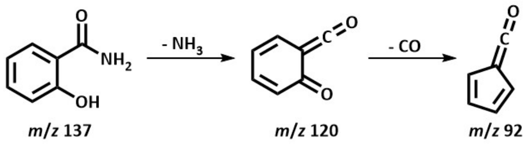
[1]Laboratory for Synchrotron Radiation and Femtochemistry, [2]Department of Chemistry and Applied Biosciences

Fulvenone is an elusive and crucial ketene intermediate in lignin catalytic pyrolysis.[1,2] It is not only responsible for the branching of the reaction pathways, but also escapes from conventional detection methods such as GC/MS and NMR. Thanks to sensitive photoelectron photoion coincidence techniques, we clearly catched the fulvenone during the catalytic pyrolysis of lignin model compounds.[1,3] This is, however, not enough and quantification is much-needed for deeper mechanistic understanding and reliable kinetics of the lignin catalytic pyrolysis process. The absolute photoionization cross section (PICS) is widely applied for quantification, especially in flame chemistry[4] and relates the signal in a mass spectrum to the mole fraction during a chemical reaction:

$$\frac{S_{C_5H_4=C=O}}{S_{Ref}} = \frac{[C_5H_4 = C = O]}{[Ref]} \times \frac{\sigma_i^{C_5H_4=C=O}}{\sigma_i^{Ref}} \times \frac{A_{C_5H_4=C=O}}{A_{Ref}}$$

Where S is the photoion signal intensities, [C_5H_4=C=O] and [Ref] are the concentrations of both reaction products, sigma$_i$ is the respective ionization cross sections and A represents the apparatus function. Salicylamide (m/z 137) is an excellent fulvenone (m/z 92) precursor, simultaneously yielding NH_3 and CO (as shown below).[5]

Ammonia is not only the reaction product, but is also used as a reference because its PICS is well known.[6] Here we investigate the pyrolysis of salicylamide at different conditions and observed another ketene intermediate at m/z 120. We characterized the ketene at m/z 120 utilizing photoion mass-selected threshold photoelectron spectroscopy (ms-TPES). At higher pyrolysis temperatures m/z 120 could be almost fully converted to the fulvenone ketene (m/z 92). By optimizing parameters (temperature and concentration), photoionization spectra were recorded for the latter species and the photon energy-dependent cross section was determined.



[1] P. Hemberger, V. B. F. Custodis, A. Bodi, et al., *Nat. Commun.* **2017**, 8: 15946.
[2] A. D. Chowdhury, J. Gascon, *Angew. Chem., Int. Ed.*, **2018**, 57, 14982–14985.
[3] Z. Pan, A. Puente-Urbina, A. Bodi, et al. *Chem. Sci.*, **2021**, 12, 3161–3169
[4] J. Wang, B Yang, T. A. Cool, *Int. J. Mass Spectrom.*, **2008**, 269, 210-220.
[5] H.-F. Grützmacher, J. Hübner, *Justus Liebigs Annalen der Chemie*, **1971**, 748, 154-162.
[6] T. J. Xia, T. S. Chien, C. Y. Robert Wu, et al., *J. Quant. Spectrosc. Radiat. Transfer*, **1991**, 45, 77-91

Ultrafast Charge Dynamics in p-Doped Conjugated Polymers - *Glycol functionalized Polythiophene P(g4 2T-T) versus workhorse P3HT*

E. Röck[1], D. Tsokkou[1], C. Müller[2], E. Järsvall[2], N. Banerji[3]*

[1]University of Bern, [2]Chalmers University of Technology, [3]Department of Chemistry, University of Bern

The major limiting factor in charge transport for molecularly doped organic semiconductors is the small fraction of mobile charge carriers. Most conductive charges are trapped by Coulomb interaction with the dopant anion. To push the relevance of p-doped conjugated polymers in optoelectronic devices, it is necessary to overcome this mobility barrier. Proposed pathways are tuning the utilized conjugated polymers in means of sites where the dopants are preferentially located, or removing the dopant ion after effective charge creation. This work focuses on the polythiophene with oligo ethylene glycol side chains P(g4 2T-T) p-doped by the well-studied electron acceptor F4TCNQ and its correlated effective charge mobility. The performance in time-resolved spectroscopy elucidates the charge dynamics that happen at ultrafast time scales. The combination of transient absorption (TA) and optical pump terahertz probe (OPTP) spectroscopy gives insight on density, lifetime, short-range mobility, and delocalization of photogenerated charges. Moreover, the characteristics yielding from the excitation of bands corresponding to neutral and charged P(g4 2T-T) results in valuable distinctions in the delocalization of charges. The well-studied P3HT is considered the workhorse amongst the conjugated polymers and is used as a complement material in this work. The optical or IR pump allows bound holes to overcome the attractive Coulomb potential emanating from the F4TCNQ anions. We demonstrate that the light-generated mobile charges in p-doped P(g4 2T-T) recombine faster, which is a measure of the interaction with the local environment. The effective THz mobility is higher than reported values for organic semiconductors, which is related to the superior morphology in terms of p-p bridging along the polymer backbone.

Measurements of np-2s transitions in the hydrogen atom

S. Scheidegger[1], J. A. Agner[1], H. Schmutz[2], F. Merkt[2]*

[1]Laboratory of Physical Chemistry, ETH Zurich, [2]ETH Zürich, Laboratory of Physical Chemistry

Precision experiments in the hydrogen atom have a long tradition and extensive studies of transitions between low lying $n \leq 12$ states were carried out [1–6]. These measurements can be used to determine values of the Rydberg constant R_∞ and the proton charge radius r_p. We present a new experimental approach to perform measurements of transition frequencies between the metastable 2s $^2S_{1/2}$ (F = 0, 1) state of H and highly excited Rydberg states with principal quantum number $n \geq 23$, with goal of a complete measurement of the *n*p Rydberg series up to the ionization threshold. With such measurements the Rydberg constant can be determined independently of the r_p.

We generate the hydrogen atoms by photodissociation of NH_3 in a capillary mounted at the orifice of a pulsed valve. The hydrogen atoms are entrained in supersonic expansions of a rare gas. The atoms enter a magnetically shielded region in which they are photoexcited to a specific hyperfine level of the metastable 2s $^2S_{1/2}$ state by a home-built frequency-tripled Fourier-transform-limited pulsed titanium sapphire laser (pulse length 40 ns). Transitions to *n*p Rydberg states are then induced by a narrow-band frequency-doubled continuous-wave titanium sapphire laser, which is phase locked to an optically stabilized frequency comb and referenced to a Cs primary frequency standard. The highly excited Rydberg states are detected by pulsed-field ionization. We will report progress on our efforts to minimize uncertainties from stray electric fields and Doppler shifts and to obtain spectral lines with a FWHM below 10 MHz.

[1] Garreau, J.C., Allegrini, M., Julien, L., and Biraben, F., J. Phys. France 51, 2293 (1990).
[2] C. G. Parthey et al., Phys. Rev. Lett. 107, 203001 (2011).
[3] A. Beyer et al., Science 358, 79 (2017).
[4] H. Fleurbaey et al., Physical review letters 120, 183001 (2018).
[5] N. Bezginov et al., Science 365, 1007 (2019).
[6] A. Grinin et al., Science 370, 1061 (2020).

Precision infrared spectroscopy using a fibre link for the distribution of the Swiss primary frequency standard

A. Shlykov[1], M. F. Roguski[1], M. Sinhal[1], Z. Meir[1], M. Bertrand[2], J. Faist[2], F. Merkt[3], E. Heiri[4], D. Husmann[5], J. Morel[5]*, S. Willitsch[1]*

[1]Department of Chemistry, University of Basel, [2]Institute for Quantum Electronics, ETH Zürich, [3] Laboratory of Physical Chemistry, ETH Zürich, [4]SWITCH, [5]Federal Institute of Metrology METAS

Trapped atoms and atomic ions are among the best-controlled quantum systems which have found widespread applications in quantum science. However, the same degree of control over molecules has so far been challenging to achieve due to their complex energy-level structure. We overcome this problem by employing a high-fidelity quantum-state detection protocol that uses a single co-trapped atomic ion as a probe for the molecular state [1]. This protocol allows us to perform highly sensitive and precise spectroscopic experiments on dipole-forbidden infrared transitions in N_2^+ driven by a quantum cascade laser. The absolute frequency stability of the measurements is provided by referencing all laser frequencies to the Swiss primary frequency standard, the Cs atomic fountain clock FoCS-2, operated by the Swiss Federal Institute of Metrology METAS in Bern [2]. The present method paves a way for establishing new methods for precision spectroscopic measurements in the infrared domain, for new frequency standards in this regime, for new ways of investigating the state-to-state dynamics of chemical reactions, and for probing spectroscopically fundamental physical questions such as temporal variation of fundamental constants.

[1] Mudit Sinhal, Ziv Meir, Kaveh Najafian, Gregor Hegi, Stefan Willitsch, *Science,* **2020,** 367, 1213-1218

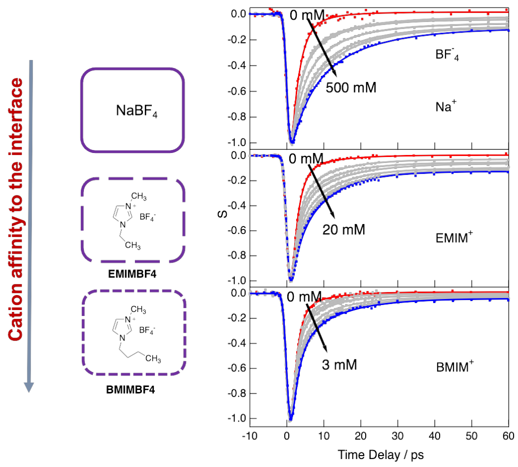
[2] Dominik Husmann et. al., *arXiv.org*, **2021,** 2104.0996

Probing Liquid Interfaces with Room-Temperature Ionic Liquids Using the Excited-State Dynamics of a Cationic Dye

J. Sissaoui[1], D. S. Budkina[1], E. Vauthey[1]*

[1]Physical Chemistry Department, University of Geneva

Interfaces involving room-temperature ionic liquids play a crucial role in many applications. However our understanding of their property is still limited. We investigated interfaces between dodecane and water/RTILs mixtures using stationary and time-resolved surface second harmonic generation. As interfacial probe, we selected a cationic dye malachite green. We find that the interfacial concentration of malachite green depends crucially on the nature of both anionic and cationic constituents. This concentration is sensitive to the overall charge of the interface and the latter depends on the relative interfacial affinity of the ions. Our results reveal that the addition of ILs to the water phase has similar effects to the addition of conventional salts. However, the IL cations have a significantly higher propensity to adsorb than small inorganic cations. Furthermore, a synergistic effect is observed between the ILs both cation and anion as the the interfacial concentration of each of them also depends on the interfacial affinity of the other.



[1] Jihad Sissaoui, Darya S. Budkina, Eric Vauthey, *Journal of Physical chemistry B* ,**2020**, *124* (46), 10546–10555.

Introducing Order and Disorder into Inverse Opals

J. Smart[1], M. Lattuada[1]*

[1]University of Fribourg, Department of Chemistry

In nature some animals make use for structural colours, instead of pigment colours, to interact or camouflage with the environment around them. Structural colour comes from the interaction of light with the structures in a material and for this reason does not fade like normal pigments do. Inspired by nature, these colours can be mimicked by arranging monodisperse colloids in crystals by making use of self-assembly. When the size of the colloids are on the order of visible light (400-700 nm) structural colours can be seen.

Colloidal crystals can be used as templates to create inverse opal structures. The amount of order and disorder in the crystalline structure allows structural colours to have different properties. In highly ordered photonic crystals the structural colour shows an angular dependence, when a low degree of disorder is introduced the structural colours begin to have a much lower angle dependence. However, once the disorder in the crystal becomes too large, the structural colour is lost and the surface appears to be white, as the light is scattered in all directions.

Controlled introduction of disorder can be done my making use of non-spherical dimpled particle templates. The dimpled particles introduce a different type of disorder into the system, the order of the disorder can be controlled by the size of the dimple in the particle itself. Increasing the dimple sizes increases the disorder in the system, until there is eventually no structural colour present. The impact of this change in the dimple size on the optical properties of the inverse structure is being looked at.

The modifications made to the template particles have a considerable impact on the self-assembly behaviour in the system. And for this reason the surface coating of the particles and the self assembly method need to be looked at and optimised for the thin film that is being produced.

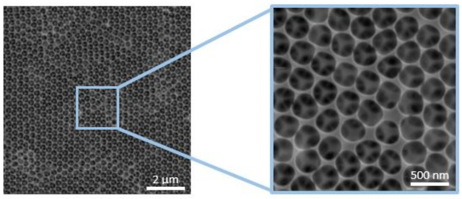


Figure 1: The two SEM images allow for the structure of pristine polystyrene template inverse opals can be seen in two different size scales. In the image with higher magnification (Right) the FCC lattice packing can be seen.

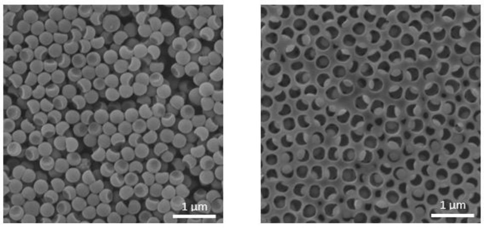


Figure 2: The dimpled particles (left) and the inverse opal structures made from these templates (right) show the disorder introduced to the system when they are compared to the order seen in Figure 1.

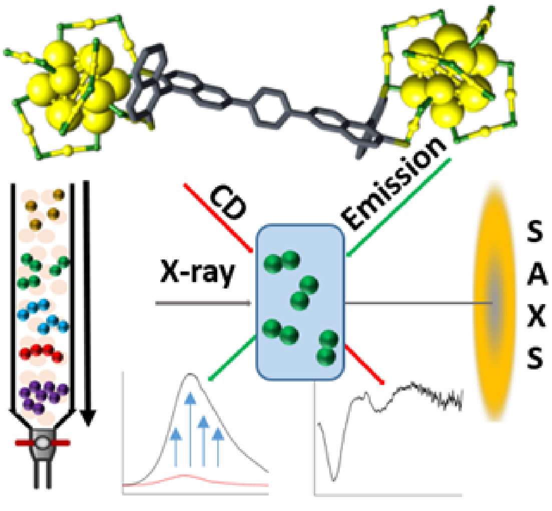
[1]Hailin Cong, Bing Yu, Jianguo Tang,ab Zejing Li and Xuesong Liu, *Chem. Soc. Rev.*, **2013**, 42, 7774
[2]Katherine R. Phillips, Grant T. England, Steffi Sunny, Elijah Shirman, Tanya Shirman, Nicolas Vogelde and Joanna Aizenberg, *Chem. Soc. Rev.*, **2016**, 45, 281--322
[3]Deyu Liu, Xinxing Peng, Binghui Wu, Xueyun Zheng, Tracy T Chuong, Jialuo Li, Shigang Sun, Galen D. Stucky, *J. Am. Chem. Soc.,* **2015**, 137, 9772−9775

Bridging $Au_{25}(SR)_{18}$ nanoclusters with a new chiral dithiol to form extremely stable dimers and trimers.

M. Swierczewski[1], F. Cousin[2], E. Banach[1], A. Ziarati[1], R. Azoulay[1], T. Bürgi [1]*, L. Lee[2]*

[1]Department of Physical Chemistry, University of Geneva, Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland, [2]Laboratoire Léon Brillouin, UMR12 CEA-CNRS, Université Paris-Saclay, CEA-Saclay, 91191 Gif-sur-Yvette Cedex, France

Thiolate-protected gold nanoclusters are atomically precise nanoparticles with a size typically lower than 2 nm. Due to their unusually high monodispersity, they exhibit interesting physical and chemical properties leading to many potential applications in sensing, catalysis and biology. The assembly of gold nanoclusters into superstructures with controlled morphologies presents an innovative pathway for fabrication of novel materials through the emergence of distinct properties as well as the enhancement of the existing optical and electronic effects via their collective action.[1-2] A new bidentate chiral ligand, (1R,1'R)-6,6'-(1,4-phenylene)di-1,1'-binaphthyl-2,2'-dithiol or diBINAS, is utilized to bridge $Au_{25}(SR)_{18}$ nanocluster monomer units to form dimers, trimers and larger multimers. Separation by size-exclusion chromatography allows the isolation of fractions that do not undergo further ligand exchange thanks to the bidentate nature of the linker. The products are, therefore, extremely stable and pure, which is confirmed by very well-defined small-angle X-ray scattering (SAXS) curves fitted using the pearl-necklace model. Additional structural details are studied by diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY NMR), transmission electron microscopy (TEM) and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). Significant changes in the optical properties brought about by the introduction of the linker are analyzed by UV-Vis and fluorescence spectroscopies, with the latter demonstrating a strong emission enhancement exhibited by the linked system. Furthermore, emergent chiral characteristics are studied by circular dichroism (CD). The high stability of the isolated products associated with the bidentate bridging is substantiated by ineffectiveness of any unlinking reaction attempts. Due to the geometry constraints of the nanocluster-ligand-nanocluster assembly relying on the favored interstaple bonding, diBINAS can be regarded as a templating molecule, which brings the bidentate linkers a step closer towards directed self-assembly.



[1] Annelies Sels, Giovanni Salassa, Fabrice Cousin, Lay-Theng Lee, Thomas Bürgi, *Nanoscale,* **2018,** *10* (26), 12754-12762.

[2] Karolina Sokolowska, Eero Hulkko, Lauri Lehtovaara, Tanja Lahtinen, *The Journal of Physical Chemistry C,* **2018,** *122* (23), 12524-12533.

Bimolecular Photoinduced Electron Transfer in Non-Polar Solvents

P. Verma[1], E. Vauthey[1]*

[1]Physical Chemistry Department, University of Geneva

Bimolecular photoinduced electron transfer (ET) in non-polar solvents is still poorly understood. In order to get a deeper insight into the relevant reaction coordinate and the nature of the product, we are applying a variety of ultrafast spectroscopic techniques. In many cases, the electronic absorption spectrum of the chromophore exhibits significant broadening and red shift upon addition of quencher, suggesting the presence of highly coupled reactants pairs. [1] Consequently, different distributions of reactant pairs can be photoselected by tuning the excitation wavelength.

We will present our investigation of the effect of the excitation wavelength on the electron transfer quenching dynamics in non-polar solvent using Broadband Fluorescence Up-conversion Spectroscopy (FLUPS) [2] with sub 100 fs resolution.

[1] Christoph Nançoz, Christopher Rumble, Arnulf Rosspeintner and Eric Vauthey, *Journal of Chemical Physics*, **152** , **2020**, 244501

[2] Mario Gerecke, Genaro Bierhance, Michael Gutmann, Nikolaus P. Ernsting, Arnulf Rosspeintner, *Review of Scientific Instruments*, **87**, 2016, 053115

Thermal Decomposition Mechanism of Vanillin, a Lignin Model Compound

X. Wu[1], S. Bjelić[1], P. Hemberger[1], A. Bodi[1]*

[1]Paul Scherrer Institute, Laboratory for Synchrotron Radiation and Femtochem

Numerous lignin valorization strategies involve thermal conversion, and reaction paths towards phenolic fine chemicals are of particular interest. Vanillin combines widespread lignin functional groups, and its chemistry is thus of interest to understand lignin's potential role as a feedstock for biomass-based aromatics.

We studied the thermal decomposition of vanillin in a low-pressure pyrolysis microreactor by combining double imaging photoelectron photoion coincidence spectrometry and vacuum ultraviolet synchrotron radiation. The majority of the former could be assigned isomer-specifically based on their photoion mass-selected threshold photoelectron spectrum together with Franck–Condon simulations and reference photoelectron spectra. The fragmentation pathways have been explored computationally to determine the unimolecular and bimolecular reactions driving thermal decomposition. The unimolecular mechanism is initiated by methyl loss, followed by sequential CO losses. The methyl-loss fragment is highly reactive and readily undergoes H-transfer in a self-reaction, which initiates the bimolecular mechanism.

The unimolecular decomposition pathways can be summarized as:

$$[\mathbf{1}] \rightarrow [\mathbf{2}] + \mathrm{CH_3} \rightarrow \begin{cases} \rightarrow [\mathbf{19}] + \mathrm{CH_3} + \mathrm{CO} \rightarrow [\mathbf{6}] + \mathrm{CH_3} + 2\,\mathrm{CO} \\ \rightarrow [\mathbf{4}] + \mathrm{CH_3} + \mathrm{CO} \rightarrow \begin{cases} \rightarrow [\mathbf{6}] + \mathrm{CH_3} + 2\,\mathrm{CO} \\ \rightarrow [\mathbf{8}] + \mathrm{CH_3} + \mathrm{CO} + \mathrm{H} \\ \rightarrow [\mathbf{12}] + \mathrm{CH_3} + \mathrm{CO} + \mathrm{H} \end{cases} \end{cases}$$

The *m/z* 81 fragment [**6**] may lose H and the two *m/z* 108 fragments [**8**] and [**12**] may lose CO sequentially to generate *m/z* 80, [**7**], which is a precursor of the final observed major product, 1-butene-3-yne (C_4H_4, *m/z* 52).

The high-energy unimolecular decomposition channels of [**2**] by H loss to [**21**] and [**22**] at *m/z* 136 cannot compete with CO loss. Instead, only [**21**] is found and shown to be the product of the bimolecular H-transfer reaction of 2 × [**2**] → [**21**] + 3,4-dihydroxybenzaldehyde at *m/z* 138. Dihydroxybenzaldehyde is quite stable thermally, but [**21**] is only weakly bound and can lose CO to produce [**12**] at *m/z* 108 over a barrier of only 1.73 eV, which merges the uni- and bimolecular pathways again. These mechanistic insights, especially the high (self-)reactivity of the methyl-loss intermediate and the resulting high preponderance of bimolecular chemistry leading to inert dihydroxybenzaldehyde will guide process design involving vanillin and vanillin-like feedstocks.

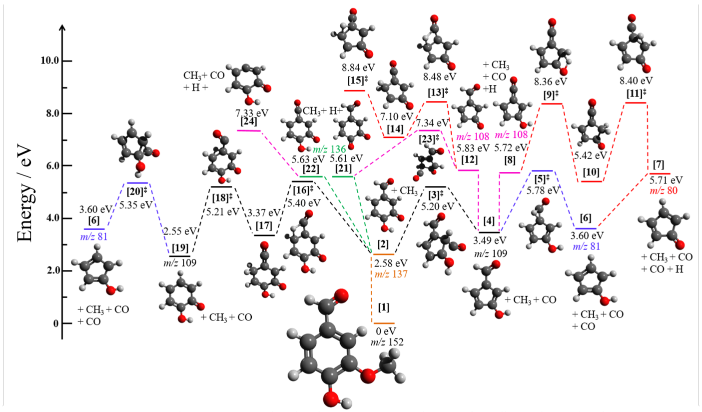


Figure 1. Computed primary unimolecular decomposition pathways of vanillin at the G4 level.

Conformationally controlled ionic Diels-Alder reactions in the gas phase

L. Xu[1], A. Kilaj[1], P. Stranak[1], J. Wang[2], J. Küpper[2,3]*, S. Willitsch[1]*

[1]Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland, [2] Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany, [3]Department of Chemistry, Universität Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

Conformers, i.e., rotational isomers, are the dominant form of isomers in complex molecules. Different conformers exhibit unique reactivities [1-3], and the study of the influence of molecular geometry on chemical reactivity is one of the eminent problems in chemistry. The Diels-Alder (DA) reaction [4] is one of the most important cycloaddition reactions. In order to explore the role of molecular conformation in DA reactions, we recently conducted a study of the conformational specificities of the prototypical ionic system *gauche/s-trans* 2,3-dibromobuta-1,3-diene(DBB) and *s-cis/s-trans* methyl vinyl ketone(MVK) reacting with trapped propene ions. The individual conformers of the neutral dienes were spatially separated in an electrostatically deflected molecular beam [1] and reacted with sympathetically cooled propene ions. Our results show that *gauche*-DBB reacted twice as fast as *s-trans*-DBB, but *s-cis*-MVK is surprisingly nearly eight times faster than *s-trans*-MVK. These surprising findings, which are at variance with the textbook mechanism for DA reactions, were rationalized using electronic-structure and adiabatic-capture calculations, which illustrate the influence of the diene conformation on the reactivity in these systems. As a further development of our experimental methodology with the aim to achieve complete conformational control over both reaction partners, we present first results on the loading and sympathetic cooling of conformationally selected ions in the ion trap.

[1] Y.-P. Chang, K. Dlugolecki, J. Küpper, D. Rösch, D. Wild, and S. Willitsch, *Science,* **2013**, 342, 98-101.

[2] D. Rösch, S. Willitsch, Y.-P. Chang, and J. Küpper, *The Journal of chemical physics,* **2014**, 140, 03B624_1.

[3] A. Kilaj, H. Gao, D. Rösch, U. Rivero, J. Küpper, and S. Willitsch, *Nature communications,* **2018,** 9(1), 1-7.

[4] O. Diels and K. Alder, *Justus Liebig's Annals of Chemistry.* **1928**; 460 (1): 98-122.

New methods for studying state and conformational effects in chemi-ionisation reactions in the gas phase

A. Mishra[1], L. Ploenes[1], P. Stranak[1], S. K. Kim[2]*, S. Willitsch[1]*

[1]Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland, [2] Department of Chemistry, KAIST, Daejeon 34141, Republic of Korea

Conformers are the dominant isomers of complex molecules. The conformation of a molecule can have pronounced effects on its chemical reactivity. However, because they often interconvert into one another under ambient conditions, individual molecular conformations are difficult to isolate. Consequently, only sparse experimental data exists on the chemical properties of distinct conformers [1]. Over the past years, we have developed experimental methods to study conformational effects in ion-molecule reactions under single-collision conditions [1]. Here, we report on an extension of these methods and present a new crossed-molecular-beam setup equipped with an electrostatic deflector which enables the spatial separation of different conformers or individual rotational states of molecules based on their effective dipole moments. The products of chemical reactions of the separated conformers are monitored by time-of-flight mass spectrometry (TOF-MS) and velocity-mapped ion imaging (VMI) [2].

As a first application of this new methodology, state- and conformationally specific chemi-ionisation reactions of OCS and hydroquinone with metastable neon atoms were investigated. Pronounced state- and conformation-specific effects on the product branching ratios of both reactions were observed. Moreover, in a collaboration with the Korean Advanced Institute of Science and Technology (KAIST), we are currently undertaking a combined study of the photochemistry, photoionisation and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene as a prototypical system. The aim of these investigations is to gain a comprehensive understanding of the role of molecular conformations in unimolecular and bimolecular reactivity. To get more insight into the reaction dynamics of these systems, we are also upgrading our existing VMI to a coincidence experiment allowing the imaging of both ions and electrons produced in chemi-ionisation reactions [3].

[1] S. Willitsch, Adv. Chem. Phys., 2017, 162, 307.
[2] L. Ploenes, P. Strank and S. Willitsch, *arXiv:2105.06427*.
[3] B. Margulis, J. Narevicius & E. Narevicius, *Nat. Commun.,* **2020**, 11, 3553.