CHIMIA

CHIMIA 2022, Volume 76
ISSN 0009-4293
www.chimia.ch
Supplementa to Issue 7-8/2022

SCS
Swiss Chemical
Society

SCS Fall Meeting 2022
Lecture, Short Talk and Poster Abstracts

Session of Physical Chemistry

September 8, 2022
University of Zurich, Irchel Campus
https://fm22.scg.ch

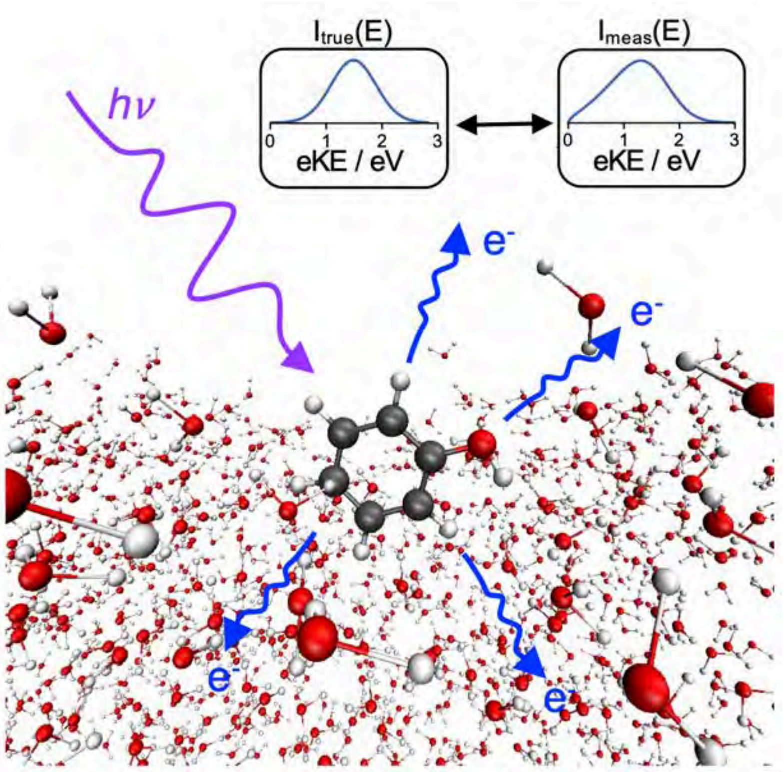
Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

UV photoelectron spectroscopy of aqueous solutions

H. H. Fielding[1]

[1]Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.;
h.h.fielding@ucl.ac.uk

Ultraviolet (UV) photoelectron spectroscopy provides a direct way of measuring valence electronic structure; however, its application to aqueous solutions has been hampered by a lack of quantitative understanding of how inelastic scattering of low energy electrons (< 6 eV) in liquid water distorts the measured electron kinetic energy distributions. We have developed a method for retrieving true UV photoelectron spectra of aqueous solutions [1]. In this talk, I will discuss our method and how we have applied it to retrieve information about the electronic structure and photooxidation dynamics of aqueous solutions of biologically relevant organic molecules [1,2].



[1] M. S. Scholz, W. G. Fortune, O. Tau and H. H. Fielding, *under review*, **2022**.
[2] O. Tau, A. Henley, A. N. Boichenko, N. N. Kleshchina, R. Riley, B. Wang, D. Winning, R. Lewin, J..M. Ward, I. P. Parkin, H. C. Hailes, A. V. Bochenkova, and H. H. Fielding,*Nature Commun.* **2022** 13, 507.

Conformationally-selected ions for reactions with conformationally-selected molecules

J. Toscano[1], L. Xu[1], S. Willitsch[1]*

[1]Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056 Basel, Switzerland

style="text-align: justify;">The different effective dipole moment of conformational isomers allows for their spatial separation by means of electrostatic deflection, enabling their individual reactivity to be investigated [1]. Recently, the conformer-specific polar cycloaddition of dibromobutadiene (DBB) with trapped propene ions has shown that both *gauche* and *s-trans* DBB conformers display capture-limited reaction rates [2]. The reaction was found to occur through both a concerted and a stepwise reaction mechanism, despite the spatial rearrangement of atoms necessary in *s-trans* DBB for the latter to take place. These results were obtained by selectively aiming the molecular beam containing either one of the two conformers at a static target of propene ions embedded within a laser-cooled Coulomb crystal of calcium ions. In order to gain further control over the reaction partners, we now wish to also select the conformational isomer of the ionic reactant. Here, we discuss the generation of conformationally-selected ionic targets of *3*-aminostyrene to enable the study of fully-conformationally-selected ion–molecule reactions. Following the detailed study of the isomer-selective ionisation of the two different *3*-aminostyrene conformers, we aim to individually load them into a Coulomb crystal to determine their stability to such environment.

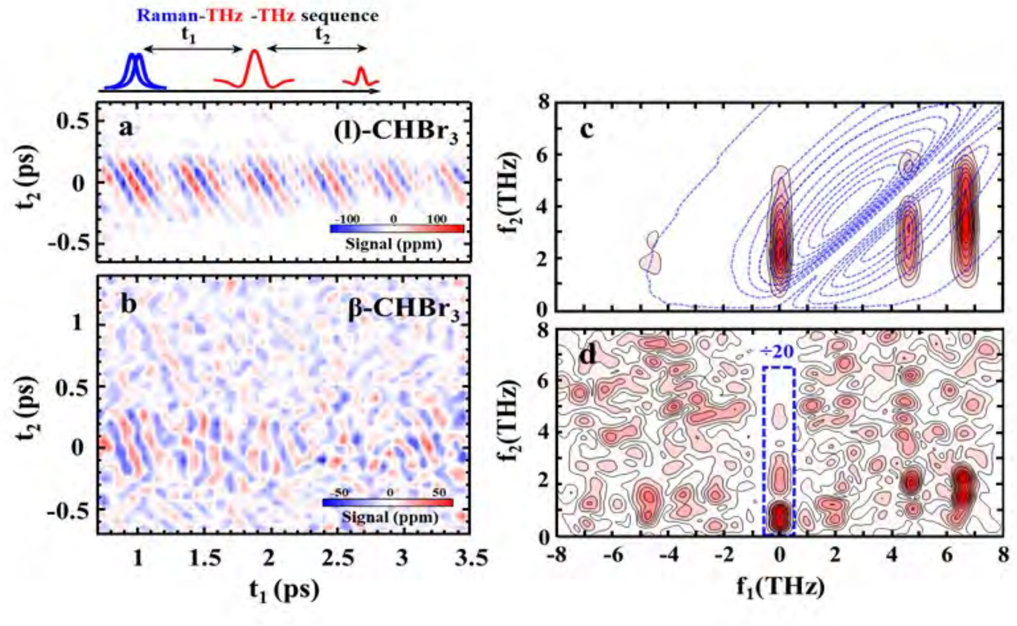
[1] Y.-P. Chang, K. Długołęcki, J. Küpper, D. Rösch, D. Wild and S. Willitsch, *Science*, **2013**, 342, 98.
[2] A. Kilaj, J. Wang, P. Straňák, M. Schwilk, U. Rivero, L. Xu, O. A. von Lilienfeld, J. Küpper and S. Willitsch, *Nat. Commun.*, **2021**, 12, 6047.

Low-frequency anharmonic couplings in bromoform revealed from 2D Raman-THz spectroscopy: From the liquid to the crystalline phase

S. J. Mousavi[1], A. Berger[1], A. Shalit[1], P. Hamm [1]*

[1]Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

Hybrid two-dimensional (2D) Raman-THz spectroscopy is a novel spectroscopic technique to study coupling between low-frequency molecular motions in the THz frequency region (0.1-10 THz) [1]. Recently, we demonstrated that this technique can be used to observe vibrational couplings between sharp intramolecular and broad intermolecular vibrational modes in liquid $CHBr_3$ and binary $CHBr_3$-MeOH mixture [2, 3]. In this work [4], 2D Raman-THz spectroscopy is used to study the crystalline β-phase of $CHBr_3$, expanding the applicability of this technique to solid samples at cryogenic temperatures. Moreover, this study elucidates the mechanism responsible for the observed cross peak features by providing new experimental evidence for anharmonic couplings between intra-/intermolecular vibrational modes. Finally, significant change in the spectral shape of the cross peaks upon the phase transition from liquid $CHBr_3$ to β-$CHBr_3$, in agreement with the corresponding THz absorption spectra, strongly supports our interpretation, and excludes the possibility of instantaneous interactions of THz field with intramolecular modes.



[1] Janne Savolainen, Saima Ahmed, and Peter Hamm, *Proc. Natl. Acad. Sci.*, **2013**, 110, 20402-20407.
[2] Gustavo Ciardi, Arian Berger, Peter Hamm, and Andrey Shalit, *J. Phys. Chem. Lett.*, **2019**, 10, 4463-4468.
[3] Andrey Shalit, Seyyed Jabbar Mousavi, and Peter Hamm, *J. Phys. Chem. B*, **2021**, 125, 581-586.
[4] Seyyed Jabbar Mousavi, Arian Berger, Peter Hamm, and Andrey Shalit, *J. Chem. Phys.*, **2022**, 156, 174501.

Chiral control of spin-crossover dynamics in Fe(II) complexes

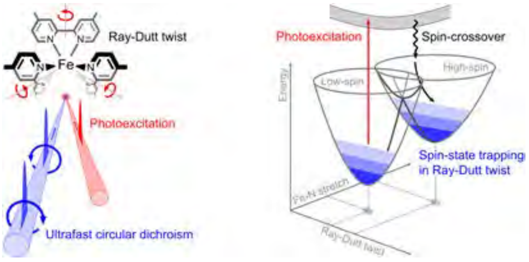
M. Oppermann[1], F. Zinna[2,3], J. Lacour[3], M. Chergui[1]

[1]Laboratory of Ultrafast Spectroscopy (LSU) and Lausanne Centre for Ultrafast Science (LACUS), École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland, [2]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Giuseppe Moruzzi 13, 56124 Pisa, Italy , [3]Département de chimie organique, Université de Genève, Quai Ernest Ansermet 30, 1211 Genève 4, Switzerland

Iron(II)-based spin-crossover (SCO) complexes hold tremendous promise as multifunctional switches in molecular devices due to a low-spin (LS) to high-spin (HS) state transition that can be triggered by light, pressure and temperature [1]. However, whilst ultrafast spectroscopy studies have achieved a detailed understanding of the photoinduced forward-SCO to the HS state, the backward-SCO mechanism has remained unresolved – despite its crucial role in governing the technologically relevant lifetime of the HS state. Through ultrafast circular dichroism experiments on a prototypical chiral Fe^{II} complex, we now show that the backward-SCO is governed by a symmetry-breaking torsional twist in addition to the well-known symmetric stretch mode of the metal-ligand bonds [2].

To this end, we characterize the back-SCO dynamics of the tris-chelate Fe^{II}(4,4'-dimethyl-2,2'-bipyridine)$_3$ in solution, associated for stereocontrol with enantiopure Δ- or Λ-TRISPHAT anions [3]. Combining ultrafast circular dichroism [4] with transient absorption and anisotropy measurements, we find that the HS state decay is accompanied by ultrafast changes of its optical activity, reflecting the coupling to an asymmetric torsional twisting mode known as the Ray-Dutt twist. Quite remarkably, the diastereoselective ion-pairing suppresses the vibrational population of the newly identified reaction coordinate, thereby trapping the HS state in the potential of the Ray-Dutt twist and achieving a four-fold extension of the HS state's lifetime.

More generally, our results finally provide a complete reaction mechanism for the Fe^{II} backward-SCO, which motivates the synthetic control of the involved torsional modes as a complementary route to manipulate the SCO dynamics of Fe^{II} complexes.



[1] G. Molnár, S. Rat, L. Salmon, W. Nicolazzi, A. Bousseksou, *Adv. Mater.* **2018**, 30, 1703862
[2] M. Oppermann, F. Zinna, J. Lacour, M. Chergui, *Nat. Chem. (in press),* DOI: 10.1038/s41557-022-00933-0
[3] J. Lacour, J. J. Jodry, C. Ginglinger, S. Torche-Haldimann, *Angew. Chem. Int. Ed.* **1998**, 37, 2379
[4] M. Oppermann, B. Bauer, T. C. Rossi, F. Zinna, J. Helbing, J. Lacour, M. Chergui, *Optica* **2019**, 6, 56

Source suppression and spin dynamics in hyperpolarized liquid state NMR spectroscopy by optically polarized crystals

F. De Biasi[1], P. Moutzouri[1], A. J. Parker[2], J. W. Blanchard[2], T. R. Eichhorn[2], I. Schwartz[2], L. Emsley[1]*

[1]Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, [2]NVision Imaging Technologies GmbH, 89081 Ulm, Germany

Nuclear magnetic resonance spectroscopy is undoubtedly one of the most versatile techniques to investigate matter at the atomic scale. Nonetheless, low sensitivity always limited the application of magnetic resonance experiments to very diluted samples. To circumvent this issue, some of us recently reported the dissolution of optically polarized naphthalene crystals doped with pentacene for the hyperpolarization of small molecules in liquids at low field.[1] This innovative method exploits the intermolecular nuclear Overhauser effect (NOE) to transfer magnetization from the extremely polarized naphthalene protons to the other species in solution, enhancing their signal by up to three orders of magnitude. Indeed, despite the very low efficiency of intermolecular cross relaxation, the starting polarization of the naphthalene protons is so high that a considerable amount of magnetization is exchanged during the process. More recent experiments confirm that it is possible to obtain significant enhancements also at higher fields. Although the use of optically polarized naphthalene provides a completely new and general way for hyperpolarization in organic solvents, it also poses some practical challenges, especially because of its huge residual magnetization that causes detrimental effects such as radiation damping and receiver saturation. Not only, because of the size dependence of longitudinal relaxation at high fields, strategies for efficient polarization of medium and large molecules in the T_1 minimum range must be used.

Here we demonstrate that conventional signal suppression sequences can be successfully implemented to overcome both radiation damping and receiver saturation. We also show that polarization of large systems at high field can be performed by tuning the experiment or by exploiting additional interactions between the source and the target species.

[1] Eichhorn, *et al.*, *J. Am. Chem. Soc.*, **2022**, 144, 2511–2519

Paramagnetic Properties of Neutral Sodium Doped Solvent Clusters

D. Borgeaud[1], J. V. Barnes[1], E. Simmen[1], H. Yang[1], B. L. Yoder[1], R. Signorell[1]*

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

Since the discovery of concentration-dependent colors of alkali metal-ammonia solutions in the early 19th century [1], excess electrons in alkali metal solutions have been found to be important in different areas. They are ubiquitous in liquid-phase chemistry [2] and play an essential role in chemical reactions [3], and biology [4]. Extensive experimental and theoretical work has been done on solvated electrons in alkali metal solutions [2]. However, the underlying correlation effects of the solvated electrons are still not well understood. While magnetic measurements have probed such effects on alkali metal solutions [5],[6], the diamagnetic and paramagnetic species have not yet been identified in such bulk phase experiments [2].

We present a study of the magnetic properties of sodium-doped ammonia, water, dimethyl ether, and methanol clusters ($Na(Solv)_n$, n=1-4) [7]. Using a pulsed Stern-Gerlach deflector, we measure the magnetic deflection of a neutral cluster beam. The experimental deflection is compared with molecular dynamics simulations based on the Zeeman interaction of a free spin ½ system.

The comparison reveals unperturbed magnetic properties of a spin ½ system for the smallest clusters $NaNH_3$ and NaH_2O. Larger clusters $Na(NH_3)_n$ (n=2-4), $Na(H_2O)_n$ (n=2-4), $Na(DME)_n$ (n=1-3) and $Na(MeOH)_n$ (n=1-4), by contrast show reduced deflection compared with a spin ½ system. These deviations from a spin ½ behavior are attributed to intracluster spin-relaxation effects -occurring on time scales similar to or faster than the experiment. The determination of spin relaxation times for these systems allows us to identify experimental trends regarding their magnetic behavior. The observed trends are discussed in terms of spin and rotational angular momentum interactions of thermally accessible rovibrational eigenstates.

[1] W. Weyl, *Ann. Phys.*, **1864**, 199, 355.
[2] E. Zurek, P. P. Edwards and R. Hoffmann, *Angew. Chem., Int. Ed.*, **2009**, 48, 8198.
[3] Bruce C. Garrett, et al., *Chem. Rev.,* **2005**, 105, 355.
[4] Elahe Alizadeh, Thomas M. Orlando, and León Sanche, *Annu. Rev. Phys. Chem.,* **2015**, 66, 379.
[5] N. W. Taylor and G. N. Lewis, *PNAS*, **1925**, 11, 456.
[6] S. Freed and N. Sugarman, et al., *J. Chem. Phys.*, **1943**, 11, 354.
[7] J. V. Barnes, et al., *Phys. Chem. Chem. Phys.*, **2021**, 23, 846.

Climeworks – from ETH start up to the world’s leading direct air capture company

C. Gropp[1,2], N. Casas[1], A. Vargas[1]

[1]Climeworks, Birchstrasse 155, 8050 Zurich, Switzerland, [2]Cornelius.gropp@climeworks.com

style="font-weight: 400;">Removing carbon dioxide from the atmosphere—legacy emissions and future unavoidable emissions—has by now become a must to meet climate goals, as pointed out by the latest IPCC reports,[1] and is set to become common practice within the next decades.

Climeworks was founded in 2009 by two PhD students from ETH and has since grown to be the leader in technological carbon removal through direct air capture (DAC). Much of Climeworks’ focus has been on building plants and advancing engineering and sorbent technologies. Here, we present Climeworks’ synergies between engineering, materials science and chemistry to advance CO2 capture from air and its safe storage. This effort is built on a platform for material development with many of the tools that modern chemistry can provide us.

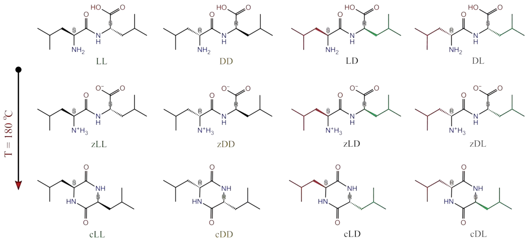
[1] https://www.ipcc.ch/reports/; accessed on August 05 2022

Solid-State Synthesis of cyclo Leu-Leu: The role of Packing

A. F. Perez Mellor[1], X. Wang[1], D. Rosa Gastaldo[1], C. Besnard [2], N. Giamboni[1], J. Brazard[1], T. Adachi[1], T. Buergi[1]*

[1]Department of Physical Chemistry, University of Geneva, Switzerland, [2]Laboratory of crystallography, University of Geneva, Switzerland

Oligopeptides are well known for their self-assembling ability and application in the nanomaterials industry [1]. The variety of self-assembled nanostructures opens up a wide range of applications in biosensors, organic semiconductors, and drug delivery [2-4]. Their supramolecular structure and chirality depend on monomers' absolute configuration (AC) [5]. It has been shown that some oligopeptides undergo cyclization under heat treatment [6]. The linear dipeptide (L)Leu-(L)Leu is one such example [7].



In this talk, I will present a comprehensive spectroscopic characterization of the cyclo Leu-Leu solid-state synthesis, see Figure. It will be divided into three parts. First, I will discuss the role of packing in the synthesis using transient absorption IR spectroscopy on the time scale of seconds. The second part will be devoted to investigating morphological changes using optical and Raman microscopy. Finally, I will conclude by evaluating the conservation of the absolute configuration of the residues using vibrational circular dichroism and nuclear magnetic resonance.

[1] Manchineella S, et al. Chempluschem (2017): 88-106. [2] Joon Seok Lee, et al. Angewandte Chemie Int Ed. (2011): 1196-1199. [3] Rondes F. Silva, et al. Langmuir (2013): 10205-10212. [4] S. Kogikoski, et al. Phys Chem Chem Phys (2016): 3223-3233. [5] Görbitz, et al. Chem. Eur. J. (2001): 5153-5159. [6] Ziganshin, M.A, et al. J Therm Anal Calorim (2016). [7] Marat A. Ziganshin, et al. J. Phys. Chem. B (2017).

The travels of hydrogen over the catalyst surface

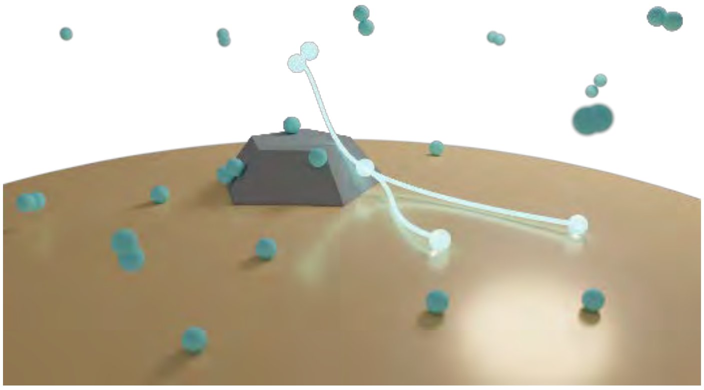
A. Beck[1], L. Artiglia[2], A. Kleibert[2], H. Frey[1], J. A. van Bokhoven[1,2]*

[1]ETH Zürich, [2]Paul Scherrer Institute

Hydrogen spillover is the surface migration of activated hydrogen atoms from a metal catalyst particle, on which molecular hydrogen dissociates, onto the catalyst support. It is of high importance for heterogeneous catalysis, hydrogen storage materials, and fuel cell technology. Its occurrence on metal oxide surfaces is established [1], yet questions remain about how far from the metal center spillover is reaching. Achieving spatial understanding of this process remains a challenging quest since the relevant materials are usually complex nanomaterials. We chose the approach to translate the complex structure of metal oxide catalysts into planar model representations [2]. This approach allows the use of surface sensitive techniques that otherwise would not provide sufficient spatial information.

By employing X-ray photoelectron emission spectroscopy (XPS) and microscopy (XPEEM), both methods which are highly sensitive to the chemical state of the surface, we were able to gather direct evidence that spillover is occurring over several microns across the oxide surface [3]. In this short communication, the propagation of hydrogen across the metal oxide originating from deposited platinum will be presented in a time resolved movie with spatial resolution of the chemical states of the oxide surface.

These findings and the derived understanding at which temperatures hydrogen spillover in affecting the surface will help to improve and exploit the process of hydrogen spillover for application.



[1] Prins R. *Chem. Rev.*, **2012**, 112(5), 2714-2738
[2] Karim W., Spreafico C., Kleibert A., Gobrecht J., Vandevondele J, Ekinci Y., van Bokhoven J. A., *Nature*, **2017**, 541(7635), 68-71.
[3] Beck A., Frey H., Kleibert A., van Bokhoven J. A. *in preparation*

Flash heating water through no man's land — Structural evolution and crystallization kinetics

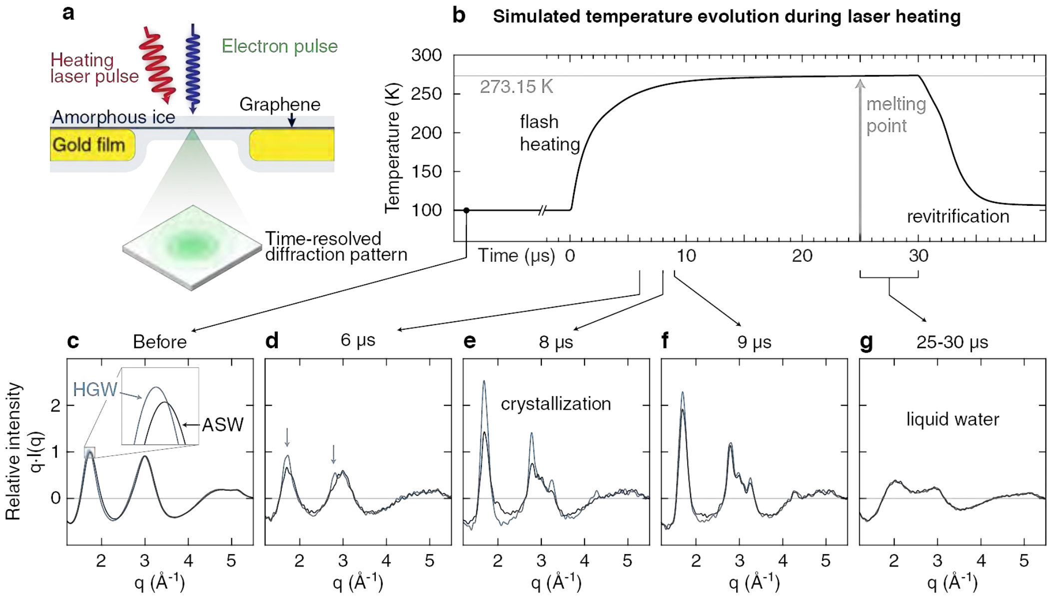
C. R. Krüger[1], G. Bongiovanni[1], N. J. Mowry [1], M. Drabbels[1], U. J. Lorenz[1]*

[1]Laboratory of Molecular Nanodynamics, EPFL, Lausanne, Switzerland

We present a new experimental scheme to study the thermodynamic and kinetic properties of water in its supercooled regime, nicknamed "no man’s land". The experimental approach is illustrated in panel a below. First, a thin layer of vapour deposited amorphous ice is grown on a graphene substrate before being flash heated with a laser. The simulated temperature evolution is depicted in panel b. After an initial steep rise, the temperature begins to level off between 5-10 µs and the sample liquifies at 25 µs. The structural evolution of water is measured during this process by recording diffraction pattern with high-brightness electron pulses of 2µs duration.[1] Finally, the laser pulse is turned off after 30 µs which results in rapid cooling (10^7 K/s) and revitrification of the sample to form hyperquenched glassy water (HGW).[2] The sample is then flash heated a second time to compare the structural evolution of ASW and HGW.

Panels c-g show the time-resolved diffraction pattern of ASW (black) and HGW (blue) during flash melting at the important time steps. Interestingly, both ices crystallize before melting, even though they revitrify after the end of the laser pulse to form HGW, suggesting that the critical heating rate to outrun crystallization is significantly higher than the respective cooling rate during hyperquenching. Moreover, we find a different structural evolution of the two ices in no man’s land as well as in their crystallization kinetics. Our data shows, that HGW crystallizes about 1.5 µs earlier than ASW.

Our experiments shed light into the complex dynamic behavior of water in no man's land and promise to help better understand the mysteries of this liquid we all depend on.



[1] P. K. Olshin, G. Bongiovanni, M. Drabbels, U. J. Lorenz, *Nano Lett.* **2020**, *21*, 612-618.
[2] J. M. Voss, O. F. Harder, P. K. Olshin, M. Drabbels, U. J. Lorenz, *Chem. Phys. Lett.* **2021**, *778*, 138812.

EPR investigation of metal oxide catalysts: ferromagnetic behaviour induced by oxygen vacancies

M. Agrachev[1], T. Pinheiro Araújo[2], C. Mondelli[2], T. Zou[2], K. M. Engel[2], R. N. Grass[2], W. J. Stark[2], O. V. Safonova[3], S. Mitchell[2], J. Pérez-Ramírez[2]*, G. Jeschke[1]*

[1]Laboratory of Physical Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland, [2]Institute of Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland, [3]Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen, Switzerland

Pure and doped metal oxides are widely used for many catalytic applications. This work mainly focuses on In_2O_3-based catalysts for CO_2 conversion to methanol through hydrogenation. The catalytic activity of these materials is thought to be related to the presence of oxygen vacancies, which act as catalytic centers. Combining In_2O_3 with ZrO_2 support and doping it with Pd provides increased stability against sintering and H_2 splitting ability, respectively.[1-2] Moreover, ZrO_2 and Pd ions could also be involved in vacancies creation and annihilation and could thus be crucial for the catalytic mechanism.

It is widely known that oxygen vacancies can trap unpaired electrons, thus becoming paramagnetic, and can therefore be studied by EPR. Isolated paramagnetic vacancies (also called color centers) give rise to sharp, usually almost isotropic signals with g factors near to g_e.[3] However, as we show here, when the density of vacancies is very high, unexpected broad signals appear, with features characteristic of ferromagnetic systems. These signals can be attributed to exchange-coupled magnetic polarons. The detailed EPR investigation of these signals provides important information about the structure and the dynamics of different kind of vacancies. Moreover, a quantitative approach to ferromagnetic signals and EPR-detected hysteresis phenomena is proposed.

The importance of these findings is related not only to metal oxide catalysis, but also to the fundamental understanding of the magnetic properties of metal oxides and provide a methodology to produce room temperature ferromagnets in a controlled fashion.

[1] Matthias S. Frei, Cecilia Mondelli, Rodrigo García-Muelas, Klara S. Kley, Begoña Puértolas, Nú López, Olga V. Safonova, Joseph A. Stewart, Daniel Curulla Ferré, Javier Pérez-Ramírez, *Nat. Commun.* **2019**, 10, 3377.
[2] Matthias S. Frei, Cecilia Mondelli, Alessia Cesarini, Frank Krumeich, Roland Hauert, Joseph A. Stewart, Daniel Curulla Ferré, Javier Pérez-Ramírez, *ACS Catal.* **2020**, 10, 2, 1133-1145.
[3] Chengsheng Yang, Chunlei Pei, Ran Luo, Sihang Liu, Yanan Wang, Zhongyan Wang, Zhi-Jian Zhao, Jinlong Gong *J. Am. Chem. Soc.* **2020**, 142, 46, 19523-19531.

At the Cutting Edge – NMR Studies Reveal Distinct Reactivities of Specific Edge Sites on Needle-Shaped γ-Al_2O_3 Nanocrystals Toward Pt(II) Precursors

L. A. Völker[1], J. Meyet[1], L. Rochlitz[1], C. Copéret [1]*

[1]ETH Zürich

Despite being a crucial component of many relevant catalytic systems such as Pt/Al_2O_3, the surface features of γ-Al_2O_3 remain poorly understood to date. Only very recently, the potential role of highly reactive edge sites was introduced to the research community. Those edge sites are proposed to be contained within the high-field signal (approx. 0 ppm) of the ^1H NMR spectrum of γ-Al_2O_3. [1] By combining the development of well-defined, needle-shaped γ-Al_2O_3 nano-crystals having a high relative fraction of edge sites with state-of the art 2D and pseudo-3D solid-state NMR spectroscopy, we have been capable to go beyond what has been previously reported and resolved two distinct hydroxyl sites in the high-field ^1H-NMR signal of our γ-Al_2O_3 material. [2]

Here, we capitalize on these findings and compare the NMR signatures of our γ-Al_2O_3material before and after grafting of [Pt(COD)Me_2]. Surprisingly, the resolved hydroxyl sites possess different reactivities toward this molecular platinum-precursor as revealed by single-quantum-double-quantum ^1H-^1H and recoupling-time encoded {^{27}Al}-^1H D-HMQC NMR spectroscopy. The herein presented analysis does not only provide a complementary tool to ^{195}Pt-NMR spectroscopy for the analysis of the surface-organometallic chemistry of platinum on alumina materials, it might also enable the tailored design of γ-Al_2O_3 nanocrystals which are ideal supports for the synthesis of mono-dispersed Pt nanoparticles.

[1] Batista A.T.F.; Wisser D.; Pigeon T.; Gajan D.; Diehl F.; Rivallan M.; Catita L.; Gay A.-S.; Lesage A.; Chizallet C.; Raybaud, P. *J. Catal.* **2019**, 378, 140-143.
[2] Völker, L. A; Meyet, J.; Berkson Z.J.; Rochlitz, L.; van Bokhoven, J. A.; Copéret, C. *J. Phys. Chem. C.* **2022**, 126, 14, 6351-6360.

Synthesis and structural determination by X-ray crystallography of metal nanoclusters

K. Ahmed Ethmane[1], A. Rosspeintner[1], E. Bordignon[1], T. Bürgi[1]*, C. Besnard[2]*

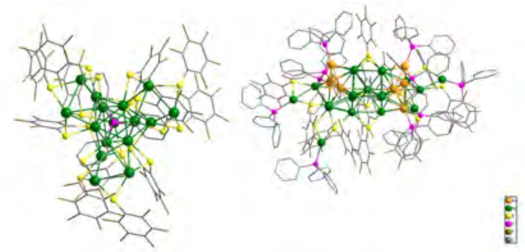
[1]University of Geneva, Department of Physical Chemistry, Quai Ernest-Ansermet 30, 1205 Genève,
[2]University of Geneva, Laboratory of Crystallography, Quai Ernest-Ansermet 24, 1205 Genève

Noble metal nanoclusters are a special class of nanomaterials with sizes varying between 1 and 3 nm which exhibit very peculiar molecule-like properties. These properties make them promising candidates for various applications including in catalysis, bioimaging or sensing. [1]

These nanoclusters are atomically precise with a number of metallic atoms ranging from around 10 to a few hundreds and are protected by a shell of organic ligands. [1]

Determining the exact structure of these compounds is essential to a good understanding of their properties and such structure determination can be achieved by X-Ray crystallography.

To investigate the structure-size relationship and the evolution of the structure with the size of nanomaterials, new nanoclusters were synthesized and crystallised. A detailed analysis of their structures was conducted after X-ray diffraction and some spectroscopic properties were measured. The new clusters are chiral. Interestingly, the chirality of the $Ag_{21}Au_8$ alloy cluster arises from the helical arrangement of the gold atoms.



[1] Meng Zhou, Chenjie Zeng, Yuxiang Chen, Shuo Zhao, Matthew Y.Sfeir, Manzhou Zhu, Rongchao Jin, *Nature Communications*, **2016**, 7, 13240

Unravelling the Mass Transport of Water at Organic Aerosol Interfaces

M. Azizbaig Mohajer[1]

[1]ETH Zürich

Interfacial mass transport plays a crucial role in defining growth rates of aerosol particles and droplets. A better understanding of the underlying kinetics is important for the delivery of pharmaceutical aerosols to human airways, industrial processes such as inkjet printing or spray drying, and cloud formation in the atmosphere. Interfacial mass transport is determined by the mass accommodation coefficient, which describes evaporation and condensation kinetics at the liquid-vapour interface in terms of a probability. Despite the widespread relevance of the accommodation coefficient, its value is still unknown for many important systems.

To address this issue, we employ Photothermal Single-Particle Spectroscopy (PSPS) to investigate the water accommodation on single optically-trapped water-miscible organic aerosol particles. PSPS combines photoacoustic spectroscopy and modulated Mie scattering, and allows the samples to be probed under ambient conditions and close to thermal equilibrium [1] [2]. Combination with a model for heat and mass transfer allows us to retrieve values for the water mass accommodation coefficient on water-miscible organics at different particle temperatures and relative humidities [1] [3]. Furthermore, the capability of PSPS to probe samples with high water content enabled us to confirm the lower limit for the mass accommodation of water on liquid water of 0.3 under ambient conditions [4].

[1] S. Roy, M. E. Diveky, R. Signorell, *J. Phys. Chem. C* **2020**, *124*, 2481–2489.
[2] M. E. Diveky, S. Roy, J. W. Cremer, G. David, R. Signorell, *Phys. Chem. Chem. Phys*. **2019**, *21*, 4721-4731.
[3] F. Graber, D-CHAB, ETH Zürich, Master Thesis, 2022, to be submitted.
[4] M. E. Diveky, M. Gleichweit, S. Roy, R. Signorell, *J. Phys. Chem. A* **2021**, *125*, 3528-3548.

Cold ion-molecule reactions between He^+ and small molecules with a quadrupole moment

F. B. V. Martins[1], F. van Swaaij[1], V. Zhelyazkova[1], F. Merkt[1]*

[1]ETH Zürich, Laboratory of Physical Chemistry

Exothermic, barrier-free ion-molecule reactions proceed with high rate coefficients even at very low temperatures. These reactions are typically described using the Langevin model, which predicts the rate coefficient to be independent of the temperature or the collision energy (E_{coll}). At near-zero collision energies, however, a strong E_{coll} dependence of the capture rate coefficients can arise because of the interaction between the charge of the ion and the electric dipole or quadrupole moments of the neutral molecule. To reach such low collision energies, we use a merged-beam approach and study ion-molecule reactions within the orbit of a highly excited Rydberg electron, which prevents the heating up of the ions by stray electric fields without influencing the reaction.

In previous studies of reactions between He^+ and either linear or symmetric top molecules, we found that for polar reactants, such as NH_3, a pronounced increase in the rate coefficient is observed with decreasing E_{coll} [1,2], whereas for N_2, which has no dipole moment but a negative quadrupole moment, the reaction yield decreases with decreasing E_{coll} [3]. In this contribution, we will present the results of recent investigations at low E_{coll} of the reactions of He^+ with molecules that have a quadrupole moment, with particular emphasis on the $He^+ + CO$ [4] and the $He^+ + C_2H_4$ reaction systems. In the former case, we examine in detail the role of the charge-dipole and charge-quadrupole interactions. The dipole moment of CO is small, and it is not obvious to predict whether the E_{coll} behavior of the rate coefficients is dominated by the charge-dipole or the charge-quadrupole interaction. In the latter case, we examine for the first time an ion-molecule reaction involving a nonpolar asymmetric molecule with a large quadrupole moment.

[1] V. Zhelyazkova, F. B. V. Martins, J. A. Agner, H. Schmutz, F. Merkt, *Phys. Rev. Lett.*, **2020**, 125, 263401.
[2] V. Zhelyazkova, F. B. V. Martins, J. A. Agner, H. Schmutz, F. Merkt,*Phys. Chem. Chem. Phys.*, **2021**, 23, 21606.
[3] V. Zhelyazkova, F. B. V. Martins, M. Žeško, F. Merkt, *Phys. Chem. Chem. Phys.*, **2022**, 24, 2843.
[4] F. B. V. Martins, V. Zhelyazkova, Ch. Seiler, F. Merkt, *New J. Phys.*, **2021**, 23, 095011.

Nanoscale Analysis of On-Surface Coordination Systems Using Tip-Enhanced Raman Spectroscopy

Z. Cai[1], L. Zheng[1], Y. Zhang[2], R. Zenobi[1]*

[1]Department of Chemistry and Applied Biosciences, ETH Zurich, [2]Hefei National Laboratory for Physical Sciences at the Microscale and Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China

Metal−organic coordination structures at interfaces play an essential role in many biological and chemical systems.[1-4] Understanding the molecular specificity, orientation, and spatial distribution of the coordination complexes at the nanometer scale is of great importance for effective molecular engineering of nanostructures and fabrication of functional devices with controllable properties. However, fundamental properties of such coordination systems are still rarely studied directly.

This presentation will focus on the application of tip-enhanced Raman spectroscopy (TERS) as a spectroscopic approach to investigate on-surface coordination species on the scale of a single molecule under ambient conditions, illustrated in Figure 1.[5] Coordination species anchored on gold surfaces modified with pyridine thiol self-assembled monolayers can be spectroscopically distinguished and mapped with *ca.* 2 nm resolution. In addition, in combination with density functional theory simulations, the adsorption configuration and molecular orientation of the coordination complexes are also revealed using TERS imaging. For instance, the tilt angles of the coordination complexes, according to the Raman spectra in Figure 1b correspond to *ca.* 90°, 60°, 45°.

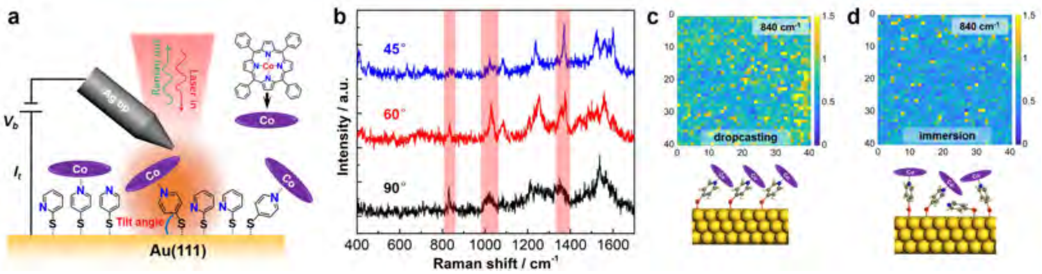


Figure 1. a) Scheme of STM-TERS probing on-surface coordination system. b) Typical TER spectra of coordination complexes with different tilt angles on a Au(111) surface. c – d) TERS peak intensity maps (840 cm^{-1}) showing the orientations of the coordination species are more homogeneous in the immersion sample.

[1] Minju Kim, Miroslaw Dygas, Yaroslav I. Sobolev, Wiktor Beker, Qiang Zhuang, Tomasz Klucznik, Guillermo Ahumada, Juan Carlos Ahumada, Bartosz A. Grzybowski, *J. Am. Chem. Soc.,* **2021**, 143, 1807-1815.
[2] Nikolay Kornienko, Yingbo Zhao, Christopher S. Kley, Chenhui Zhu, Dohyung Kim, Song Lin, Christopher J. Chang, Omar M. Yaghi, Peidong Yang, *J. Am. Chem. Soc.,* **2015**, 137, 14129-14135.
[3] Mark Kuil, Theresa Soltner, Piet W. N. M. van Leeuwen, Joost N. H. Reek,*J. Am. Chem. Soc.,* **2006**, 128, 11344-11345.
[4] Melissa L. Merlau, Maria del Pilar Mejia, SonBinh T. Nguyen, Joseph T. Hupp, *Angew. Chem. Int. Ed.,* **2001**, 40, 4239-4242.
[5] Zhen-Feng Cai, Li-Qing Zheng, Yao Zhang, Renato Zenobi, *J. Am. Chem. Soc.,* **2021**, 143, 12380-12386.

High-resolution spectroscopy of metastable helium atoms using beam-manipulation methods

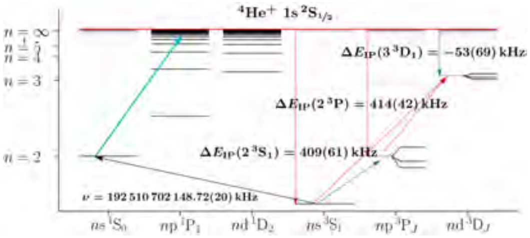
G. Clausen[1], L. Gabriel[1], J. A. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]Laboratory of Physical Chemistry, ETH Zurich

The metastable He ($(1s)^1(2s)^1$) atom in its singlet (^1S) or triplet (^3S) states is an ideal system to perform tests of ab-initio calculations of two-electron systems that include quantum-electrodynamics. The recent determination of the ionization energy of the metastable 2 ^1S state of ^4He [1] confirmed a discrepancy between the latest theoretical values of the Lamb shifts in low lying electronic states of triplet helium [2] and the measured 3 $^3D \leftarrow 2\ ^3S$ [3] and 3 $^3D \leftarrow 2\ ^3P$ [4] transition frequencies. To find the reasons behind these discrepancies, it is necessary to carry out new determination of the ionization energies of the low-lying tripet states of helium, both experimentally and theoretically.

Currently, we focus on the development of a new atomic-beam manipulation method for the 2 ^3S state of He, with the aim of determining its ionization energy with unprecedented accuracy. The interaction of the triplet state (which has a nonzero total electronic spin) with magnetic fields is exploited to slow down supersonic beams of 2 ^3S He to low velocities using the technique of multistage Zeeman deceleration. In addition, the closed-cycle 2s ^3S - 2p ^3P transition is used to transversally cool the beam.

We present measurements and simulations of the velocity distribution of the He atoms in the 2 ^3S state after Zeeman deceleration and transverse laser cooling. This combination strongly reduces Doppler and transit-time broadening and enables the measurement of transitions from the 2 ^3S state to np Rydberg states with linewidths of about 1 MHz. Extrapolation of the np series yields the ionization energy with sub-MHz accuracy.



[1] G. Clausen, P. Jansen, S. Scheidegger, J. A. Agner, and F. Schmutz, H.and Merkt, *Phys. Rev. Lett*. **2021,** 127, 093001.
[2] V. Patkóš, V. A. Yerokhin, and K. Pachucki, *Phys. Rev. A*, **2021**, 103, 042809.
[3] C. Dorrer, F. Nez, B. de Beauvoir, L. Julien, and F. Biraben, *Phys. Rev. Lett.*, **1997** 78, 3658.
[4] P.-L. Luo, J.-L. Peng, J. Hu, Y. Feng, L.-B. Wang, and J.-T. Shy, *Phys. Rev. A*, **2016**, 94, 062507.

Enhanced stability and solubility of photoacids in binary solvent mixtures

A. de Vries[1], M. Reiter[1], K. Goloviznina[2], M. Salanne[2], M. R. Lukatskaya[1]*

[1]ETH Zurich, Electrochemical Energy Systems Laboratory, [2]Physicochimie des Électrolytes et Nanosystèmes interfaciaux

Metastable photoacids are a unique class of organic molecules that can reversibly lower pH of the solution under UV-visible light. Merocyanine-type photoacids can decrease the pH by up to 3.5 units in less than 30 seconds (pH-jump), and then reverse to the original pH in darkness within 15 minutes through thermal relaxation [1, 2]. The non-invasive nature of these light switchable proton emitters renders highly relevant applications in functionalized surfaces, such as membranes [3] and sensors [4], or pH-driven reactions such as hydrogel formation [5] or CO_2 absorption/release [6]. Despite the pK_a tunability with substituents modifications [7], merocyanine-type photoacids are generally limited by their low chemical stability due to hydrolysis (half-life is 16 hours) and low solubility in water (0.19 mM) [3]. In aprotic organic solvents such as dimethyl sulfoxide (DMSO), photoacids display higher chemical stability and solubility [1], however pH-jump in such solvents is not reversible.

Herein we propose the use of the water-DMSO solvent mixtures in combination of photoacids to achieve the ‘best of both worlds’: high reversibility of pH-jump as well as high chemical stability and solubility. By combining pH-jump, solubility and stability studies, we demonstrate that solubility can be enhanced by 2 orders of magnitude, and half-life increased by 1 order of magnitude in DMSO-water mixtures. UV-Vis absorption, NMR, SAXS and MDS were used to reveal the role of H-bonding networks and modified solvent structure to enable this enhancement. Besides optimizing for specific properties, binary solvent mixtures provide an additional degree of freedom to tune photoacid properties such as pK_a and relaxation kinetics that can also be applied to other types of photoacids.

[1] Cesare Berton, Daniel Maria Busiello, Stefano Zamuner, Euro Solari, Rosario Scopelliti, Farzaneh Fadaei-Tirani, Kay Severin Cristian Pezzato, *Chemical Science.,* **2020**, 11, 8457-8468.
[2] Jonathon Beves, Laura Wimberger, Joakim Andréasson, *Chemrxiv*, **2022**.
[3] William White, Christopher D. Sanborn, David M. Fabian, Shane Ardo, *Joule 2.1,* **2018**, *94-109.*
[4] Thaaer Khalil, Arwa Alharbi, Clayton Baum, Yi Liao, *Macromolecular Rapid Communications,* **2018**, 39, 1800319.
[5] Amos Meeks, Michael M. Lerch, Thomas B. H. Schroeder, Ankita Shastri, Joanna Aizenberg, *Journal of the American Chemical Society*, **2021**, 219-227.
[6] Robert Bennett, Sarah Clifford , Kenrick Anderson , Graeme Puxty, *Energy Procedia*, **2017**, 114, 1-6.
[7] Nawodi Abeyrathna,Yi Liao, *Journal of Physical Organic* Chemistry, **2017**, 30.8: e3664.

Zero-quantum-defect method using the Stark effect in Rydberg states of para-H_2

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

[1]Laboratory of Physical Chemistry, ETH Zürich, Switzerland

Molecular hydrogen is the simplest molecular four-body system, and its ionization energy is an important benchmark quantity for the calculation of quantum-electrodynamics corrections [1]. The bottleneck in the experimental determination of the ionization energy using high-*n* Rydberg states is the extrapolation of the Rydberg series to their limit. Currently, this extrapolation is performed using multichannel quantum defect theory (MQDT), with a precision limited to about 500 kHz [2].

In order to overcome this limitation, we propose an alternative method based on the Stark effect. By applying relatively weak (below 300 mV/cm) static electric fields, Rydberg states of different values of *l* are mixed, providing access to the highest-*l* states which have vanishing quantum defects. These high-*l* states form a nearly degenerate linear Stark manifold, to which transitions can be driven by near infrared radiation (Fig. 1). By extrapolating to zero field, the zero-quantum-defect positions ($-R_{H2}/n^2$ relative to the ionization threshold) are obtained and used instead of MQDT to determine the ionization energy. We show that this method leads to an one-order-of-magnitude improvement in the accuracy of the determination of ionization energy of para-H_2.

The proposed scheme can be extended to excited rovibrational states of molecular hydrogen, and therefore enables experimental determination of rovibrational intervals with unprecedented accuracy. As illustration, we report on the determination of the fundamental vibrational interval of $H_2{}^+$ at sub-MHz accuracy.

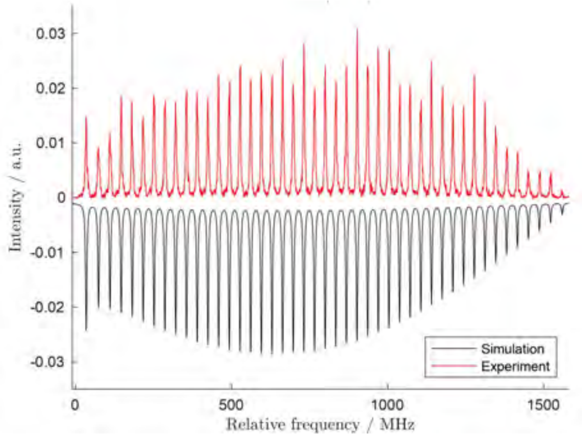


Fig. 1: Measured spectrum to the Stark manifold (n = 48, v^+= 0) from the initial GK $^1\Sigma_g{}^+$ (v^+ = 0, N^+ = 2) state (red) and simulation using transition frequencies calculated in a matrix-diagonalisation approach and intensities modelled as the square of the f character (black). The frequency scale is referenced to an arbitrary value.

[1] Mariusz Puchalski, Jacek Komasa, Paweł Czachorowski, and Krzysztof Pachucki, *Physical Review Letters*, **2019**, 122, 103003
[2] Maximilian Beyer, Nicolas Hölsch, Joël Hussels, C.-F. Cheng, Edcel J. Salumbides, Kjeld S. E. Eikema, Wim Ubachs, Christian Jungen, and Frédéric Merkt, *Physical Review Letters*, **2019**, 123, 163002

Probing Photocatalytic Reactions at the Single-particle and Single-photon Level

L. G. Feld[1,2], G. Rainò[1,2], Y. Sahin[1,2], D. Dirin[1,2], M. V. Kovalenko[1,2]*

[1]Institute of Inorganic Chemistry, Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich, 8093 Switzerland, [2]Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, 8600 Switzerland

Colloidal quantum dots (QDs) are compelling photocatalysts for organic reactions owing to their tuneable energy levels, large absorption cross-sections, and the absence of the Marcus inverted regime due to Auger-assisted charge transfers (CT) [1]. The presence of CT events alters the lifetime and the intensity of the QD fluorescence and can thus be tracked by photoluminescence (PL) spectroscopy. For photocatalytic reactions driven by emissive QDs, single-particle spectroscopy is particularly insightful because reactions of colloids are inherently inhomogeneous and CT events are rare under common reaction conditions. Unlike ensemble PL studies, single-particle spectroscopy can access timescales ranging from nanoseconds to seconds. Therefore, photophysics of single CT events, diffusion of reactants and catalyst ageing can be captured in a single experiment with nanometre resolution, whilst resolving inhomogeneities and rare events. Here, we present our work on lead halide perovskite ($APbX_3$, A=FA/Cs, X=Cl/Br/I) QDs by means of single-particle spectroscopy. Owing to the broad timescales covered by single-particle spectroscopy and the QD acting both as photocatalyst and sensor, we gain new insights into the dynamics which could drive further design improvements for QD-driven photocatalytic reactions.

[1] Haiming Zhu, Ye Yang, Kaifeng Wu, Tianquan Lian, *Annual Review of Physical Chemistry*, **2016**, 67, 259–281.

Polaritonic chemistry with instanton theory

M. R. Fiechter[1], J. O. Richardson[1]*

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

The field of polaritonic chemistry, focused on the interaction of molecules with the quantized light field of a cavity, has gained a lot of attention recently. Particularly interesting is the observed enhancement or suppression of chemical reaction rates upon tuning the cavity to vibrational resonance with the molecule, even if the cavity contains no photons; the mechanism of this is currently still not fully understood.

So far, studies have either focused on strongly simplified models, which can be treated fully quantum-mechanically but may not be representative for the real world; or treated the full molecule and cavity system, but assumed the nuclear and light degrees of freedom to behave classically, and therefore missed important quantum effects such as tunnelling and zero-point energy fluctuations.

The middle way between these two approaches is provided by instanton rate theory, which is an approximation to path-integral quantum mechanics; it singles out one least-action path and takes into account some of the fluctuations around it via a prefactor. It captures tunnelling and zero-point energy-related effects and since it is exact for an harmonic oscillator, it should describe the light mode(s) very accurately. Moreover, unlike quantum mechanics, the expense of an instanton calculation does not scale exponentially with system size, making it computationally tractable even for large molecules. Additionally, the instanton path is the most probable tunnelling path, therefore it gives us some insight into the mechanism of the reaction.

In this poster presentation, I will outline how we plan to use instanton theory to calculate cavity-modified rates and what we hope to learn from it, and show some preliminary results.

Phosphate ion triggered modifications of oil/water interfaces

M. Frigerio[1], S. Salentinig[1]

[1]Department of Chemistry, University of Fribourg, Chemin Du Musée 9, 1700 Fribourg, Switzerland

Oil/water interfaces are regions of excess free energy ubiquitous in colloids. The energy required for emulsification of oil in water is proportional to the interfacial tension. Certain ions were found to reduce the surface tension in a surfactant-free way [1]. This can help to reduce the consumption of surfactants while ensuring the decrease in surface tension and costs associated to the emulsification process from a practical point of view. However, the role of ions and the enhancement in interfacial features is still matter of debate as there are many factors, such as the polarizability [2] that come into play. Here we show that phosphate buffer, a commonly used buffer system in many studies, can significantly alter the lipid-water under certain pH conditions. Spinning drop tensiometry demonstrated the pH-triggered reduction of the interfacial tension between oil and water in presence of phosphate buffer. Monohydrogen phosphate (MHP) even appeared to crystallise at the water-triolein interface (Figure 1), in contrast to a plethora of other ions that were studied. Ellipsometry and Brewster angle microscopy showed the MHP triggered formation of layers at the interface, with a refractive index that is comparable to supersaturation conditions of the MHP. Moreover, stabilizer-free GMO cubosomes are used as a platform to analyse the integrations of the ions into lipid-water interfaces. Small angle X-ray scattering showed their structural transformation from double diamond Pn3m-type cubic phase in water [3] to primitive Im3m-type upon addition of MHP. Complementary techniques such as molecular dynamics and interfacial tension measurements all point in the same direction. Our results pave the way for a more systematic study on the interfacial role of ions in processes of biological relevance [4] such as calcium removal of long chain fatty acids from oil/water interface in lipid digestion.

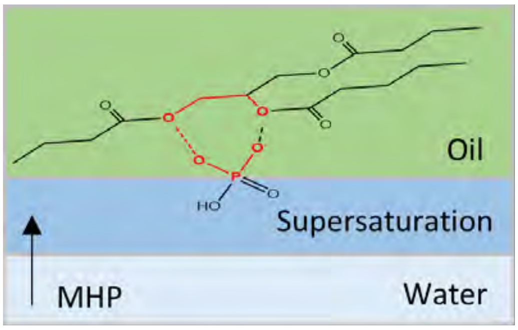


Figure 1. Sketch diagram for supersaturation conditions established upon MHP adsorption at the interface and following crystallization.

[1] Badizad Mohammad Hasan et al., *Journal of Colloid and Interface Science*, **2020**, 575, 337-346.
[2] Chang Tsun-Mei, Liem X. Dang, *Chemical Reviews*, **2006,** 4, 1305-1322.
[3] Zabara Mahsa et al., *Advanced Functional Materials*, **2019**, 35, 1904007.
[4] Salentinig Stefan et al., *Soft Matter*, **2011**, 2, 650-661.

Femtosecond broadband spectroscopic study of planarization dynamics of 9,10 -bis(phenylethynyl)anthracene

I. Fureraj[1], D. S. Budkina[1], E. Vauthey[1]*

[1]University of Geneva

Most arylethynyl-based chromophores are characterised by a non-mirror image relationship of their electronic 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[1]. 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[2,3]. For this, we use femtosecond broadband fluorescence up-conversion spectroscopy with sub 100 fs resolution and tunable excitation, as well as femtosecond time resolved absorption spectroscopy. These methods allow 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. TD-DFT calculations and low-temperature stationary measurements in the rigid environment of polymer films support the interpretation of the time resolved data.

[1] Mikhail I. Sluch, Godt, Adelheid Godt, Uwe H. F. Bunz, Mark A. Berg. *J. Am. Chem. Soc.* **2001**, *123* (26), 6447–6448.
[2] Marcia Levitus, Miguel A. Garcia-Garibay. *J. Phys. Chem. A* **2000**, *104* (38), 8632–8637.
[3] Youn Jue Bae, Gyeongwon Kang, Christos D. Malliakas, Jordan N. Nelson, Jiawang Zhou, Ryan M. Young, Yi-Lin Wu, Richard P. Van Duyne, George C. Schatz, Micheal R. Wasielewski. *J. Am. Chem. Soc.* **2018**, *140* (45), 15140–15144.

Fabrication of nano-masked test samples for chemical etching relevant to microchip fabrication: An electron beam lithography approach

L. Galvez-Vazquez[1], P. Moreno Garcia[1], M. Galvez Vazquez[1], P. Broekmann[1]*

[1]University of Bern

Controlled removal of metal surfaces through additive assisted chemical etching is a highly relevant process for surface finishing in microchip manufacturing. [1] Herein, we introduce a novel and complementary SEM-AFM-ICP-MS approach that provides insights into characteristic features of metal corrosion phenomena (roughness, texture, erosion rate, and homogeneity).

By means of a simplified electron beam lithography procedure, [2] we manufacture microarrays (nanomasks) of passivated regions resistant to corrosion on the surface of metallic model systems. These nanomasks are thin, transparent, and practically non-invasive. Upon chemical etching of these surfaces, only the non-masked sample regions are eroded. This procedure leaves intact sample locations protruding out of the new, partially eroded sample surface (Figure 1). Each of these "original" sample regions is then characterized and compared with the eroded locations. This enables a closer and *visual* inspection at the nature of the corrosion phenomena. Validation of the method was demonstrated through chemical etching experiments on chemically etched Mo and W samples under harsh and mild erosion conditions.

Additionally, the method can also be applied to studies on metal corrosion inhibition. We demonstrate this latter issue through the prevention of electrochemical oxidation on Cu and Co model systems.

Importantly, our approach requires equipment usually available in any research institution and can be applied to many experimental platforms (steel, Cu, Fe, Mo, W, etc.). Additionally, the method can also be applied to studies on metal corrosion inhibition.

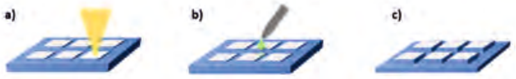


Figure 1. a) Exposure of specific regions to the electron beam (gray areas) promotes surface passivation and as result, a nanomasks array is fabricated. The blue area represents the area that was not exposed to the electron beam. b) Nanomasked samples subjected to chemical etching. c) Upon chemical etching, only the non-masked sample regions are eroded whereas the masked areas remain intact.

[1] J.C Love, K.E Paul, G.M Whitesides, *Advanced Materials* **2001,** *13* (8), 604-607.
[2] Beibei Luo, Yunsheng Fang, Jia Li, Zhen Huang, Bin Hu, Jun Zhou, *ACS Applied Materials & Interfaces* **2019,** *11* (13), 12195-12201.

Electrolyte engineering for Zn-ion batteries: Concentration-dependent Zn^{2+} coordination structure and its implication on Zn metal anode reversibility

D. Gomez Vazquez[1], J. Yoo[1], O. Borodin[2], T. P. Pollard[2], J. Mars[3], H. Steinrück[4], S. E. Bone[5], M. Lukatskaya[1]*

[1]ETH Zürich, [2]US Army Research Laboratory, [3]CU Boulder, [4]Paderborn University, [5]SLAC National Accelerator Laboratory

Aqueous secondary zinc ion batteries (ZIBs) are promising systems for grid storage because of their high energy density, low cost, and low safety concern. However, ZIBs have major limitations at their Zn metal anode because it suffers from both, side reaction of water splitting and dendrite formation which affect their coulombic efficiency (CE) and long-term stability, respectively. Recent approaches in electrolyte engineering have shown promising improvements in the cyclic reversibility of Zn metal anodes, including water-in-salt (WIS) electrolytes. While WIS electrolytes effectively increase CE of Zn metal anode through unique solvation structure and suppressed water splitting, its high salt usage, and increased electrolyte viscosity put other limitations on advanced ZIB systems. To implement beneficial effects from WIS into realistic ZIB systems, additional fundamental understanding is required of the correlation between electrolyte concentration, Zn^{2+} coordination environment, electrolyte structure, and resultant Zn plating/stripping efficiency, which has not been properly addressed in the field. Herein, we investigate the electrochemical properties of Zn plating/stripping as a function of electrolyte concentration and structure using a mixed cation Zn^{2+}-K^+ acetate (OAc) electrolyte: $Zn_{0.2}K_{0.8}OAc_{1.2}\cdot nH_2O$ where “n” was variated from 1.5 to 50. Upon increase in concentration we observed a change in the Zn^{2+} coordination environment and bulk electrolyte properties (e.g. thermal, conductivity and viscosity). We identify optimal electrolyte composition at n=10. In this *salt-solvate* electrolyte state we benefit from both WIS-like Zn^{2+} coordination environment and high conductivity and enable high CE >99% during Zn plating/stripping.

Quantifying London Dispersion Interactions in Onium Ions

V. Gorbachev[1], A. Savoy[1], L. Fritsche[1], P. Chen[1]*

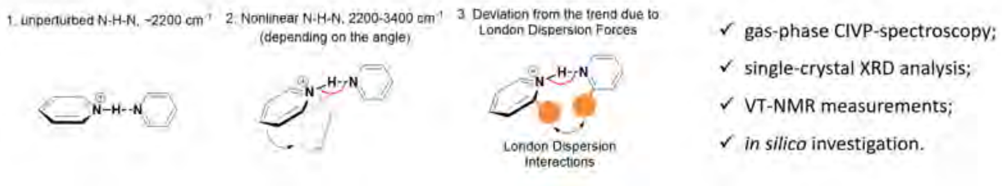
[1]ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

The quantitative evaluation of non-covalent interactions in medium to large organic molecules has remained difficult despite becoming increasingly cited as a design principle in the construction of catalysts and materials.[1,2] Despite encouragingly accurate calculations for small molecules, experimental benchmarks for large molecules in the gas phase remain scarce. There is evidence that accurate results for small molecules may not extrapolate reliably to large molecules due to inadequate treatment of the London dispersion interactions.[3] The present proposal introduces a new experimental probe of non-covalent interactions as well as provides a new benchmark against different computational and experimental methods.

The investigated set of compounds consists of a range of small to large proton-bound pyridine dimers and protonated bipyridines. These systems were experimentally studied in solid-state by single-crystal X-ray diffraction, in condensed phase by VT-NMR, and in the gas phase by CIVP-spectroscopy. We also performed density functional theory calculations, including an extensive search and analysis of accessible conformations as well as BOMD-simulations that treat such mobile systems' dynamic behavior.

We observed a correlation between calculated and experimental N-H stretching frequency, N-H-N bond angle, and ^{1}H chemical shift. This would indicate that IR and NMR can be used to assess the bending of the hydrogen bond in such systems.

The onium cations can adopt various conformations, whose energies map interaction potentials. Substituents on their proton-bound dimers interact non-covalently through dispersion forces. The proton-bound dimer acts like a molecular balance where the non-covalent interaction is set against the bending potential in an ionic hydrogen bond. In the case of asymmetric pyridine dimers, the non-covalent interactions between substituents can bend the N-H-N bond, as shown by X-ray diffraction analysis. The bending of the intermolecular hydrogen bond leads to a significant shift in the IR frequency, which allows us to quantify London dispersion forces.



- ✓ gas-phase CIVP-spectroscopy;
- ✓ single-crystal XRD analysis;
- ✓ VT-NMR measurements;
- ✓ *in silico* investigation.

[1] J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed.,* **2015**, 54, 12274–12296.
[2] V. Gorbachev, A. Tsybizova, L. Miloglyadova, P. Chen, *J. Am. Chem. Soc.,* **2022**, 144, 20, 9007–9022.
[3] R. Pollice, M. Bot, I. J. Kobylianskii, I. Shenderovich, P. Chen, *J. Am. Chem. Soc.,* **2017**, 139, 37, 13126–13140.

Energy-dependence of reactions of D_2^+ + NH_3 and D_2^+ + CH_3F

R. Hahn[1], J. Agner[1], H. Schmutz[1], F. Merkt[1]*

[1]ETH Zürich, Laboratory of Physical Chemistry

Fast, exothermic and barrierless ion-molecule reactions drive rich chemistry in the cold (~10-150 K) and tenuous (particle number densities of less than 10^6 cm^{-3}) environment of the interstellar medium [1,2]. Ion-molecule reactions involving H_2^+ in particular play a crucial role in the chemistry of interstellar clouds, initiating complex reaction chains which lead to the synthesis of all hydrocarbons. Precise knowledge of the reaction rate coefficients, product branching ratios and kinetic-energy distributions of the products are thus important for astrochemical kinetic models. These 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 [2,3,4].

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 H_2^+ (or D_2^+) ions by neutral H_2 (D_2) molecules 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. 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 deflected using a curved chip-based surface-electrode deflector. This deflector can also be used to set the velocity of the Rydberg species (v_{Ryd}). By tuning v_{Ryd} relative to the velocity of the ground-state molecules (v_{GS}), we can tune the collision energy in a large range (between ~ $k_{\mathrm{B}} \times 150$ mK and ~ $k_{\mathrm{B}} \times 70$ K). The reaction product ions are collected in a time-of-flight (TOF) mass spectrometer and the reaction rates and branching ratios monitored for a range of collision energies. The use of short-pulse valves (pulse duration ~ 20 µs) for the pulsed supersonic beams ensures excellent velocity dispersion at the reaction-observation volume.

We report on experimental studies of low-energy ion-molecule reactions between D_2^+ and NH_3 as well as D_2^+ and CH_3F. In these barrier-free exothermic reaction systems, we observe different product channels and a strong energy dependence of the reaction rates on the collision energy.

[1] K. Höveler , J. Deiglmayr, J. A. Agner, H. Schmutz, and F. Merkt,*Phys. Chem. Chem. Phys.*, **2021**, 23, 2676
[2] K. Höveler, J. Deiglmayr and F. Merkt, *Molecular Physics*, **2021**, 119:17-18
[3] F. Merkt, K. Höveler , J. Deiglmayr.*, J Phys. Chem. Lett.,* **2022**, 13, 3, 864–871.
[4] K. Höveler , J. Deiglmayr, J. A. Agner, R. Hahn, V. Zhelyazkova and F. Merkt, in press.

Methodological and Instrumental Developments in Improving the Resolution Limit of PFI-ZEKE Photoelectron Spectroscopy

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

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

The spectral resolution in pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy is related to the state selectivity in the ionization process of the Rydberg states. The selectivity is determined by the applied electric-field pulse sequence. Hollenstein *et al.* [1] used discrete electric-field pulses with increasing field strength in combination with a preceding field pulse of opposite polarity. By using such field pulse sequences with the smallest possible field step size (i.e., approximately 9 mV/cm), a spectral resolution of 0.06 cm^{-1} could be achieved. To improve the resolution further, Harper *et al.* [2] recently suggested replacing the sequence of field steps by a linearly increasing field, as used earlier by Reiser *et al.* [3], in combination with a prepulse of opposite polarity and obtained promising results on the PFI-ZEKE photoelectron spectrum of NO and CO_2. Using a home-built narrow-bandwidth long-pulse laser system (pulse lengths up to 50 ns) in combination with a pulsed field ramp [2, 3], we explore the resolution limit of this approach. To avoid overlap of spectral lines, we chose atomic systems, Ar and Kr, as test systems and recorded PFI-ZEKE photoelectron spectra of transitions from the metastable states $(n\mathrm{p})^5((n+1)\mathrm{s})[3/2]_2$ $(^3\mathrm{P}_2)$ and $(n\mathrm{p})^5((n+1)\mathrm{s'})[1/2]_2$ $(^3\mathrm{P}_0)$ of the neutral rare-gas atom to the $(n\mathrm{p})^5\ ^2\mathrm{P}_{1/2,\ 3/2}$ states of the corresponding ion, with n=3, 4 for Ar and Kr, respectively. This system also offers the advantage of precisely known ionization energies [4] with which the ionization energies determined with the new method can be compared.

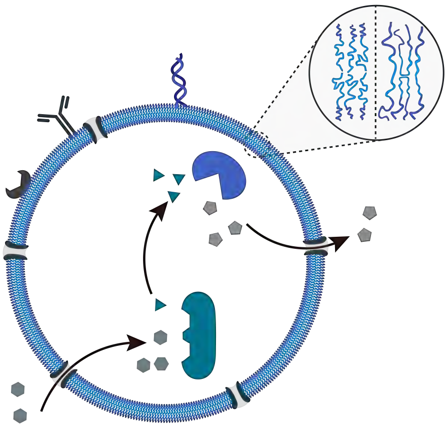
[1] U. Hollenstein, R. Seiler, H. Schmutz, M. Andrist, and F. Merkt, *J. Chem. Phys.* **115**, 5461--5469 (2001).
[2] O. J. Harper, N. L. Chen, S. Boyé-Péronne, and B. Gans, *Phys. Chem. Chem. Phys.* **24**, 2777-2784 (2022).
[3] G. Reiser, W. Habenicht, K. Müller-Dethlefs, and E. W. Schlag, *Chem. Phys. Lett.* **152**, 119–123 (1988).
[4] V. L. Sukhorukov, I. D. Petrov, M. Schäfer, F. Merkt, M.-W. Ruf, and H. Hotop, *J. Phys. B: At. Mol. Opt. Phys.* **45**, 092001 (2012) and references therein.

Polymer GUVs for High-Throughput Screening

L. Heuberger[1], C. G. Palivan[1]*

[1]Department of Chemistry, University of Basel

Biological systems use compartmentalization strategies to generate microenvironments with controlled biochemical compositions. These environments serve as a protective method from undesired influences from outside of the compartment and to keep diffusing elements in proximity.[1] Giant unilamellar vesicles (GUVs) are micrometer-sized vesicles used to mimic biological compartments that can be made from polymers. 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. Double-emulsion microfluidics enables production of monodisperse GUVs with controllable cargo, polymer membrane structure, and membrane functionalization at high throughput [2]. By adjusting the inner composition, enzymatic cascades, smaller vesicles, organelles and entire living organisms can be encapsulated within GUVs.



In the work presented, GUVs produced using PDMS-*b*-PMOXA block copolymers. By inserting outer membrane porin F (OmpF) or the pore-forming peptide melittin into the synthetic membrane, GUVs can be selectively permeabilized. This enables their use as catalytic microcompartments or cellular models. This approach shows the versatility of double-emulsion templated polymer GUVs for studying compartmentalized biological systems, deepening insights into fundamental biological processes. Thanks to their size being comparable to cells, GUVs can be screened using flow cytometry. Using these techniques, tens of thousands of GUVs can be analyzed, making them a convenient alternative to water/oil/water double emulsions.

[1] Roodbeen, R.; Van Hest, J. C. M. Synthetic Cells and Organelles: Compartmentalization Strategies. *BioEssays* **2009**, *31* (12), 1299–1308.

[2] dos Santos, E. C.; Belluati, A.; Necula, D.; Scherrer, D.; Meyer, C. E.; Wehr, R. P.; Lörtscher, E.; Palivan, C. G.; Meier, W. Combinatorial Strategy for Studying Biochemical Pathways in Double Emulsion Templated Cell-Sized Compartments. *Adv. Mater.* **2020**, *32* (48), 2004804.

IDTBT polymers studied with *in-situ* time-resolved spectro-electrochemistry

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

[1]Department of Chemistry, University of Bern

In the last decades, the field of organic bioelectronic grew tremendously, mainly because they combine advantageous properties such as their soft and flexible nature, versatile processing and synthetic tunability. Allowing for a wide range of applications at the interface of biology and electronics, encompassing wearable to implantable devices, which e.g., can work as sensitive biomedical sensors and circuit elements.[1,2] In the last decade, the research on bioelectronics was mainly focused on device fabrication and on the different material options. Therefore, there is still a lack of in-depth understanding on the fundamental effects occurring during the operation of bioelectronic devices.[3] A semiconducting material which recently sparked large interest due to its high mobility of up to 1 $cm^2V^{-1}s^{-1}$ in organic field effect transistors (OFET) is IDTBT, a donor-acceptor copolymer with a planar and near-torsion-free backbone allowing for such high charge carrier mobility.[4] Four IDTBT polymers, differing in their amount of alkyl versus glycol side chains were chosen to control the local morphology, conformation an ion-affinity of IDTBT. With *in-situ* time-resolved Vis-NIR spectro-electrochemistry we could assign different bands in the absorption spectrum to the different kinds of species present during the doping process (neutral segments, polarons, bipolarons). Additionally, by use of Multivariate Curve Resolution (MCR) analysis, the evolution of the species as a function of time could be determined and an overview of the IDTBT redox kinetics was established.

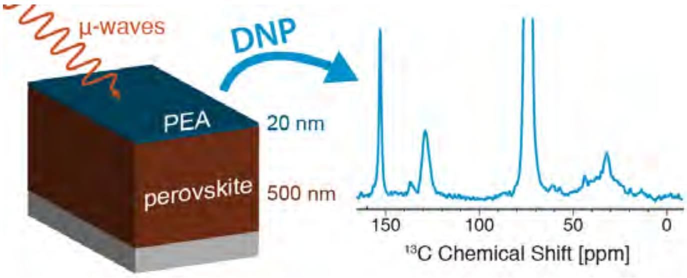
[1] Jonathan Rivnay, Róisín M. Owens, George G. Malliaras, *Chemistry of Materials*, **2014**, 26, 679-685.
[2] David Nilsson, Nathaniel Robinson, Magnus Berggren, Robert Forchheimer, *Adv. Mater.*, **2005**, 17 (3), 353-358.
[3] Jaeyub Chung, Aditi Khot, Brett M. Savoie, Bryan W. Boudouris, *ACS Macro Letters*, **2020**, 9 (5), 646-655.
[4] Xinran Zhang, Hugo Bronstein, Auke J. Kronemeijer, Jeremy Smith, Youngju Kim, R. Joseph Kline, Lee J. Richter, Thomas D. Anthopoulos, Henning Sirringhaus, Kigook Song, Martin Heeney, Weimin Zhang, Iain McCulloch, Dean M. DeLongchamp, *Nature Communications*, **2013**, 4, 2238.

DNP-enhanced NMR of Passivating Agents on Hybrid Perovskite Thin Films

M. A. Hope[1], A. Mishra[1], L. Emsley[1]*

[1]Institut des Sciences et Ingénierie Chimiques, EPFL

Hybrid organic–inorganic perovskites show great promise as materials for solar cells. While a lack of long-term stability currently limits their application, this can be greatly improved by the use of surface and bulk modulators. Nevertheless, to optimise the stability and efficiency of perovskite solar cells, a greater understanding is required of how these species interact with the perovskite and modify the optoelectronic properties. NMR has been an ideal approach to answer these kinds of problems for bulk samples, but its application to perovskite thin-films is limited by the extremely low sample masses, which is compounded by the typically low concentrations of the modulators. Dynamic nuclear polarization (DNP) is emerging as an effective method to enhance NMR sensitivity, but the performance when applied to hybrid perovskites has been rather poor to-date. Here, we determined the factors that limit the efficiency of DNP NMR on perovskite samples by systematically studying layered hybrid perovskite analogues. We identify that the fast-relaxing dynamic cation is the major culprit for the poor performance, which we show can be mitigated by deuteration. Consequently, we demonstrate ^{1}H DNP enhancements up to a factor of 100, which can then be harnessed to enhance signals from dopants or additives present in very low concentrations. Notably, by combining this methodology with cutting-edge DNP hardware, we were able to record the NMR spectrum of a 20 nm passivating layer on a single perovskite thin-film and determine its structure. This pushes the frontiers of NMR for hybrid perovskites, enabling the characterization of surface and bulk modulators in technologically relevant thin-film samples.

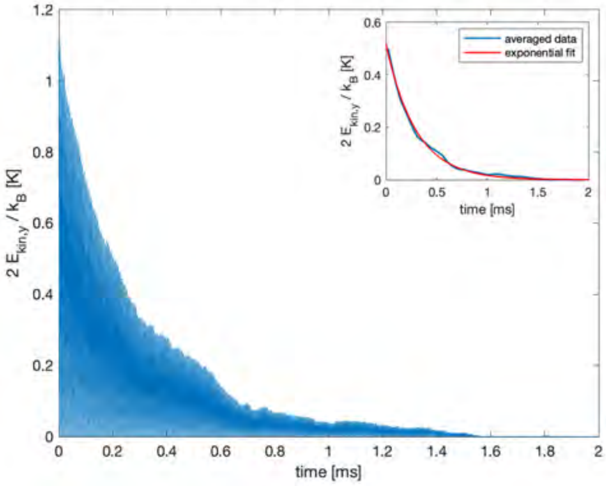


Laser Cooling of Ions in Strongly Inhomogeneous Magnetic Fields

R. Karl[1], Y. Yin[1], S. Willitsch[1]*

[1]University of Basel, Department of Chemistry, Klingelbergstrasse 80, 4056 Basel

The capability to cool and translationally control ions, atoms and molecules has recently enabled collision experiments and studies of chemical reactions at temperatures of a few millikelvin [1]. Interesting quantum phenomena occur at such temperatures and intermolecular interactions as well as reaction mechanisms can be studied with high precision [2]. At the frontier of cold collision experiments are hybrid traps in which charged and neutral species are trapped simultaneously [3]. In our experiment, we combine a RF trap for ions with a quadrupole magnetic trap for neutral molecules. In the RF trap, molecular ions are sympathetically cooled by a Coulomb crystal of laser-cooled calcium ions. After overlapping the RF trap with the magnetic trap, the calcium ions experience different Zeeman shifts due to the inhomogeneous B-field depending on their instantaneous position in the trap. This poses challenges for their efficient laser cooling.



To understand the internal and external dynamics of laser-cooled ions in inhomogeneous B-fields, molecular-dynamics simulations were conducted on the basis of 8-level rate equations. The simulations reveal the presence of dark states and the occurrence of dark resonances and highlight the interplay between Zeeman and Doppler shift for optimal cooling conditions. Based on the simulations, optimised cooling schemes for the trapped ions were designed inspired by magneto-optical traps.

[1] S. Willitsch, in Ad. Chem. Phys., Eds. S. Rice, A. Dinner, Wiley Interscience, **2017**, 162, 307-340.
[2] A. Dörfler, el al., Nat. Commun., **2019**, 10, 5429.
[3] P. Eberle, et al., J. Phys. Conf. Ser., **2015**, 635 012012.

QCL Dual-Comb Spectrometer Measurements of cold $CHCl_2F$ and CF_4

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

[1]ETH Zürich, Physical Chemistry, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland, [2]IR Sweep AG, Laubisrütistrasse 44, 8712 Stäfa, Switzerland

The IR spectra of the environmentally relevant molecules CF_4 and $CHCl_2F$ have been measured in pulsed, skimmed supersonic beams using quantum cascade laser (QCL) dual comb spectroscopy [1]. The low rotational temperature of the beams and the narrow expansion cone after the skimmer have made it possible to record the spectra of the ν_7 CH-bending fundamental of $CHCl_2F$ and the ν_3 CF-stretching fundamental of CF_4 with high resolution and sensitivity in the mid-IR range from 1200 cm^{-1} to 1290 cm^{-1}. The narrowest lines have a full width at half maximum of 18 MHz (0.0006 cm^{-1}), and the observed line width is likely dominated by Doppler broadening in the skimmed molecular beam. The wavenumber calibration was performed using line positions in the ν_1 fundamental of N_2O recently measured by Hjältén et al. [2]. The results of a new, detailed examination of the rovibrational transitions in the $CHCl_2F$ ν_7 band and the ν_3 fundamental of CF_4 are compared with previous results obtained using high resolution FTIR spectroscopy [3, 4, 5] and diode laser spectroscopy of seeded cw and pulsed supersonic jets [6, 7]. The results demonstrate the potential of QCL dual-comb spectroscopy for broadband acquisition of mid-infrared spectra at high sensitivity and high spectral and temporal resolution.

[1] J. A. Agner, S. Albert, P. Allmendinger, U. Hollenstein, A. Hugi, P. Jouy, K. Keppler, M. Mangold, F. Merkt, M. Quack (in preparation 2022).
[2] A. Hjältén, M. Germann, K. Krzempek, A. Hudzikowski, A. Głuszek, D. Tomaszewska, G. Soboń, A. Foltynowicz, *JQSRT*, **2021**, 271, 107734.
[3] M. Snels and M. Quack, *J. Chem. Phys.,* **1991**, 95, 6355.
[4] S. Albert, S. Bauerecker, M. Quack, A. Steinlin, *Mol. Phys.,* **2007**, 105, 541.
[5] S. Albert, K. K. Albert, M. Quack, *J. Mol. Struct.,* **2004**, 695−696, 385.
[6] M. Caviezel, V. Horká-Zelenková, G. Seyfang, M. Quack (in preparation 2022).
[7] M. Snels, V. Horká-Zelenková, H. Hollenstein, 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. 1022−1067, Wiley, Chichester, 2011.

Inverting glucuronidation of hymecromone *in situ* by catalytic nanocompartments

M. Korpidou[1], V. Maffeis[1,2], I. Dinu[1,2], C. Schoenenberger[1,2], W. P. Meier[1,2]*, C. G. Palivan[1,2]*

[1]Department of Chemistry, University of Basel, Mattenstrasse 24a, BPR 1096, Basel, Switzerland, [2] NCCR-Molecular Systems Engineering, Mattenstrasse 24a, BPR 1095, Basel, Switzerland

Glucuronidation, one of the main processes of metabolism is the conjugation of endogenous or exogenous molecules with glucuronic acid. The conjugation with glucuronic acid leads to the formation of water-soluble derivatives which can then be excreted and eliminated from the body (1). In the case of therapeutic compounds, when this process takes place rapidly, their half-lives become shorter and their therapeutic effects wear off quickly. On the other hand, administration of higher doses of therapeutic compounds to overcome this limitation result in harmful effects such as drug abuse or even addiction (2). Notably, inverting compound glucuronidation can be achieved by β-glucuronidase (GUS), the enzyme responsible for glucuronide moiety cleavage. In our study, catalytic nanocompartments (CNCs) made of PMOXA10-*b*-PDMS25 block copolymer can encapsulate β-glucuronidase, while the polymer membrane is permeabilized with melittin (mel), a pore-forming peptide (3). CNCs have shown to be beneficial in shielding the encapsulated enzymes from their surroundings, prolonging their activity and reducing immunogenicity (4). Our results showed that when the glucuronide conjugate of hymecromone (4-MUG) is given, GUS-melCNCs successfully produced hymecromone both in phosphate buffered solution and cell culture medium. Furthermore, GUS-melCNCs were non-cytotoxic when incubated with HepG2 cells and were able to produce the drug *in situ* over 24 hours. Our data suggests that such catalytic nanosystem that can locally revert a drug metabolite into its active form, has a potential to produce pharmacologically active compounds locally and on demand.

(1) L. A. Stanley, in *Pharmacognosy: Fundamentals, Applications and Strategy*, eds. S. Badal and R. Delgoda, Academic Press, 1st edn., 2017, pp. 527–545.
(2) B. Sproule, B. Brands, S. Li and L. Catz-Biro, *Canadian Family Physician*, 2009, **55**, 68–69.
(3) M. Korpidou, V. Maffeis, IA. Dinu, CA. Schoenenberger, W. P. Meier and C. G. Palivan, *Journal Materials Chemistry B*, 2022, **10**, 3916-3926.
(4) F. Bialas, D. Reichinger and C. F. Becker, *Enzyme and Microbial Technology*, 2021, **150**, 109864

High-resolution spectroscopy of the ground state of $MgKr^+$ and its low-lying electronically excited states

C. Kreis[1], M. Holdener[1], M. Génévriez[2], F. Merkt[1]*

[1]ETH Zürich, Laboratorium für Physikalische Chemie, [2]Université Catholique de Louvain, Institute of Condensed Matter and Nanosciences,

Diatomic molecules RgM consisting of a rare-gas atom Rg and an alkaline-earth-metal atom M and their singly and doubly-charged cations RgM^+ and RgM^{2+} have unusual chemical properties that are related to the low first and second ionization energies of M and the high ionization energy of Rg. In the case of MgAr, the second ionization energy of Mg is lower than the first ionization energy of Ar. Consequently, $MgAr^{2+}$ is thermodynamically stable and Rydberg series of $MgAr^+$ can be observed that converge on the $X^{2+}\ {}^1\Sigma^{2+}$ ground state of $MgAr^{2+}$ [1]. We want to extend this study to MgKr, where the second ionization energy of Mg is higher than the first ionization energy of Kr, and therefore $MgKr^{2+}$ is predicted to be metastable.

In this contribution, we present the results of spectroscopic investigations of $MgKr^+$ in its ground and low-lying electronically excited states that complement earlier studies of this cation [2,3].

Pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectra of the $X\ {}^2\Sigma^+$ ground state of $MgKr^+$ were recorded following single-photon excitation from the $a\ {}^3\Pi_0$ metastable state of MgKr. Vibrational channel interactions enabled the observation of the lowest vibrational levels of $MgKr^+$ and the determination of an accurate value of the adiabatic ionization energy of metastable MgKr ($38183 \pm 2\ \text{cm}^{-1}$). Using isolated-core multiphoton Rydberg dissociation (ICMRD) spectroscopy [4], spectra of several low-lying electronically excited states of $MgKr^+$ were observed that are associated with the Kr + Mg^+ (nl) dissociation limits with n=3,4 and l=s, p and d. These states may be regarded as the lowest members of Rydberg series converging on the ground state of $MgKr^{2+}$. These studies represent first steps towards studying the doubly charged cation $MgKr^{2+}$.

[1] D. Wehrli, M. Génévriez, F. Merkt, *Physical Chemistry Chemical Physics*, **2021**, 23, 10978, and references therein
[2] J. G. Kaup and W. H. Breckenridge, *Journal of Chemical Physics*, **1997**, 107, 2180.
[3] J. S. Pilgrim, C. S. Yeh, K. R. Berry, M. A. Duncan, *Journal of Chemical Physics*, **1994**, 100, 7945.
[4] M. Génévriez, D. Wehrli, F. Merkt, *Molecular Physics*, **2019**, 118, 11.

Combined electrochemical and thermochemical approach to determine the fundamental reaction processes of the CO_2 reduction reaction

P. M. Leidinger[1], T. J. Schmidt[1], J. A. van Bokhoven[1,2], J. Herranz[1]*, L. Artiglia[1]*

[1]Paul Scherrer Institut, Forschungsstrasse 111, CH-5232 Villigen PSI, Switzerland, [2]Institute of Chemical and Bioengineering, ETH Zurich, Zurich, Switzerland

The valorization of carbon dioxide is one of the main research topics in the current time, since it is highly relevant for the development of sustainable energy cycles within the scope of net-zero CO_2-emissions for the future. The reaction of CO_2 on silver catalysts can take place either electrochemically (to carbon monoxide) or thermochemically (to methanol), and it is fundamentally interesting to determine the similarities and differences between the molecular activation processes and intermediates defining the product selectivity in each of these reaction environments. The aim of the present study is to identify the surface reaction processes and active sites determining the product composition, turn over frequency and deactivation pathways of the CO_2 reduction reaction using silver-based catalysts. This is achieved by using ambient pressure X-ray photoelectron spectroscopy (APXPS) on different catalysts from a model-catalytic system (i.e. polycrystalline silver) towards industrially applicable supported substrates. To attain the best possible correlation between experimental results and processes under industrially relevant conditions, experiments are performed using solid-gas and solid-liquid interface setups combined with *ex situ* reactor/electrochemical cell studies.

Investigations on the chemical behavior of cesium and iodine in lead-bismuth liquid metal solution

L. Liu[1], . Zivanovic[1,2], E. Karlsson[1], D. Herrmann[1], A. Vögele[1], J. Neuhausena[1]

[1]Paul Scherrer Institut, [2]ETH Zurich

Lead-bismuth eutectic (LBE) is a eutectic alloy composed of 44.5 at% Pb and 55.5 at% Bi. It is of particular interest as a possible coolant for the Generation IV nuclear reactors and accelerator-driven systems (ADS) given its good thermophysical properties (low melting point, low vapor pressure, and good thermal conductivity) and inertness towards reactions with water and air. However, the behavior of radionuclides present in the coolant, originating from the activation of the liquid metal itself and the potential contamination with fission products, are not well understood. In particular, the release of radionuclides from LBE is a key issue for its safe application and a significant challenge for the licensing of LBE-cooled reactors. In the framework of the “Horizon 2020” PASCAL project, we are interested in the radioisotopes of Cs and I, which are among the most problematic fission products. Compared to the single elements dissolved in LBE, modeling of the chemical equilibrium of the LBE/O/Cs/I system has indicated that Cs and I may show increased evaporation from LBE attributed to the formation of CsI. This thermodynamic prediction needs to be experimentally verified since it is not evident that the chemical equilibrium required to form CsI will be established quickly.

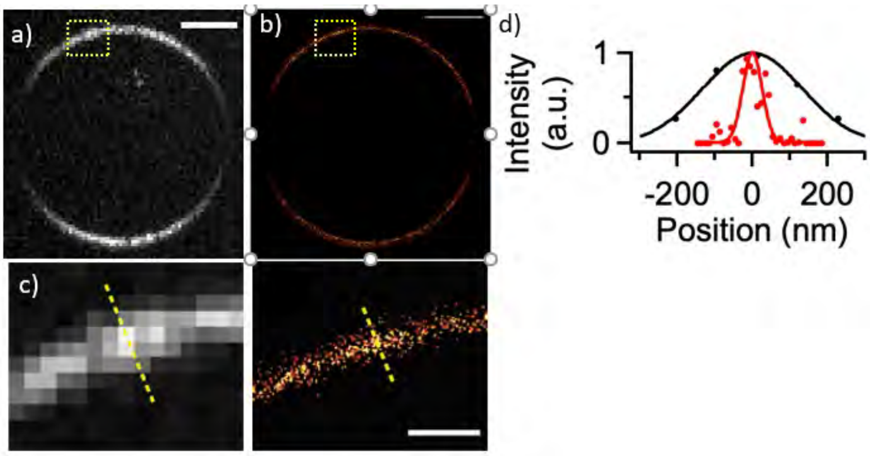
To address this question, on one side, the solubility of the CsI salt in LBE is determined to get a deeper insight into the quaternary system. On the other side, the species evaporated from I-containing LBE samples, Cs-containing LBE samples and Cs-I-containing LBE samples are investigated through thermosublimatography experiments to verify the formation of CsI in LBE.

Super-Resolution Microscopy with Mechanosensitive Membrane Tension Probes

J. Maillard[1,3], E. Drab[1], J. Garcia-Calvo[1], N. Sakai[2], S. Matile[2], A. Fürstenberg[1,3]*

[1]University of Geneva, Department of Physical Chemistry, [2]Department of Organic Chemistry, [3] Department of Inorganic and Analytical Chemistry

The mechanical properties of cells are crucial parameters that regulate key functions and therefore, dysregulation in sensing their environment have implications in various diseases. Although it is generally accepted that membrane tension underlie many different cellular processes such as cell adhesion, endocytosis, exocytosis, phagocytosis, intracellular membrane trafficking and cell division, measuring in vivo forces like tension remains technically challenging. Newly designed oligothiophenes fluorescent probes displaying ground-state planarization at room temperature have led to the development of push-pull probes as mechanosensitive molecules, called “flippers”[1,2]. These probes insert easily into lipid membranes, where they display red-shifted absorption and a much stronger fluorescence emission in the liquid ordered (L_o) lipid phase than in the liquid disordered (L_d) phase due to the forces imposing a planarization of the chromophore already in its ground state. In this contribution, we evaluate different flipper derivatives for single-molecule localization microscopy imaging and report imaging below the diffraction limit with several mechanosensitive probes using the PAINT method (Point Accumulation for Imaging in Nanoscale Tomography)[3,4]. This work paves the way to the imaging of local forces with nanometric precision in cell biology.



Cation Dynamics in Hybrid Perovskites from Solid-state NMR Spectroscopy

A. Mishra[1], M. A. Hope[1], M. Cordova[1], L. Emsley[1]*

[1]Laboratory of Magnetic Resonance, Institut des Sciences et Ingéniere Chemiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

The dynamic response of the ionic lattice affects key electronic properties such as charge-carrier mobilities and exciton binding energies in hybrid perovskites. This dynamic response has been experimentally shown to affect the reorientation of the cation in the cuboctahedral cavity. Solid state NMR has been used widely within the perovskite community to study cation incorporation, phase segregation, halide mixing, disorder, and dynamics. Herein, we show how quadrupolar solid-state NMR relaxometry under magic-angle spinning can be used to uniquely determine cation dynamics in hybrid perovskites. The experimental data can be fitted by considering a rotational diffusion model. This allows the activation energies (E_a) and the correlation times (τ_c) for motion about each principal axes of the cation to be disentangled. We use this model to characterize cation dynamics in current state-of-the-art multi-cation perovskites such as $GUA_xMA_{1-x}PbI_3$, $MA_xFA_{1-x}PbI_3$, $Cs_xFA_{1-x}PbI_3$ and, $Cs_xFA_yMA_{1-x-y}PbI_3$. Surprisingly, we find that the FA (formamidinium) dynamics is invariant to the composition, whereas MA (methylammonium) dynamics changes significantly. Overall, this methodology provides a comprehensive understanding of the cation dynamics in hybrid perovskites.

Studying rotational-state and conformational effects in chemi-ionisation reactions

A. Mishra[1], L. Ploenes[1], P. Straňák[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 [2,3]. Extending our methodology to neutral reactions, we have recently built a new crossed-molecular-beam setup. This setup is 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) [4].

As the first application of this new method, rotational-state and conformationally specific chemi-ionisation reactions of carbonyl sulfide (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. Our result suggests that OCS molecules in the rotational ground state $j = 0$ are a factor of 2.5 more reactive for dissociative ionisation than Penning ionisation compared to the $j = 1$ state [4,5]. Similarly, cis-hydroquinone shows a stronger propensity for dissociative ionization in comparison to Penning ionisation than trans-hydroquinone. Monte-Carlo trajectory simulations showed that the formation of the Penning ionised product depends on the initial conformational and rotational state of hydroquinone whereas the formation of the dissociative ionised product is independent of the initial conformational and rotational state. The disentanglement of conformational and rotational-state effects can be difficult to analyse due to the involvement of several rotational states [5]. However, choosing conformers that can be chemically separated and have high interconversion barriers could disentangle the conformational and rotational state dependencies. Therefore, we chose to study the chemi-ionisation reaction of 1,2-dibromoethylene (DBE), the conformers of which can be chemically separated. Moreover, in a collaboration with the Korean Advanced Institute of Science and Technology (KAIST), we are also currently undertaking a comparative study of the photochemistry, photoionisation and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene (DBE) as a prototypical system. These investigations aim at gaining a comprehensive understanding of the role of molecular conformations in unimolecular and bimolecular reactivity.

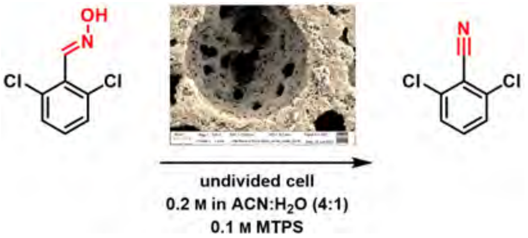
[1] S. Willitsch, *Adv. Chem. Phys.*, **2017**, 162, 307
[2] Y.-P. Chang, K. Dlugolecki, J. Küpper, D. Rösch, D. Wild, S. Willitsch, *Science*, **2013**, 342, 98
[3] A. Kilaj, J. Wang, P. Straňák, M. Schwilk, U. Rivero, L. Xu, O. A v. Lilienfeld, J. Küpper, S. Willitsch, *Nat. Commun.*, **2021**, 12, 6047
[4] L. Ploenes, P. Straňák, H. Gao, J. Küpper and S. Willitsch, *Mol. Phys.*, **2021**, 119, 1965234
[5] L. Ploenes, P. Straňák, S. Willitsch, in prep., **2022**

Leaded bronze foams: a novel high surface area electrocatalyst material for cathodic electrosynthesis

P. Moreno-García[1], T. Prenzel[2], M. Gálvez-Vázquez[1], L. Gálvez-Vázquez[1], S. R. Waldvogel, [2], P. Broekmann[1]*

[1]University of Bern, [2]Johannes Gutenberg University Mainz

Typical heavy metals used as cathode materials for electro-organic reduction reactions are lead, mercury, and cadmium, as they exhibit a large over-potential for the hydrogen evolution reaction (HER).[1] However, all three metals are prone to cathodic corrosion forming highly toxic organometallic compounds, which might contaminate the product. In previous work we have shown that leaded bronze, which is an easily available and inexpensive flat cathode material, combines an excellent performance in electrosynthesis with a significantly increased mechanical and chemical stability.[2] In this work we report on the development and electrocatalytic performance of a novel leaded bronze foam-type cathode material that keeps the catalytic properties of flat leaded bronze samples and exhibits ultra large specific area for efficient electroorganic transformations. Its manufacture is based on the dynamic hydrogen bubble template (DHBT) method,[3,4] an efficient and inexpensive strategy to prepare functional porous materials that consists of the superposition of metal deposition and hydrogen evolution at the surface of the support material. We exemplarily demonstrate the improved catalytic performance of these leaded bronze foams by means of a direct, halogen-free synthesis of nitriles from oximes with yields up to 84%. These cathode materials keep promise as an excellent and improved alternative to substitute heavy metal cathodes used for electrosynthesis of fine chemicals, pharmaceutical active agents, and late-stage functionalization.



[1] Christoph Gütz, Valentine Grimaudo, Michael Holtkamp, Marius Hartmer, Janina Werra, Lisa Frensemeier, Anton Kehl, Uwe Karst, Peter Broekmann, Siegfried R. Waldvogel, *ChemElectrochem* 2018, 5, 247-252

[2] Christoph Gütz, Maximilian Selt, Markus Bänziger, Christoph Bucher, Christina Rçmelt, Nadine Hecken, Fabrice Gallou, Tomás R. Galvão, Siegfried R. Waldvogel, *Chem. Eur. J.* 2015, 21, 13878-13882

[3] Pavel Moreno-García, Nicolas Schlegel, Alberto Zanetti, Alena Cedeño López, María de Jesús Gálvez-Vázquez, Abhijit Dutta, Motiar Rahaman, Peter Broekmann, *ACS Appl. Mater. Interfaces* 2018, 10, 37, 31355-31365

[4] Blake J. Plowman, Lathe A. Jones, Suresh K. Bhargava, *Chem. Comm.* 2015, 51, (21), 4331-4346

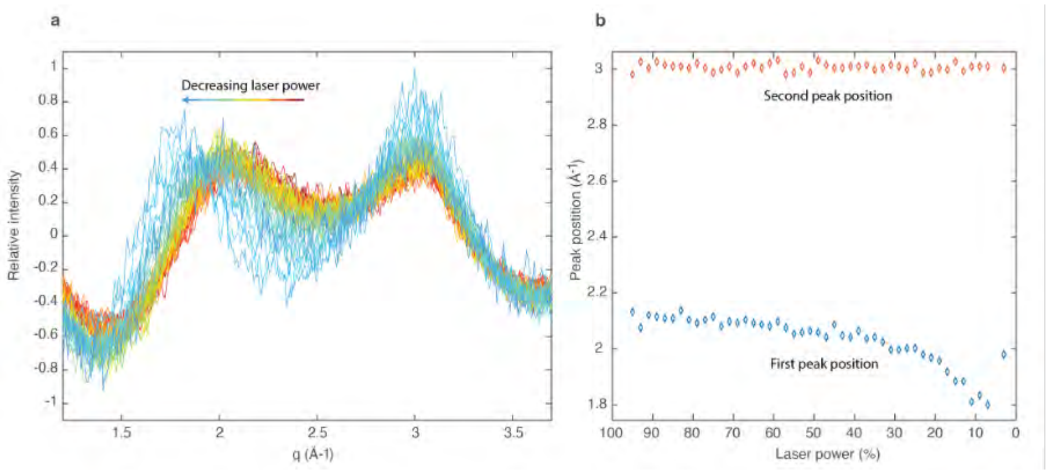
The Structure of Water in No Man's Land

N. Mowry[1], C. Krüger[1], M. Drabbels[1]*, U. J. Lorenz[1]*

[1]Laboratory of Molecular Nanodynamics, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Water is the most researched liquid in history yet still perplexing scientists with its abnormal behavior, giving water the nickname – “the most anomalous liquid.”[1] For example, the density of water increases as it is cooled, reaching a maximum at 4 ˚C (277 K), the compressibility of water sees a minimum at 46 ˚C (319 K)[2] and the specific heat rises sharply as water is supercooled.[3] These behaviors raise the question that scientists have been trying to answer for decades: why does water exhibit such anomalous behavior the colder it gets? The answer, at least in part, lies within the supercooled regime. Researchers believe this is because water exists in a so called ‘two-state liquid,’ where both a high-density liquid and low-density liquid water coexist together in a metastable state, giving water abnormal behavior as it gets colder.[4] In the temperature range between 235 K and 150 K, supercooled water can crystalize as fast as several microseconds, and therefore not accessible experimentally by traditional approaches, giving this temperature range the name ‘no man’s land.’

We have developed a technique to probe the structure of water at these temperatures, using a modified transmission electron microscope that provides high temporal and spatial resolution. To perform these experiments, a small gold mesh sample grid with graphene placed on top is cooled down to 100 K and water is condensed onto it and rapidly cooled to become amorphous solid water. By heating this sample with a laser pulse to different temperatures, we can acquire diffraction patterns by means of an electron pulse, which can provide detailed information on the structure of water at a specific temperature. The attached two panel figure shows the one-dimensional diffraction patterns at different laser powers (Figure 1a) as well as the peak position change as a function of laser power (Figure 1b). By analyzing the change in peak position, experimental data can begin to expose the structural changes of water in no man’s land.



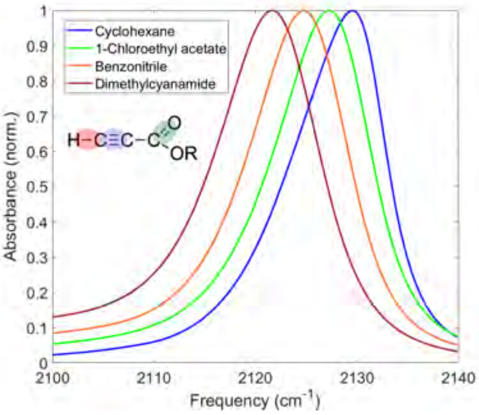
[1] Pettersson, L. G. M., Henchman, R. H. & Nilsson, A. Water—The Most Anomalous Liquid. *Chem. Rev.* **116**, 7459–7462 (2016).
[2] Kumar, P., Han, S. & Stanley, H. E. Anomalies of water and hydrogen bond dynamics in hydrophobic nanoconfinement. *J. Phys.: Condens. Matter* **21**, 504108 (2009).
[3] Maruyama, S. Thermal Properties of Supercooled Water Confined within Silica Gel Pores. in *AIP Conference Proceedings* vol. 708 675–676 (AIP, 2004).
[4] Gallo, P. *et al.* Water: A Tale of Two Liquids. *Chem. Rev.* **116**, 7463–7500 (2016).

Vibrational Spectroscopy of New Molecular Probes for Interfacial Sensing

M. Parra[1], B. Dereka[1]*

[1]University of Zurich, Department of Chemistry

Surface physical and chemical processes play a significant role in the performance of many energy conversion technologies such as batteries and photovoltaic cells, as well as catalysis for water splitting and CO_2 reduction. Characterisation of microscopic processes, molecular motions and fluctuations at solid-liquid interfaces is a challenging task, partly due to the limited number of methods capable of tracking structural dynamics and the high complexity of the interfacial region. For example, the best descriptions of the electric double layer formed at solid-liquid interfaces are merely static, and real-time experimental evidence of solute dynamics and its interplay with the immediate surrounding environment is needed. Recent rapid progress in ultrafast spectroscopy is changing this, with the development of techniques capable of studying ultrafast dynamics at the interface with a high degree of surface sensitivity [1]. In particular, time-resolved infrared (IR) spectroscopy is a powerful tool that combines both structural sensitivity and time resolution to visualise the dynamics of molecular interactions in real time. With the implementation of this technique for interfacial analysis, tethering of appropriate molecular probes with adequate vibrational markers could allow the characterisation of molecular environments at various lengths from the surface. We are developing an approach of multiplexed vibrational probes combining several characteristic markers placed at different positions and with different orientations in a molecule. We plan to tether these probes to conducting films via different approaches depending on the specific surface chemistry. Sensitivity of these makers towards specific and non-specific interactions is a highly desirable feature when probing interfaces. As a first step, steady-state FTIR spectra were measured for esters of propiolic acid in a selection of solvents with varying parameters. Specific local vibrational modes (C≡C, C=O and C–H stretches, see Figure) were chosen as suitable candidates for IR probes. Solvent-induced variations of vibrational frequencies (Fig. 2) due to the electric field and H-bonding interactions exerted by the solvent were disentangled by correlating the frequencies corresponding to each vibrational mode with the Kamlet-Taft parameters (accounting for the solvent ability to donate (α) or accept (β) H-bonds) and the solvent's Onsager function (incorporating the effect of non-specific interactions resulting from the vibrational Stark effect (VSE) [2,3]). These results obtained in liquid solution pave the way toward the characterisation of the molecular vibrational modes interacting with their environment and serve as a reference for the future quantification of the interfacial properties.



FTIR spectra showing the C≡C stretching band of methyl propiolate in four different solvents. **Inset**: Ester of propiolic acid showing the vibrational markers of interest highlighted in red (C-H), blue (C≡C) and green (C=O).

[1] Jan Philip Kraack, Peter Hamm, *Chemical Reviews*, **2017**, 117, 10623–10664.
[2] Stephen Fried, Steven Boxer, *Accounts of Chemical Research*, **2015**, 48, 998–1006.
[3] Nicholas Levinson, Stephen Fried, Steven Boxer, *Journal of Physical Chemistry B*, **2012**, 116, 10470–10476.

Prediction of mycotoxin response of DNA-wrapped nanotube sensor with machine learning

Y. Rabbani[1,2], S. Behjati[1], B. Lambert[1], S. Sajjadi[1], M. Shariaty-Niassar[2], A. A. Boghossian[1]*

[1]Institute of Chemical Sciences and Engineering (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015-Lausanne, Switzerland, [2]Transport Phenomena & Nanotechnology (TPNT) Lab., School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, 111554563, Iran

DNA-wrapped single-walled carbon nanotubes (SWCNTs) have demonstrated great versatility in their use as optical sensors. SWCNTs emit a near-infrared fluorescence that is responsive to even the slightest changes in the nanotube environment, enabling sensors that can respond to single-molecule fluctuations within the vicinity of their surfaces. The fluorescence response and surface interactions of these sensors are determined by the DNA wrapping sequence. However, the lack of information on the relationship between the DNA sequence and its effect on the SWCNT fluorescence remains a bottleneck for designing sequences that are specific to analytes of interest. We have recently demonstrated the use of directed evolution to control the fluorescence response of SWCNTs through DNA design. Iterative cycles of DNA mutation, screening, and selection allowed us to evolve sequences that yield DNA-wrapped SWCNT sensors with a desired fluorescence response to mycotoxins.

In this work, we apply the screening results of the DNA libraries used in this approach to train machine learning (ML) algorithms. Artificial neural network (ANN) and support vector machine (SVM) methods were used to predict the response of ssDNA-SWCNT sensors to the mycotoxin. The reliability of the model was further assessed through cross-validation. The SVM model with cross-validation was able to accurately classify the various DNA sequences as yielding either a high or low fluorescence response with 81% accuracy. The model was further tested on alternative DNA sequences outside the initial training dataset, which was able to accurately classify the data with 95% accuracy. The application of ML algorithms to directed evolution libraries of DNA thus allows one to accurately map the performances of these sensors within a particular sequence space. The computational success of this mapping provides a framework for replacing current empirical approaches with the rational design of DNA sequences for SWCNT sensing.

Keywords: ssDNA-SWCNT, Mycotoxin, Directed Evolution Method, Machine learning

Precision spectroscopy and coherent manipulation of single trapped molecular N_2^+ ions

M. F. Roguski[1], A. Shlykov[1], M. Sinhal[1], R. Karl[1], P. Paliwal[1], S. Willitsch[1]*

[1]University of Basel, Department of Chemistry, Klingelbergstrasse 80, 4056 Basel, Switzerland

Manipulation of single trapped molecules on the quantum level has gained notable interest in recent years. Their complex energy-level structure with rotational and vibrational degrees of freedom provides a plethora of transitions with various properties but also presents challenges towards molecular state initialisation, manipulation and readout. Building on the methods known for trapped atomic species, we follow a quantum-logic protocol that uses a single co-trapped atomic ion as a probe for the molecular state. We demonstrated a quantum non-demolition state detection on N_2^+ with fidelities exceeding 99% without destroying the state itself.[1] Currently, we are implementing precision-spectroscopic measurements on a narrow infrared quadrupole transition referenced to the Swiss primary frequency standard at METAS in Berne via an optical fibre link. Future work will involve coherent manipulation of the molecular long-lived hyperfine-Zeeman transitions. The presented methods pave a way for the implementation of molecular qubits with excellent coherence properties, for establishing new frequency standards in the mid-IR regime, for investigating state-to-state dynamics of chemical reactions, and for exploring beyond-standard-model physics by tracking a possible temporal variation of fundamental constants.

[1] Mudit Sinhal, Ziv Meir, Kaveh Najafian, Gregor Hegi and Stefan Willitsch, Science, **2020**, 367, 1213–8.

2DRaman-THz spectroscopy with single-shot THz detection

S. Shukla[1], M. Duchi[1], A. Shalit[1], P. Hamm[1]*

[1]University of Zürich, Winterthurerstrasse 190, 8057, Zürich, Switzerland

Hybrid two-dimensional (2D) Raman-THz spectroscopy is a novel spectroscopic technique to study coupling between low-frequency molecular motions in liquid samples in the THz frequency region (0.1-10 THz) [1]. Often in these liquids the signal to noise ratio is quite small leading to long data acquisition times (of the order of days) [2]. In this work we present the development of a multi-channel (single shot) THz detection scheme using crossed echelons (Fig. 1a) which brings the data acquisition from days to hours. We characterize the setup using 2D response on liquid $CHBr_3$; which has a coupling signal between its intramolecular vibrational modes and intermolecular librational modes [2]. We demonstrate a speed-up factor of 34 times in data acquisition as compared to conventional step scanning method [3].

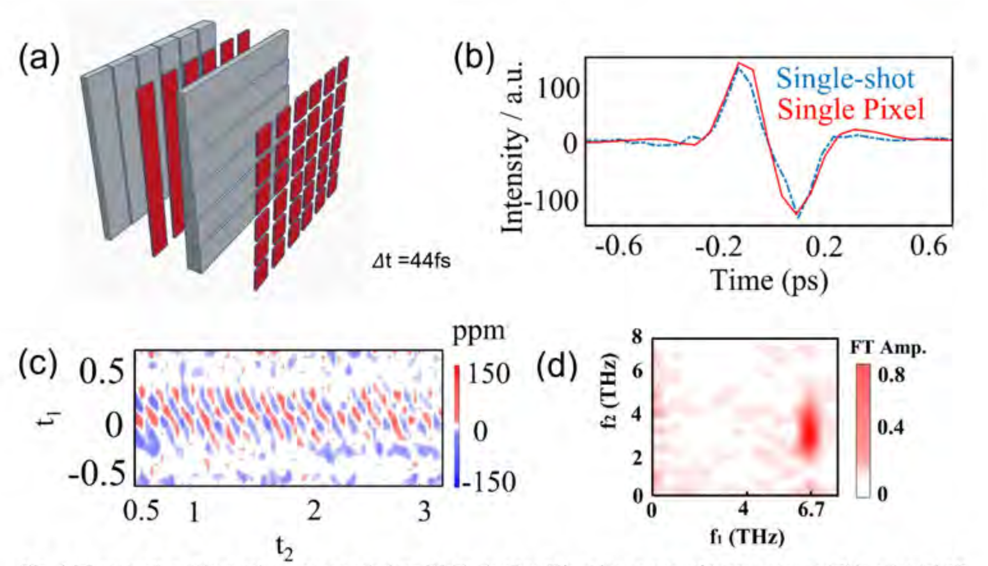


Fig. 1 (a) generating delays using crosses echelons (b) Single Shot THz pulse compared to step scanned THz pulse (c) 2D Raman THz signal revealing vibrational dynamics in liquid bromoform (d) Fourier transform of vibration dynamics shows a peak at 6.7 THz

Figure 1(a) shows two sets of crossed echelons of increasing thicknesses generating beamlets (pixels) which are delayed by 44 fs with respect to each other. This gives a time window of 1.4 ps. Figure 1(b) shows multi-channel detected single shot THz pulse in comparison with step scanned THz pulse on a single pixel. 2D Raman THz response of liquid $CHBr_3$ is shown in Figure 1(c). Vibrational dynamics extending along the Raman axis beyond pulse overlap at 0. Fourier transforming these dynamics reveals a frequency of 6.7 THz shown in Figure 1(d). By comparing the data quality (Signal to noise ratio) of the single shot method with the step scan method (data taken for 2 hours), we see an enhancement factor of 5.8 in Signal to Noise, translating to speed up factor of 34 in data acquisition times [3].

[1] Savolainen, J. et al., *Proc. Natl. Acad. Sci. U. S. A.* **2013**, 110, 20402−20407.
[2] Ciardi, G. et al., *J. Phys. Chem. Lett.* **2019**, 10, 4463-4468.
[3] Duchi, Marta, et al., *J. Chem. Physics* **2021**, 155.17: 174201.

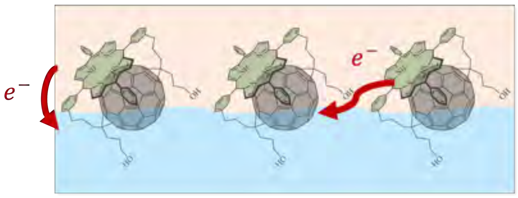
Photoinduced Electron Transfer in a Porphyrin-Fullerene Dyad at a Liquid Interface

J. sissaoui[1], A. Efimov[2], T. Kumpulainen[3], E. Vauthey[1]*

[1]Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, Geneva, Switzerland, [2]Faculty of Engineering and Natural Sciences, Tampere University, Korkeakoulunkatu 8, Tampere, Finland, [3]Department of Chemistry/Nanoscience Center, University of Jyväskylä, Survontie 9 C, Jyväskylä, Finland

Organic Photovoltaics (OPVs) have gained increasing attention during the past decades as an alternative energy source. These devices rely on absorption of photons by small organic molecules followed by charge transfer at the interface in the donor and acceptor materials. Therefore, understanding the charge-separation process at interface of two materials with different dielectric properties is of paramount importance for the future development of superior devices.

We approach this problem using the excited-state properties of an amphiphilic porphyrin-fullerene dyad and of its porphyrin analogue adsorbed at water/dodecane interface using second harmonic generation (SHG). The Polarized SHG experiments confirm the results of MD simulations. The interfacial orientation of the porphyrin subunit is different for the dyad and the porphyrin analogue. Time-resolved SHG measurements reveal a concentration dependence of the excited state dynamics of both compounds upon Q-band excitation implying the occurrence of intermolecular quenching processes. A significantly slower ground-state recovery of the dyad compared to the porphyrin analogue is observed, in agreement with the population of a longer-lived state, most probably a charge separated state.



A cryogenic hybrid trap for cold ion-molecule reactions

P. Vahramian[1], C. Von Planta[1], D. Haas[1], C. Mangeng[1], R. Karl[1], D. Zhang[2], T. Kierspel[1], Y. Ying[1], S. Willitsch[1]*

[1]University of Basel, [2]Institute of Atomic and Molecular Physics, Jilin University, Changchun, China

At cold (~ mK) translational temperatures, the physics of ion-molecule chemical reactions is a vastly uncharted territory.
Their manipulation and control has made rapid progress in the past years [1], both for neutral [2] and charged [3] molecules, reaching even the coherent control on the internal state at the single particle level [4].

The goal of our experiment is to study the chemistry of cold, reactive collisions between simultaneously trapped neutral polar molecules (e.g. OH) and molecular or atomic ions (e.g. Ca+ and N2+).
Employing state-of-the-art techniques, we aim at overlapping physically the two trapped species, while retaining control over the internal state of the ion and observing state-dependent reaction rates in the millikelvin temperature range.

As initial step we will study collisions between atomic ions and polar molecules.
In a later stage, molecular ions would be cooled and coherently manipulated by means of auxiliary Ca+ ions and quantum--non demolition measurement techniques, as recently demonstrated [4].

In my poster I will introduce the experiment developed in the previous years.
The heart of the setup is a cryogenic hybrid trap consisting of a linear RF ion trap and a static magnetic trap for neutral molecules, where long-term trapping of Stark decelerated paramagnetic radicals has already been demonstrated [2].

Moreover I will report on the recent implementation of an advanced switching scheme of the Stark decelerator, first developed in [5], that increases the number of molecules trapped by a factor of 7, greatly enhancing the number of collisions expected to be observed and the statistic of the experiment overall.

[1] Dulieu, Olivier, et al. "Physics and chemistry of cold molecules." Physical Chemistry Chemical Physics 13.42 (2011): 18703-18704.
[2] Haas, Dominik, et al. "Long-term trapping of Stark-decelerated molecules." Communications Physics 2.1 (2019): 1-7.
[3] Willitsch, Stefan. "Chemistry with controlled ions." Adv. Chem. Phys 162 (2017): 307-340.
[4] Sinhal, Mudit, et al. "Quantum-non demolition state detection and spectroscopy of single trapped molecules." Science 367.6483 (2020): 1213-1218.
[5] Reens, David, et al."Beyond the limits of conventional Stark deceleration." Physical Review Research 2.3 (2020): 033095.

Bimolecular Photoinduced Electron Transfer in Non-Polar solvents

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

[1]Department of Physical Chemistry, University of Geneva, 30 Quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland

Bimolecular photoinduced electron transfer (ET) in non-polar solvents is still poorly understood. To get a deeper insight into the relevant reaction coordinate, the effect of molecular interactions between donor and acceptor and the nature of the quenching 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, 2] One can thus anticipate that the red-edge absorption is due to chromophores with one or several quencher molecules. Consequently, different distributions of reactant pairs can be photo-selected by tuning the excitation wavelength. (see figure)

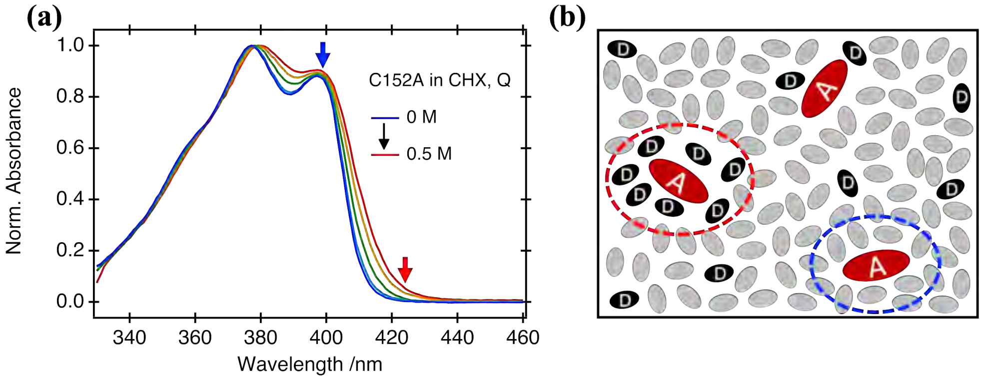


Figure: **(a)** Absorption spectrum of the coumarin C152A in cyclohexane with increasing concentration of quencher (Q) **(b)** Pictorial representation for possible distribution of electron donor (D) and acceptor (A) in a non-polar solvent.

We will present our investigation on the dynamics and the nature of the ET quenching product in non-polar solvents with donor-acceptor pairs experiencing different interactions, namely dispersion and dipole-dipole interactions. For this we applied broadband fluorescence up-conversion and transient absorption (TA) spectroscopy with sub 100 fs resolution using tunable excitation wavelength. We will show that significantly different ET dynamics are observed depending on the excitation wavelength.

[1] Christoph Nançoz, Christopher Rumble, Arnulf Rosspeintner and Eric Vauthey, *Journal of Chemical Physics*, **2020**, 152, 244501.
[2] Romain Letrun and Eric Vauthey, *The Journal of Physical Chemistry Letters*, **2014**, 5 (10), 1685-1690.

Femtosecond laser-induced fragmentation mechanism of gold nanoparticles in water

C. Yan[1], G. Bongiovanni[1], P. K. Olshin[1], J. M. Voss [1], M. Drabbels [1], U. J. Lorenz[1]*

[1]Laboratory of Molecular Nanodynamics, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Laser irradiation of plasmonic nanoparticles in water gives rise to a range of phenomena that includes particle reshaping and fragmentation. Despite many experimental and theoretical studies, there is still a debate about the fundamental mechanisms involved during ultrafast laser-induced fragmentation of plasmonic nanoparticles in liquid. Here, we use in situ electron microscopy to observe the fragmentation of gold nanoparticles in water under femtosecond laser irradiation, which reveals that the process occurs through the emission of individual progeny particles. This observation is consistent with a mechanism that involves Coulomb fission of an ionized and melted particle. Prolonged laser irradiation gives rise to a variety of secondary phenomena such as solution-mediated etching and growth processes. This work provides valuable insight into the complexity of the interaction of nanoparticles with laser radiation and highlights the importance of in situ observations to disentangle the mechanisms of related phenomena.

A generalised-dividing-surface diabatic instanton rate theory

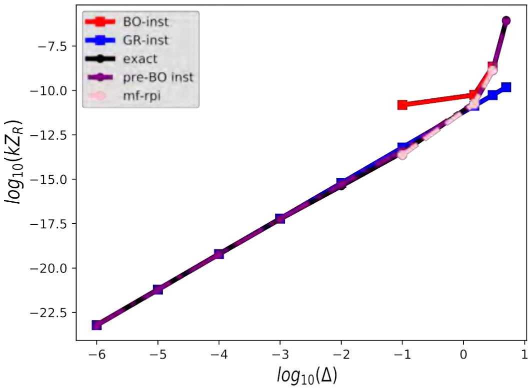
R. A. Zarotiadis[1], J. O. Richardson[1]*

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

The accurate prediction of (quantum) rates and rate mechanisms is key to advance our understanding of chemical reactions in a variety of disciplines, ranging from astrophysics to photosynthesis.

For many chemically-relevant reactions, it is well-known that either the Born-Oppenheimer approximation is a valid choice or that the reaction takes place in the nonadiabatic regime. In either of these limits well-established instanton rate theories exist. [1, 2]

A priori however, the distinction into adiabatic and nonadiabatic regimes is not straightforward or cannot be made strictly. Here a universal rate theory is desirable. Many such attempts have been made, a prominent one being mean-field ring-polymer instanton (mf-rpi) theory. We show the pitfalls of this approach, namely that it does not recover the golden-rule behaviour in the nonadiabatic limit and that the instanton collapses prematurely (see figure). We introduce our new instanton rate theory, which is developed to describe the different contributions to the generalised flux-flux correlation function using separate instantons.



Our new, general instanton rate theory is derived from the flux-flux correlation function and inspired by a generalisation of the flux-operator as introduced in [3], it can therefore go beyond the theories designed for either limits while still correctly recovering them if appropriate.

[1] Richardson, J. O., Int. Rev. Phys. Chem., 2018, 37:2, 171-216
[2] Richardson, J. O., Bauer, R., Thoss, M., J. Chem. Phys., 2015, 143, 134115
[3] Lawrence, J. E., Manolopoulos D. E., J. Chem. Phys., 2020, 152, 204117

Ion-molecule reactions near 0 K: the effect of the unpaired electron in NO on the He^+ + NO reaction rate coefficients

V. Zhelyazkova[1], F. B. Martins[1], S. Schilling [1], F. Merkt[1]*

[1]ETH Zurich

We present experimental results and calculations of the capture rate coefficient based on the adiabatic-channel model [1-2] for the He^+ + NO reaction at collision energies between 0 and ~ $k_B\cdot 10$ K. To avoid heating by stray electric fields, the He^+ ion is replaced by a He atom in a Rydberg state [He(*n*)]. We employ a merged-beam set-up, in which a 50-electrode curved Rydberg-Stark deflector and decelerator is used to merge the Rydberg helium atoms with a supersonic beam containing the NO molecules [2]. The reaction product ions are collected in a time-of-flight mass spectrometer for a range of collision energies (E_{coll}) varied by changing the velocity of the He(*n*) atoms with the deflector.

Although NO has only a small dipole moment (μ_e = 0.159 D), we observe a strong enhancement of the total reaction yield below ~$k_B\cdot 1$ K, with the total capture rate coefficient reaching a value of ~$3k_L$ (k_L is the Langevin rate constant) at the lowest energies accessible (~$k_B\cdot 100$ mK). Our results are well described by calculations based on the adiabatic-channel model [1-2]. NO has an electronic configuration of $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2px,y})^4(\sigma_{2pz})^2(\pi^*_{2px,y})^1$, with a single unpaired electron in a π orbital. The electronic ground state of NO has X $^2\Pi_{1/2}$ character, and the projection of the orbital angular momentum on the internucler axis is $\Lambda = \pm 1$. The two possible values of Λ lead to two states of opposite parity (a Λ-doublet), the degeneracy of which is lifted by interactions with higher-lying electronic states [3]. The observed enhancement of the reaction rate coefficient is attributed to the repulsion between the opposite-parity components of each rotational state in NO in the electric field of the ion, which leads to states experiencing a strong linear and negative Stark shift.

To emphasise this effect, we also present results on the He^+ + CO reaction. Carbon monoxide has a similar dipole moment to nitric oxide (μ_e = 0.112 D), but a X $^1\Sigma^+$ ground electronic state and thus no Λ-doubling. The total product ion yield of the He^+ + CO reaction exhibits a *decrease* with decreasing E_{coll} attributed to the negative quadrupole moment of CO (Q_{zz} = -2.839 DÅ).

[1] J. Troe *J. Chem. Phys.* **105**, 6249 (1996).
[2] D. C. Clary, *Ann. Rev. Phys. Chem.* **41**, 61 (1990).
[3] G. Herzberg. Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules. D. Van Nostrand Company, 2nd edition, 1963.

Performance of chemoresistive nanosensors in the detection of gas-phase impurities after irradiation with gamma-rays and alpha particles.

G. Zonta[1], M. Astolfi[1], S. Gherardi[2], C. Malagù[1], M. Kasprzak[3], P. Steinegger[4,5], N. M. Chiera[4]*

[1]Department of Physics and Earth Science, University of Ferrara, Italy, [2]SCENT S.r.l., Italy, [3] Department of Radiation Safety and Security, Paul Scherrer Institute, Switzerland, [4]Laboratory of Radiochemistry, Paul Scherrer Institute, Switzerland, [5]Department of Chemistry and Applied Biosciences, ETH Zürich, Switzerland

In the past years, chemoresistive gas sensors based on hybrid metal-oxides nanocomposites have received increasing attention due to their fast and high sensitivity to specific volatile compounds, low production cost, small dimensions, and simple integration to pre-existent analytical systems. Recently, an array of chemoresistive gas sensors, based on screen-printed metal oxide semiconducting films, has been developed at the University of Ferrara (Italy), and used as a non-invasive preventive screening technique for colorectal cancer [1, 2]. This array of sensors showed a detection sensitivity at the ppb level for volatile organic compounds of oncological interest [3]. In particular, the nanostructured semiconductor sensors ST25 (based on a mixture of SnO_2, TiO_2, and Au nanoparticles) and STN (made of a mix of SnO_2, TiO_2, and Nb_2TiO_7) showed the best sensing response, i.e., the highest sensitivity detection coupled to a high specificity when applied to various gas mixtures [4]. The need of monitoring the composition of gas mixtures is of utmost importance in radiochemical experiments with transactinides and their lighter homologues. At the single-atom level conditions, residual impurities (e.g., H_2O, O_2, CO, etc.) in the gas carrier can lead to the synthesis of undesired compounds, with a consequent decrease of the expected gas-chromatographic yields. In order to gain knowledge on the influence of gas impurities on the chemistry of transactinides, the chromatographic gas-loop system TRACY (Trace-Gas Reaction Analyzer for Chemistry) has been developed at Paul Scherrer Institute, Switzerland [5]. One of the great advantages of TRACY is its contained dimension, which allows its transport and use at worldwide heavy-ion accelerator beamlines. At present, the TRACY device is coupled to a mass-spectrometer for the monitoring of the gas-composition. However, the employment of a mass-spectrometer shows several disadvantages, such as impractical transport, high maintenance costs, and inability to identify polyatomic or molecular interferences having the same charge-to-mass ratio. Therefore, alternative mass-detection techniques are highly desired.

In the project herein presented, we assessed the performance of the ST25 and STN chemosensors in the detection H_2O impurities in the TRACY gas-loop system, with the objective of employing these sensors as an efficient and cheaper alternative to on-line mass-spectrometer devices. Since the sensors are destined for use in a radioactive environment, we tested the detection sensitivity of the ST25 and STN nanostructured semiconductors towards H_2O and CO before and after irradiation with alpha particles and gamma-rays. The irradiated samples were characterized by scanning electron microscopy to evaluate the effect of irradiation on their morphology and microstructure. Preliminary results showed a fast and efficient response of the sensors in their novel use. The performance of the ST25 and STN sensors before and after irradiation will be discussed.

[1] Malagù, C., Fabbri, B., Gherardi, S., et al. *Sensors*, **2014**, 14, 18982-18992. [2] Anania, G., Fabbri, B., Gaiardo, A., et al. *Procedia engineering*, **2016**, 168, 113-116. [3] Zonta, G., Anania, G., Fabbri, B., et al. *Sensors and Actuators B: Chemical*, **2015**, 218, 289-295. [4] Astolfi, M., Rispoli, G., Anania, G., et al. *Molecules*, **2021**, 26, 466. [5] Ionescu, P., Sato, T.K., Steinegger, P., et al. *Laboratory of Radiochemistry*, **2020**, 184, p.5.

Single molecular insights into receptor binding energetics of SARS-CoV2-variants

A. Ray[1,3], M. Koehler[1], R. Moreira[2], B. Juniku[1], A. Poma[2]*, D. Alsteens[1]*

[1]Nanobiophysics lab, Université catholique de Louvain, Belgium 1348, [2]Lodz University of Technology, Lodz, Poland 90-924, [3]Ankita.ray@uclouvain.be

The emergence and spread of a novel coronavirus (CoV) that is a causative agent for severe acute respiratory syndrome (SARS) has impacted global health and economy tremendously. It has garnered considerable attention because of its ability to evade the host immune surveillance and retain its infectivity while undergoing mutagenesis at an alarming rate . The virus infects by attaching its homotrimeric spike glycoprotein (consisting of S1 and S2 subunits) to the angiotensin converting enzyme 2 (ACE2) receptor molecules present in human respiratory epithelial cells. After a period of evolutionary stasis, there has been an emergence of different mutants of SARS-CoV-2 with varying degrees of transmissibility and antigenicity in the late 2020s. Mutations in genetic material of CoV-2 have led to the development of variants with unusual epidemiological characteristics and some of these mutants are recognized as 'variants of concern' (VOCs) by the World Health Organization (WHO). Mutants detected in the United Kingdom (B.1.1.7, Alpha), Republic of South Africa (B.1.351, Beta), Japan-Brazil (B.1.1.248 , Gamma), and India (B.1.617, Delta) are expected to display altered affinity towards the ACE2 receptors, thereby affecting its severity in a population. Since genomic mutations confer unusual biophysical properties to the native virus which can manifest in resistance towards vaccines or altered resistance to recombinant neutralizing antibodies, a definitive understanding of the binding interaction is of pivotal importance in the development of vaccines against the SARS-CoV-2 mutants. We have reported the use of atomic force microscopy (AFM) to map the interaction forces between the AFM tips functionalized with the S-glycoprotein of RBD and the ACE2 receptors on model surfaces . By single-molecule force spectroscopy (SMFS), we have shown that there is a high affinity (~ 120 nM) guided by specific multivalent interactions at the RBD/ACE2 interface . By leveraging the power of force-distance (FD) curve-based AFM and steered MD calculations, we have derived the kinetic and thermodynamic parameters between the ACE2 receptors on model surface with RBD of four different SARS-CoV-2 mutants (alpha, beta, gamma, and delta respectively) to shed a light on the molecular basis of increased transmissibility and pathogenicity.

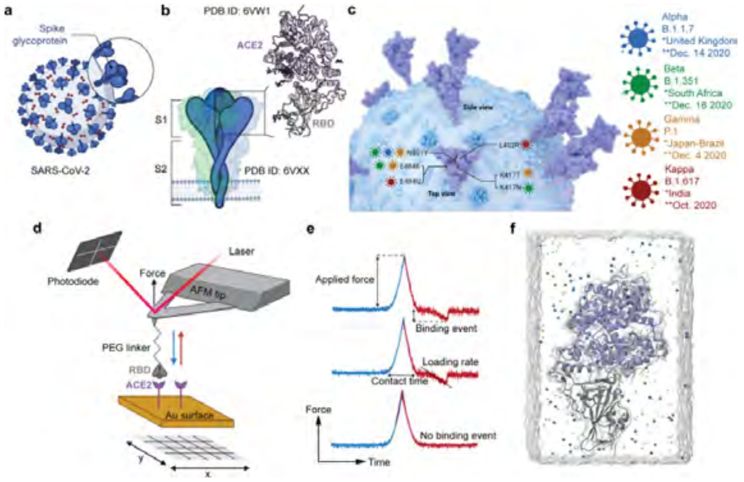


Figure 1. (a) Schematic of a SARS-CoV-2 virus particle expressing spike glycoprotein. (b) S-glycoprotein comprising of S1 and S2 subunits. (c) 3D rendering of a viral particle showing the different VoCs with key spike mutations. (d) Schematic of probing RBD mutant binding to ACE2 receptors by AFM. (e) Representative AFM force-time curves from which loading rate (LR) can be determined (LR= ΔF/ Δt) (upper curve). (f) Cartoon for the interaction between RBD-ACE2 for MD simulation.

[1] Koehler Melanie, Ray Ankita, Poma Adolfo, Alsteens David, *Nature Comm*, **2021**, 12:6977
[2] Simpson Joshua, Ray Ankita, Alsteens David, Chem Comm, **2022**, 58,5088.
[3] Yang Jinsung, Petitjean Simon, Alsteens David, *Nature Comm*, **2020**, 11:4541

Unraveling the Photoinduced Symmetry-Breaking Charge Separation (SB-CS) process in a PDI-based Cage

E. Sucre-Rosales[1], E. Vauthey[1]*

[1]University of Geneva, Physical Chemistry Department - Sciences II, 30, Quai Ernest Ansermet,
1211 Geneva 4

To be delivered