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More than a solvent: donor-acceptor complexes of room-temperature ionic liquids and electron acceptors

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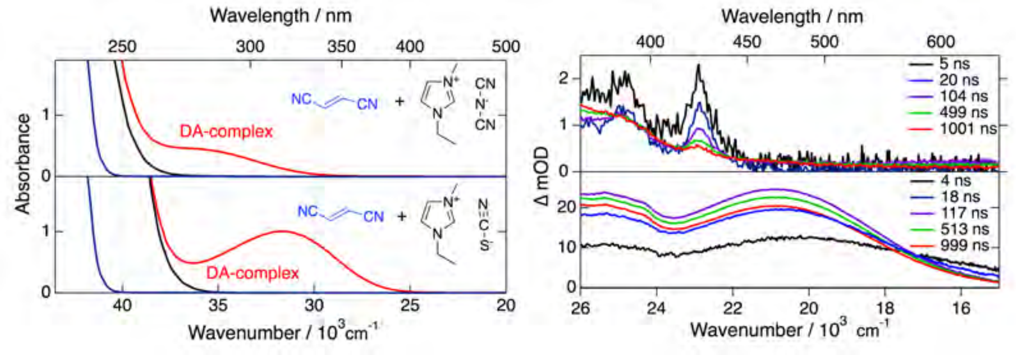
Room-temperature Ionic liquids (RTILs) are considered as green alternatives to “conventional” solvents due to their low volatility, high intrinsic conductivity and good solubility for inorganic and organic solutes. Besides their applications, the elucidation of solvation and reaction dynamics in this unusual solvent is matter of interest. [1] The interaction of charged solvent molecules with solutes should impact the driving force, equilibrium and kinetics of elementary photochemical processes, especially those involving charged species such as electron or proton transfer reactions. The quantification of these effects, especially in bimolecular reactions, has turned out to be rather complex due to the high viscosity of RTILs which requires elaborate data analysis and may hide the impact of solvent-solute interactions on a molecular level. [2] Furthermore, it has to be questioned if the reactivity and stability of RTILs are sufficient to treat them as inert solvent if reactive intermediates are formed during e.g. photoinduced electron transfer.



In our communication, we will show the appearance of broad charge-transfer (CT) absorption bands upon addition of electron donors (EDs) to solutions of RTILs in acetonitrile. These broad bands reveal the formation of ground-state donor-acceptor (DA) complexes between the anions of the RTILs and the EDs. Using time resolved transient absorption spectroscopy from fs to ns, we will explain the processes following the CT excitation and discuss the species involved. Based on this data we will show that the CT absorption does not only open a pathway for RTIL photo-degradation, relevant in e.g. dye sensitized solar cells, but can also lead to data misinterpretations in photoinduced bimolecular quenching experiments.

[1] Castner Jr., E. W., Margulis, C. J., Maroncelli, M. & Wishart, J. F., *Annu. Rev. Phys. Chem.,* **2011,** 62, 85–105.

[2] Koch, M., Rosspeintner, A., Angulo, G. & Vauthey, E., *J. Am. Chem. Soc.,* **2012,** 134, 3729–3736.

Combined spectroscopic studies of functionalized clusters for ion sensing

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Ultra-small thiolate-protected gold nanoclusters of the formula of $Au_m(SR)_n$ have gained tremendous interest in recent years. Several sizes have been synthesized and characterized with several physico-chemical methods [1,2]. Recently, ligand exchange reactions are commonly used for post-synthetic functionalization of gold clusters [3-5]. This reaction allows one to impart new properties to the clusters, opening the door for applications. Furthermore, the choice of ligand and control over the reaction conditions allow tailoring of optical and electrochemical properties and tuning of solubility. The aim of this research was to study the ligand exchange reaction between achiral $Au_{25}(2\text{-PET})_{18}$ and a thiolated 18-crown-6 ligand (L). The ligand contains two thiol groups, which ensures firm anchoring to the cluster. The exchanged cluster works as a potential ion sensor for K^+ and NH_4^+ present in solution even in trace amounts. The optimized reaction conditions allow to obtain several $Au_{25}(2\text{-PET})_{18-2x}L_x$ exchange species that are easily separated by size exclusion chromatography. The ion sensing was successfully achieved using 10-5000ppm KBr and NH_4Cl solutions. The reaction was followed in situ by NMR, UV-vis, HPLC and FTIR. MALDI-TOF mass spectrometry analyses show the presence of incorporated ions onto the crown ether macrocycle.

[1] H. Häkkinen, M. Walter, and H. Grönbeck, *J. Phys. Chem. B*, vol. 110, no. 20, pp. 9927–31, May 2006.
[2] H. Qian, Y. Zhu, and R. Jin, *ACS Nano*, vol. 3, no. 11, pp. 3795–803, Nov. 2009.
[3] S. Knoppe, R. Azoulay, A. Dass, and T. Bürgi, *J. Am. Chem. Soc.*, vol. 134, no. 50, pp. 20302–5, Dec. 2012.
[4] L. Beqa, D. Deschamps, S. Perrio, A.-C. Gaumont, S. Knoppe, and T. Bürgi, *J. Phys. Chem. C*, vol. 117, no. 41, pp. 21619–21625, Oct. 2013.
[5] S. Knoppe, A. C. Dharmaratne, E. Schreiner, A. Dass, and T. Bürgi, *J. Am. Chem. Soc.*, vol. 132, pp. 16783–16789, 2010.

Donor Effect on Photo-induced Electron Injection Process in D-π-A Type Diketopyrrolopyrrole Dyes on TiO_2 Surface

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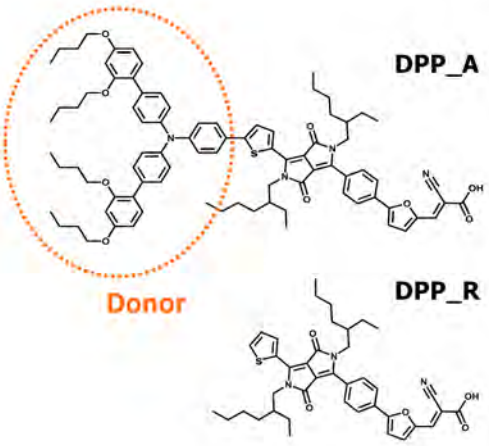
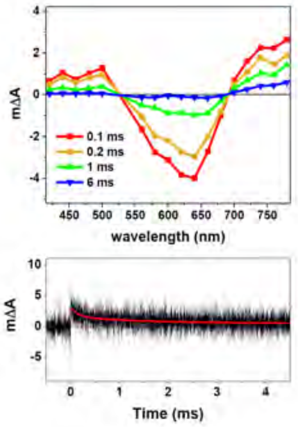
Blue colored diketopyrrolopyrrole (DPP) based dye, where the DPP core acts as a π-bridge in Donor-π-Acceptor (D-π-A) architecture, is an attractive redox sensitizer for dye-sensitized solar cells (DSSCs) based on mesoporous TiO_2 anodes, as it encompasses high-performance and aesthetic properties.[1] Despite its successful use in practical devices, much has still to be understood regarding the detailed mechanisms and dynamics, by which charge separate upon photoexcitation, within the molecule and across the dye-semiconductor junction. In particular, the effect of donor moiety, which is designed to enhance the dipolar characteristic of sensitizer, still need to be explored regarding to photodynamic processes. Detailed investigation in this field involve the use of steady-state and time-resolved ultrafast transient absorption measurements.

The role of donor in electron injection and recombination processes of electronic excited states of the (D-p-A)-structured dye adsorbed on a redox-active metal-oxide surface, such as TiO_2, were scrutinized by femtosecond pump-probe laser spectroscopy. Since kinetic competition between various electron transfer, charge transport, and recombination processes controls the photon-to-electron conversion efficiency in DSSCs,[2] these observations are expected to help determine the crucial factors that still limit the photovoltaic performances of organic dye-based solar cell systems and foster new, improved designs.[3]





[1] Holcombe, T. W.; Yum, J. H.; Kim, Y.; Rakstys, K.; Gräztel, M. J. Mater. Chem. A, **2013**, 1, 13978-13983.
[2] Moser, J.-E. in 'Dye-sensitized solar cells', K. Kalyanasundaram, Ed.; EPFL Press, Lausanne, **2010**; Chapter 11 , pp. 403-456.
[3] Hardin, B. E.; Snaith, H. J.; McGehee, *M. D. Nature Photon.* **2012**, 6, 162–169.

Crystal Structure Prediction and NMR Powder Crystallography

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Structure activity relationships are the basis of development in modern chemical sciences, which depends on the capacity for atomic-level characterization. While it is straightforward to determine structures from single crystals, when the sample is a powdered solid, in many cases structure determination is difficult if not impossible. This is a major handicap in the development of complex materials. For example, the drug delivery properties of a pharmaceutical compounds are governed by the three-dimensional packing in the crystal structure, and the overall architecture of the formulation.

Over the past few decades computational crystal structure prediction (CSP) methods have seen great improvement and have been successfully used to predict and confirm single and multicomponent systems [1]. Recently they have been combined with solid-state NMR and DFT chemical shift calculations to provide a tool for structure determination in powders [2-4]. The main bottleneck for these methods today is the computational cost that grows sharply as the systems get bigger and more complex.

We present how solid state NMR measurements can be used to accelerate CSP. As an example we correctly determine the crystal structure of the medium-sized organic molecule ampicillin, where the ordinary approach fails to determine the correct structure.

[1] A. Reilly, R. Cooper, C. Adjiman et al, *Acta Crystallogr B Struct Sci Cryst Eng Mater*, **2016**, 72, 439-459.
[2] M. Baias, C. Widdifield, J.-N. Dumez et al, *PCCP*, **2013**, 15, 8069-8080.
[3] M. Baias, A. Lesage, S. Aguado, et al, *Angew. Chemie - Int. Ed.*, **2015**, 54, 5971-5976.
[4] E. Salager, G. M. Day, R. S. Stein, C. Pickard, B. Elena, L. Emsley, *JACS*, **2010**, 132, 2564-2566.

Excited-State Dynamics of Radical Ions

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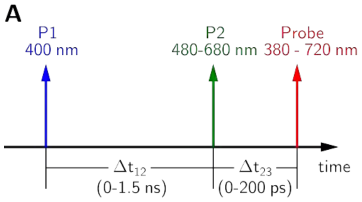
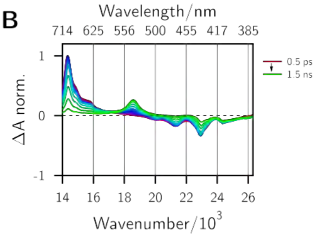
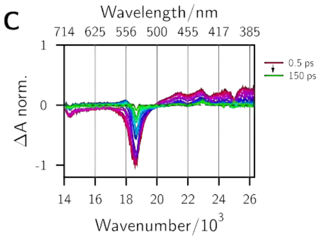
Excited radical ions states are relevant to many important photoinduced processes, such as enzyme-catalysed reactions[1], photosynthesis[2] and indeed all electron-transfer reactions. Despite their importance in these reactions, their excited-state dynamics in solution are little studied.

In previous studies, rapid decays of the radical excited states have often been observed. These do not appear to correlate with the energy gap - for example, the roughly 2.0 eV energy gaps of the 1,4-benzoquinone radical anion and the Wurster's Blue cation were found to have lifetimes at room temperature of "at least" 63 ns[3] and roughly 200 fs[4] respectively. The short lifetimes are instead ascribed to conical intersections or photochemical reactions that can occur on very rapid timescales.[4]

As such, questions arise about the excited-state dynamics of radical ions. How prevalent are conical intersections? Do the molecular structure and the solvent have clear systematic effects? In order to answer these questions, Pump-Pump-Probe (PPP) Spectroscopy[5] (Figure A) has been used.







This is a technique where a pump first triggers a photochemical or photophysical process - an example is shown in Figure B of a transient absorption experiment in which perylene is quenched by an electron acceptor to form the perylene cation (new band at ~540 nm). Another pump pulse, tuned to the band of interest (in this case the band at 540 nm) is then used at a given delay after the first in order to achieve transient absorption measurement on the new species. In this way, anions and cations can be generated by photoinduced electron transfer and then their excited dynamics studied. An example of this PPP spectroscopy is shown above in Figure C, where the perylene cation prepared by photochemical reaction is studied.

Here, we will present results on organic radical ions studied by PPP spectroscopy. The advantages and disadvantages of the technique will be discussed, as will the excited-state dynamics of the radicals and their implications to natural and industrial processes.

[1] W. Buckel, *Angew. Chem. Int. Ed.*, 2009, **48**, 6779–6787.
[2] W. Lubitz, F. Lendzian and R. Bittl, *Acc. Chem. Res.*, **2002**, 35, 313–320.
[3] A. R. Cook, L. A. Curtiss and J. R. Miller, *J. Am. Chem. Soc.*, **1997**, 119, 5729–5734.
[4] J. Grilj, E. N. Laricheva, M. Olivucci and E. Vauthey, *Angew. Chem. Int. Ed.*, **2011**, 50, 4496–4498.
[5] S. Pagès, B. Lang and E. Vauthey, *J. Phys. Chem. A*, **2006**, 110, 7547–7553.

Improving the sensitivity of DNP NMR of microcrystalline solids by flip-back recovery of bulk proton magnetization

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Solid-state NMR is an important analytical technique, commonly used for collecting information about the structure and dynamics of biomolecules and powdered solids, such as pharmaceuticals and inorganic materials. One of the main drawbacks of ssNMR is its relatively low sensitivity, especially for nuclei like ^{13}C and ^{15}N, which have low gyromagnetic ratios and low natural abundance. DNP methods can improve the sensitivity of NMR of microcrystalline solids by using ^{1}H spin diffusion to transfer polarization from the surface of the particles and towards the center.[1] These systems often have long polarization build-up times and require long recycling periods to reach maximum sensitivity, which imposes a practical limitation on the enhancements routinely achieved.

We have shown how the sensitivity of hyperpolarized cross-polarization experiments on microcrystalline solids can be improved by pushing the bulk proton magnetization remaining after decoupling back to the direction of the main magnetic field.[2] Three powdered solids, theophylline, L-histidine monohydrochloride monohydrate and salicylic acid, with build-up times spanning two orders of magnitude were used for the experiments and in all cases sensitivity gains up to a factor of three were obtained. In addition, the flip-back pulse shortens the recycle periods needed and consequently reduces experimental time.

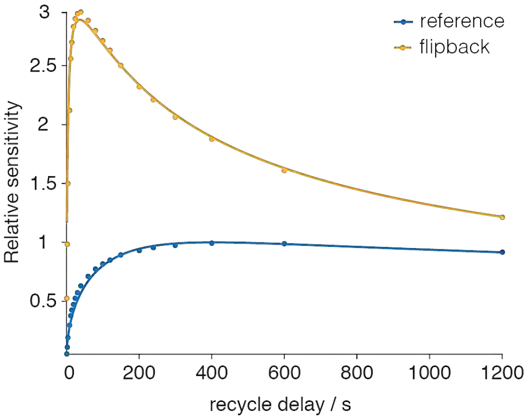

Figure 1. Experimentally observed sensitivity improvements of salicylic acid. The flip-back cross-polarization experiment (yellow) is compared to the same experiment without the flip-back pulse (blue) and the curves are fit to the data using a biexponential recovery model for longitudinal I-spin magnetization. The sensitivity is normalized to maximum sensitivity without a flip-back pulse.

[1] Rossini et al., *J. Am. Chem. Soc.*, **2012,** 134, 16899-16908.

[2] Tegenfeldt and Haeberlen, *J. Magn. Reson.*, **1979,** 36, 453-457.

High Resolution Gigahertz and Terahertz Spectroscopy and Theory of Parity Violation and Tunneling for 1,2-dithiine ($C_4H_4S_2$) as a Candidate for Measuring the Parity Violating Energy Difference between Enantiomers of Chiral Molecules

I. Bolotova[1], S. Albert[1], F. Arn[1], Z. Chen[2], C. Fabri[2], G. Grassi[2], L. Horny[2], P. Lerch[3], M. Quack[2]*

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Electroweak parity violation leads to a slight energy difference between the enantiomers of chiral molecules (on the order of 100 aeV to 1 feV depending on the molecule) and also to a slow time dependent intramolecular process changing parity with time on the order of *ms* to *ks* [1, 2]. Recently we have identified 1,2-dithiine (Figure 1) as a possible candidate for measuring $\Delta_{pv}E$ using the experimental set up described in [3]. Here we report spectroscopic and theoretical studies needed for the preparation of such experiments on 1,2-dithiine ([4, 5] and references therein). We shall also refer to the evolution of the biomolecular homochirality, which may be related to parity violation [6].

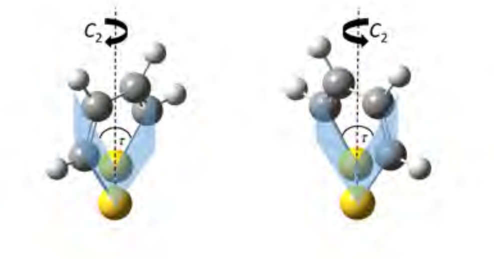

Figure 1. Two enantiomers of 1,2-dithiine ($C_4H_4S_2$), left P, right M enantiomer.

[1] M. Quack Fundamental Symmetries and Symmetry Violations from High-Resolution Spectroscopy, Vol. 1, pp. 659-722 in Handbook of High Resolution Spectroscopy, M. Quack and F. Merkt eds., Wiley Chichester **(2011)**.
[2] M. Quack, J. Stohner, M. Willeke, *Annual Review of Physical Chemistry*, **2008**, 59, 741.
[3] P. Dietiker, E. Miloglyadov, M. Quack, A. Schneider, G. Seyfang, *Journal of Chemical Physics*, **2015**, 143, 244305.
[4] S. Albert, I. Bolotova, Z. Chen, C. Fabri, L. Horny, M. Quack, G. Seyfang, D. Zindel, *Physical Chemistry Chemical Physics*, **2016**, 18, 21976.
[5] S. Albert, F. Arn, I. Bolotova, Z. Chen, C. Fabri, G. Grassi, Ph. Lerch, M. Quack, G. Seyfang, A. Wokaun, D. Zindel, *Journal of Physical Chemistry Letters*, **2016**, 7, 3847.
[6] M. Quack, *Advances in Chemical Physics*, **2014**, 157, 247.

* Further authors are G.Seyfang, A.Wokaun, D.Zindel

High-resolution FTIR spectroscopy of trisulfane HSSSH: a candidate for detecting parity violation in chiral molecules

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According to traditional quantum chemistry involving only the electromagnetic force the ground state energies of the enantiomers of chiral molecules as well as the energies of equivalent excited quantum states are exactly identical by symmetry. When the parity violating weak "nuclear" force causing beta-decay is included in the "electroweak quantum chemistry", one predicts an energy difference $\Delta_{\mathrm{pv}}E_0$ between the ground states of enantiomers and a corresponding reaction enthalpy $\Delta_{\mathrm{pv}}H_0^{\Theta}$ for the stereomutation reaction converting *P* and *M* enantiomers in the case of axially chiral molecules, [1, 2]:

$$P = M \qquad \Delta_{\mathrm{pv}}H_0^{\Theta} = E_0(M) - E_0(P) = N_{\mathrm{A}}\Delta_{\mathrm{pv}}E_0 \qquad (1)$$

We report the first successful high-resolution analyses of the Fourier transform infrared (FTIR) spectrum of trisulfane. A band centered at 861.0292 cm^{-1} can be assigned unambiguously to the chiral *trans* conformer by means of ground state combination differences in comparison with known rotational spectra. A second band near 864.698 cm^{-1} is tentatively assigned to the *cis* conformer by comparison with theory. The results are discussed in relation to their importance for experimental attempts to measure the parity violating energy difference $\Delta_{\mathrm{pv}}E$ between the ground states of enantiomers of chiral molecules, [3, 4].

[1] M. Quack Fundamental Symmetries and Symmetry Violations from High-Resolution Spectroscopy, Vol. 1, pp. 659-722 in Handbook of High Resolution Spectroscopy, M. Quack and F. Merkt eds., Wiley Chichester **2011**.
[2] C. Fabri, L. Horny, M. Quack, *ChemPhysChem*, **2015**, 16, 3584.
[3] P. Dietiker, E. Miloglyadov, M. Quack, A. Schneider, and G. Seyfang, *Journal of Chemical Physics* **2015** 143, 244305.
[4] S. Albert, I. Bolotova, Z. Chen, C. Fabri, M. Quack, G. Seyfang, D. Zindel, Physical Chemistry Chemical Physics **2017**, 19, 11738.

Understanding the crowd: how specific is the influence of crowding particles on the activity of RNAs?

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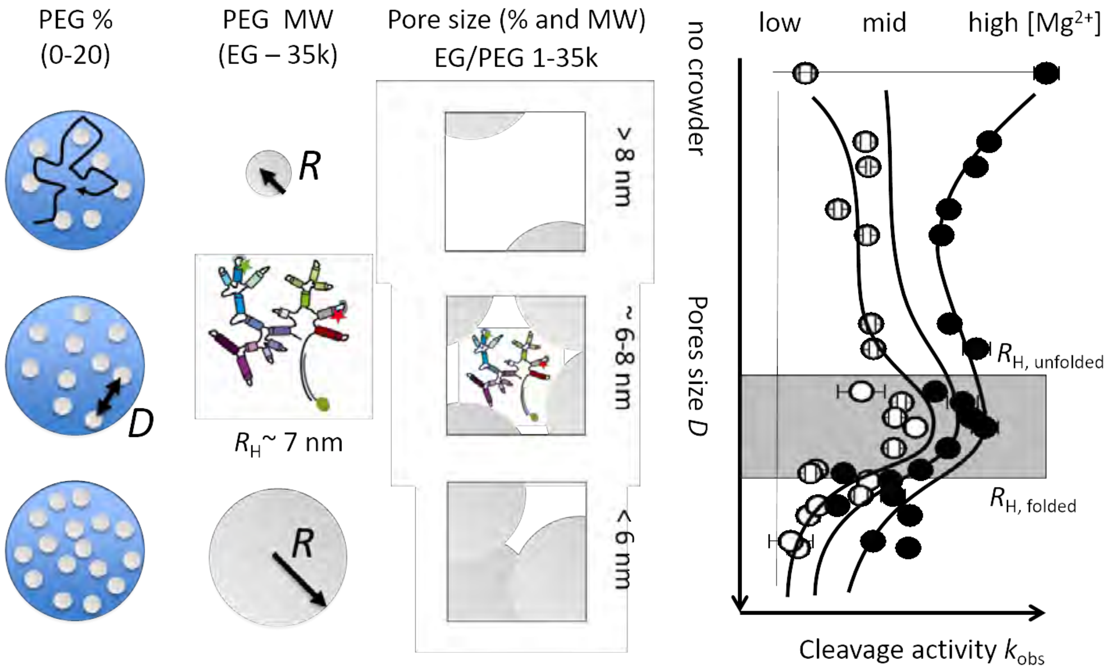
[1]University of Zürich, [2]University Konstanz

Ribozymes are catalytic active RNAs requiring a high magnesium(II) concentration to show folding and function *in vitro* [1,2]. In contrast, *in vivo* conditions are characterized by a highly crowded cellular environment and much lower ion concentration. Molecular crowding agents are used to *mimic* the cellular environment. However, particular physical/chemical properties explaining the co-solutes or the macromolecular crowders influence on folding and function of RNAs are poorly understood. In this study, we gain new insights on how polymer properties like dielectric constant, viscosity, diffusion and pore size influence the activity and folding of a large non-coding RNA, the group IIB intron ribozyme of *S. cerevisiae* [3,4]. We combined bulk activity assays, smFRET and NMR diffusion experiments screening the influence of volume fraction (%) and molecular weight (MW) of different crowding particles. We unveiled an optimal pore size of the crowder, i.e. the average distance of the crowding particles in solution, that matches the size of the ribozyme to maintain its catalytic activity even at lower magnesium(II) concentration.



Financial support from the European Research Council (MIRNA N° 259092 to R.K.O.S.), the Swiss National Science Foundation (to R.K.O.S.), and the Forschungskredit Grant of the University of Zurich (FK-14-096 and FK-15-095 to R.B.) are gratefully acknowledged.

[1] Richard Börner, Danny Kowerko, Helena Guisett-Miserach, Michelle F. Schaffer, Roland K.O. Sigel, *Coord. Chem. Rev.*, **2016**, 327-328, 123-142.
[2] Miriam Steiner, Krishanthi S. Karunatilaka, Roland K.O. Sigel, David Rueda, *Proc. Natl. Acad. Sci. U.S.A.,* **2008,** 105, 13853.
[3] Erica Fiorini, Richard Börner, Roland K.O. Sigel, *Chimia*, **2015**, 69(4), 207. [4] Richard Börner, Erica Fiorini, Birgit Köhn, Michael Kovermann, Roland K.O. Sigel, **2017,** in preparation.

Investigation of PDZ2/RagEF peptide interactions by 2D infrared spectroscopy using wild type and modified photoswitchable peptide ligands

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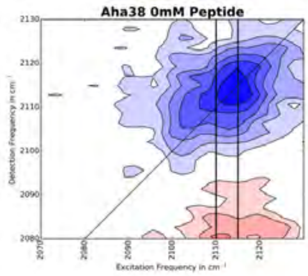
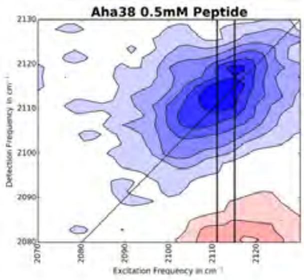
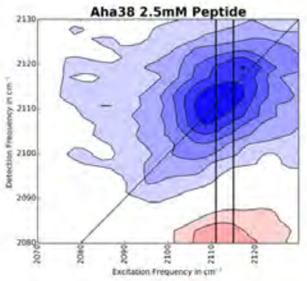
Unnatural amino acid azidohomoalanine (Aha) has been shown to be an environment-sensitive infrared probe [1]. In order to monitor protein-ligand interactions between PDZ2 domain of human phosphatase 1E and its peptide ligands, two different mutants of PDZ2 domain were expressed where Aha was incorporated in two specific positions on the opposite sides of the binding groove of the PDZ2 domain. Our results have shown that a 5 wavenumber red shift of the Aha signal occurred as a consequence of peptide binding.







Furthermore, it has been previously shown that covalent bridging of alpha helical peptides by photoswitchable azobenzene molecule linked to two cysteine residues, can induce helix unfolding upon light isomerization of photoswitch [2]. After inducing the conformational change of peptide by photo-isomerization the affinity of Aha labeled PDZ2 for the given peptide may change enough to enable peptide unbinding from the protein in a controlled manner. Here we investigate two conceptually different phtoswitchable peptide candidates, and their binding affinities.

[1] Bloem, Robbert, et al. *The Journal of Physical Chemistry B,* **2012,** 116.46: 13705-13712.
[2] Koziol, Klemens L. et al. *Current opinion in structural biology,* **2015,** 34 , 1-6.

Reliable distance distributions in the nanometer range from 5-pulse Double Electron Electron Resonance (DEER)

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Double Electron Electron Resonance (DEER) enables determination of distance distributions in the nanometer range by Electron Paramagnetic Resonance (EPR). In DEER, a refocused echo is recorded at the observation frequency while the distance to a partner spin is probed by time-dependent excitation at a second frequency (the pump frequency). Due to the dipolar interaction between the two spins, the observed echo is modulated with a frequency which depends on the distance between the two spins. The accessible observation window and thus distance range can be significantly prolonged by the use of dynamically decoupled multi-pulse versions of this experiment [1,2]. Such experiments, however, are not free of artefacts. On coherent spectrometers, artefacts due to additional coherence transfer pathways occur and can be removed by systematic change of the pulse phases [3]. On both coherent and incoherent spectrometers, overlap of the observer and pump frequency bands causes additional signals of dipolar origin, hereafter called band overlap artefacts. Furthermore, incomplete population inversion in the pump band gives rise to a so-called partial excitation artefact.

Using the 5-pulse DEER experiment with pulses from an arbitrary waveform generator (AWG), we show how pulse parameters can be optimized in order to suppress or completely remove the artefacts due to band overlap, so that only the partial excitation artefact remains. For removal of the partial excitation artefact, we present a data processing procedure that works without previous knowledge of the artefact amplitude or shape and without sensitivity loss. Two 5-pulse DEER traces are recorded in which the artefact position is shifted with respect to the wanted signal. Using the difference of the two traces, the artefact is identified and corrected for. Artefact removal is demonstrated for both simulated and experimental data acquired at different frequencies, for shaped as well as rectangular pump pulses, for a variety of distance distributions and spin environments. The algorithm is stable down to low S/N ratios and in the regime of moderate background decay. We show that 5-pulse DEER recorded with optimized pulse parameters and, if necessary, artefact-corrected by our algorithm gives access to correct distance distributions and a prolonged distance range.

[1] Peter P. Borbat, Elka R. Georgieva, Jack H. Freed, *J. Phys. Chem. Lett.,* **2013**, 4, 170.
[2] Philipp E. Spindler, Izabela Waclawska, Burkhard Endeward, Jörn Plackmeyer, Christine Ziegler, Thomas F. Prisner, *J. Phys. Chem. Lett.,* **2015**, 6 (21), 4331–4335.
[3] Claudia E. Tait, Stefan Stoll, *Phys. Chem. Chem. Phys.*, **2016**, 18, 18470-18485.

Hybrid Organic-Inorganic Perovskites Studied with Ultra-Broadband Time-Resolved Terahertz Spectroscopy

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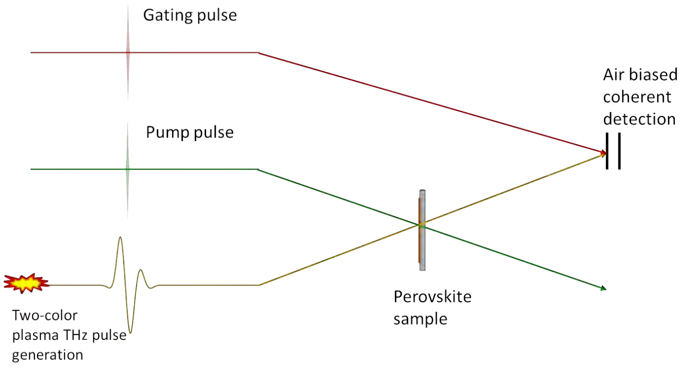
The fundamental study of charge carrier dynamics has been shown to be central to the design of novel and improved photovoltaic systems. Understanding the mechanisms for charge carrier recombination, migration and transfer can pave the way forward for future developments. With this objective in mind, many spectroscopic techniques have been employed in the past. Particularly, THz time-resolved spectroscopy, based on optical rectification in non-linear crystals, has been used to study charge carrier and pseudo-particle dynamics in third generation photovoltaics, such as dye-sensitized solar cells[1] and perovskite solar cells [2].



A promising new technology based on gas photonics has been under heavy development for the last decade to obtain and detect broadband THz pulses [3], with early generation results dating back to the early 2000s. Improvements such as the introduction of the air biased coherent detection(ABCD) technique, and the use of different gas media [3] have greatly increased the signal to noise ratio. Thus, the technology has reached a state where optical pump-THz probe time-resolved spectroscopy can be successfully performed, providing enhanced time resolution and spectral bandwidth with respect to the classical optical rectification methods.

We present the first measurements carried out on multigrain methylammonium lead iodide perovskite thin films with optical pump-broadband THz probe spectroscopy. This technique allows us to unveil the first steps of charge carrier generation thanks to its sub-ps time resolution and extend the photoconductivity analysis up to a frequency of 20 THz.

[1] Brauer, J. C. *et al.*, *J. Phys. Chem. C,* **2015**,119**,** 26266–26274.
[2] Johnston, M. B. & Herz, L. M., *Acc. Chem. Res.,* **2016**, 49, 146–154.
[3] Lu, X. & Zhang, X.-C., *Front. Optoelectron.,* **2014**, 7, 121–155.

NMR Studies of Hierarchical Protein Dynamics

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A fundamental challenge in biology is to understand the complex interaction between protein motion and function. Due to the complexity of this interaction and the wide range of timescales on which protein motion occurs, this task remains hard or even impossible. Recently, Lewandowski and coworkers have shown that temperature dependent magic angle spinning multinuclear solid state NMR relaxation measurements, at temperatures ranging from 105 to 280K, can provide a window into the hierarchy of dynamic processes in proteins.[1] Other available methods often focus only on a specific transition and are limited. In contrast, solid-state NMR allows simultaneous access to a wide range of observables (here we observe sixteen different probes (4 relaxations parameter for 4 different nuclei) within one protein).

We have reproduced those results[1] with a high accuracy, validated the previously proposed model and extended the method of this studies to a different system to conclude on the universalism of those dynamics.

The reproduced experiments allowed us to map the energies related to the “glass transition”. Similar transitions in the relaxation patern can be observed for different probes within the protein and the solvent. We propose that internal motion can be model as a two-component system, where the higher energy motion (20-30 KJ.mol$^{-1)}$ dominates the lower energy motion (5-10 KJ.mol$^{-1)}$ with rising temperature.

Quantitative description of motions occurring in the protein and the solvent are dependent on the applied magnetic fields. Thus, we have validated our previous model using different fields strength, in order to obtain field-independent data: 9.4, 11.7, 14.1 and 18.8 T (400, 500, 600 and 800 MHz). Our model accurately predicts the results found for all the used fields strength.

A different protein (SH3) has also been studied, in order to see if the proposed model can predict fundamental properties shared by all soluble peptides. Our results show similar (but not identical) behavior for both proteins. We thus conclude, that small soluble protein show several similar dynamical properties, which can be accurately described by the presented model.

[1] Lewandowski, Józef R, Meghan E Halse, Martin Blackledge, Lyndon Emsley, *Science,* **2015,** 348, 578-81.

Towards 2D Raman-THz spectroscopy of supercooled water

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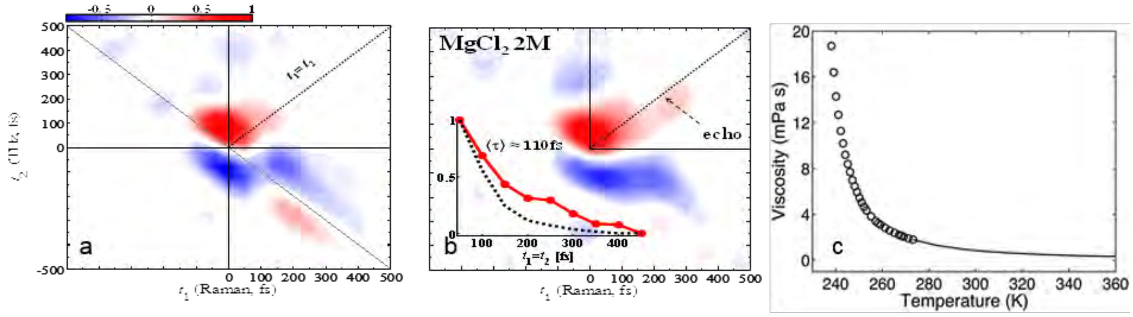
Two dimensional Raman-THz spectroscopy, as a new multidimensional spectroscopic technique directly in the THz regime [1], was proposed and used in our group to explore the low-frequency intermolecular modes dynamics in liquid water and aqueous salt solution [1][2]. This new approach has given new insights to the relaxation dynamic of complex collective hydrogen bond networks; the amount of inhomogeneity in the system is quantified by the time persistence of the “echo” signal along the diagonal $t_1=t_2$ [1] (Fig.1 (a)). The series of measurement of aqueous salt solution has revealed that the extent of the diagonal feature is directly related to the increase or decrease of viscosity driven by different kind of dissolved ions in water; in particular, as salts “structure” water (i.e. viscosity increases), the echo feature becomes more pronounced [2] (Fig. 1 (b)). To have a more complete picture regarding the appearance of this extended diagonal component and its connection to viscosity, next step is to measure the response of supercooled water. Cooling water below its freezing point leads essentially to the same viscosity change [3] of “structure making” salts but it comes without the addition of any external compound. For this reason and for the purpose of directly relating the appearence of the "echo" with viscosity effects , supercooled water is even a more reliable and direct probe of the structure of intermolecular hydrogen bond network.



[1] Savolainen, J., Ahmed, S. & Hamm, P. *Proc. Natl Acad. Sci.* USA 110, 20402–20407 **(2013)**.
[2] Shalit A., Ahmed S., Savolainen J. and Hamm P., *Nat. Chem*. **(2016)**.
[3] Y. A. Osipov, et al *Russ. J. Phys. Chem.* **51**, 748–749 **(1977)**.

Photophysical Study of Perovskite Organic Blends for Applications in Light Emmiting Diodes

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Solid-state heterojunction photovoltaic cells and white light emitting diodes are the most promising solutions in the modern, global energetic needs. Among the different materials that fulfil the desirable conditions for serving as active materials for the above-mentioned applications, a new class of materials called perovskites, has gained a lot of attention during the current decade. The numerous advantages of perovskites, including high absorption coefficient, high photoluminescence quantum yield~~s~~, good transport properties, bandgap tunability and solution-processability, have situated them among the most intensively studied and the most promising candidates for solar cells and light emitting diodes.

Despite their advantages, perovskites stability and control of their synthesis conditions need to be further improved before their implementation in commercially available devices. Concerning their application in white light-emitting diodes that is less studied compared to the solar cells, except from their stability, also charge injection and light-extraction efficiencies must be improved, while the non-radiative recombination losses that lead to a decreased photoluminescence quantum yield need to be reduced.

In the present work, an attempt towards the improvement of the photoluminescence properties of methylammonium lead bromide ($MAPbBr_3$) thin films is attempted. For this purpose either a high molecular weight polymer or a low molecular weight Spiro Fluorene derivative was mixed into the precursor solution in different weight ratios with the perovskite and the resulted solutions were spin-coated as thin films. It is shown that additive containing films showed a large increase in their photoluminescence quantum yield of the perovskite. To further investigate the reasons for this improvement perovskite films with and without the addition of the additives were investigated with several transient techniques of ns-time-resolved photoluminescence, ns- and fs- transient absorption spectroscopy. We attribute the increase of the photoluminescence quantum yield of the perovskite to the enhanced excitonic recombination due to the creation of quantum confinement upon the addition of the additives. Furthermore, proofs for the trap passivation of the perovskite are provided.

Mechanistic elucidation on the stability of SnO_2 NPs under electrochemical CO_2 reduction condition: An in operando Raman Spectroscopy study

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In this present study we demonstrate degradation effects on the basis of a direct electro-reduction process of CO2 taking place on a SnO2 NP catalyst supported on reduced graphene oxide (rGO). The field of CO2 electro-catalysis is rapidly growing due to the global demand for new technologies which allow for the reduction of CO2 in the atmosphere and to store at the same time excesses of electric energy from wind and solar sources in form of a reduced carbon compound. In this respect, an electrochemical approach towards the conversion of CO2 into more valuable products seems to be highly promising. The SnO2 NP catalyst supported on reduced graphene oxide (rGO) shows a superior activity and selectivity towards the formation of formate with Faradaic efficiencies (FEs) above 80%. However, our study also demonstrates that the Faradaic efficiencies crucially depend on the applied electrode potential and the pH of the electrolyte. The SnO2 NPs themselves undergo at cathodic potentials an electro-reduction reaction transforming the SnO2 (Sn^{IV}) into metallic tin (Sn^{0}). This chemical transition can be monitored potential and time dependent by *in operando* (this is, during an ongoing CO2 electroreduction) Raman spectroscopy (Fig.1). This ***catalyst degradation*** is accompanied by a significant drop down of the Faradaic efficiency of formate formation. Highest efficiencies are actually obtained under conditions where the NP is neither fully oxidized nor fully reduced and consist of a Sn/SnO2 composite. The post-electrolysis characterization of the catalyst material reveals a full recovery of the SnO2. This result emphasizes once more the importance of an *in operando* identification of the catalytically active species as basis for the elucidation of reaction mechanisms.

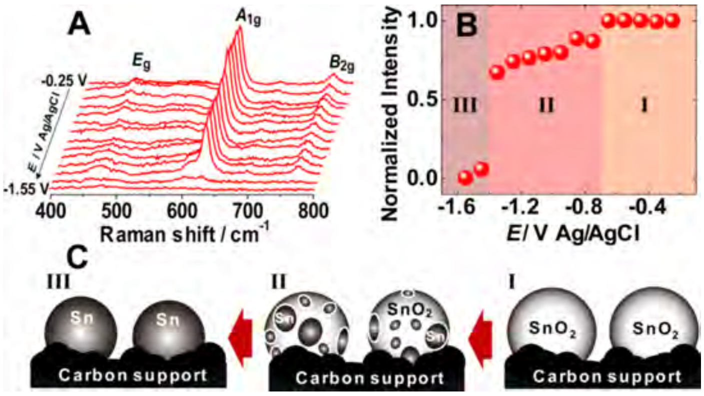

Fig.1 In operando Raman studies at varied potential (A) The relative intensities of the SnIV-related A1g Raman peaks (B). In the three distinct potential regions represented by the shaded background, the catalyst is in the form of fully oxidized SnO2 (I), a partially reduced compound of mixed oxidation state (II) and completely reduced metallic Sn (III), as illustrated by the scheme of (C).

[1] A.Dutta, A. Kuzume, M. Rahaman, S.Vesztergom, P. Broekmann,. *ACS Catal*. **2015,** 5 (12), 7498−7502

[2] M. Sackmann, A. Materny *J. Raman Spectrosc*. **2006**, 37, 305−310

[3] I. E. Wachs, C. A. Roberts *Chem. Soc. Rev.,* **2010,** 39, 5002–5017

Binding Properties of Polymer Nanoparticles Encapsulating Porphyrinic Photosensitizers

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The concept of photodynamic therapy (PDT) for anticancer treatment is based on the formation of highly reactive singlet oxygen ($^1O_2$) via energy transfer from a light excited photosensitizer ultimately leading to localized cell death. Due to their intrinsic phototoxicity and high tumor accumulation, porphyrinic compounds including porphyrins and chlorins have evolved as important family of photosensitizers in PDT. However, one of their drawbacks originates from a high aggregation tendency of most porphyrinic compounds. Polymer systems have been identified as an elegant and simple way to cope with the undesired effects of aggregation. As an example, Photolon®, which is a polyvinylpyrrolidone (PVP) - chlorin e6 (Ce6) complex, has been approved for medical application in PDT. [1]

Previously, we have reported and characterized a series of naturally derived porphyrins by NMR spectroscopy keeping the focus on their aggregation models, propensity to form aggregates, carrier systems and their interactions with membrane models. [2, 3]

The aim of this study is to investigate the efficacy of different polymer systems regarding their disaggregating capability and binding strength of porphyrin compounds using NMR and UV spectroscopy as main techniques. A step towards understanding the loading efficiency of the polymer matrices can be accomplished by characterization of parameters such as the association (binding) constant of porphyrin-polymer ensembles. Particularly, we have calculated and compared the binding constants of polymer matrices either based on block copolymer micelles (BCMs) or PVP with a chlorin (SerCe) and a deuteroporphyrin IX derivative (DPIXDSME). The results indicate different binding motives of the polymer matrices with respect to the porphyrinic compounds. Moreover, the stability and reactivity of the polymer-encapsulated porphyrins were probed by NMR spectroscopy mimicking physiological conditions. They were found to be different for BCMs and PVP and correlated with the association constants. The protective role of the polymer carrier system towards blood plasma proteins plays an important role in the drug delivery process. The binding differences reported in this contribution may have a considerable impact on the pharmacokinetic properties of the corresponding delivery systems.

[1] H.A. Isakau, M.V. Parkhats, V.N. Knyukshto, B.M. Dzhagarov, E.P. Petrov, P.T. Petrov, *J. Photochem. Photobiol*. B, **2008**, 92, 165-174.
[2] M. Vermathen, M. Marzorati, P. Bigler, *J. Phys. Chem*. B, **2013**, 117, 6990-7001.
[3] M. Hädener, I. Gjuroski, J. Furrer, M. Vermathen, *J. Phys. Chem*. B, **2015**, 119, 12117-12128.

Fast data sorting to distinguish unique single molecular break junction trajectories

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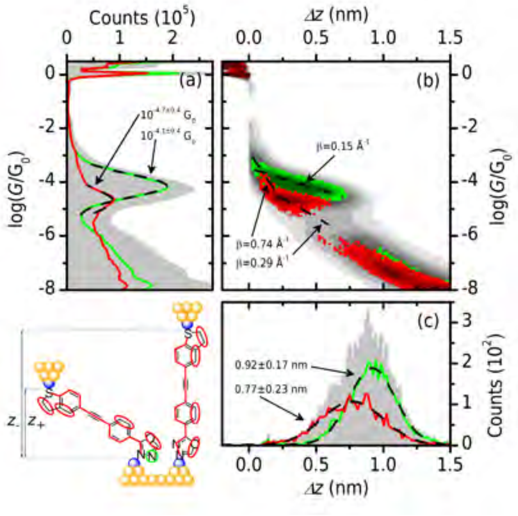
A simple and fast analysis method to sort large data sets into groups with shared distinguishing characteristics is described, and applied to single molecular break junction data. The method successfully sorts data sets without the need to assert any specific hypothesis about the expected features within the data. The method is applied to mixtures of two molecules with identical anchor groups, similar lengths, but either a π (high conductance) or σ (low conductance) bridge. The mixed data is sorted into break junctions containing one molecule or the other. The method also distinguishes between two junction geometries in measurements of the π bridged molecule alone[1].



[1] J.M. Hamill, X.T. Zhao, G. Mészáros, M.R. Bryce, and M. Arenz **(2017)**. “Fast data sorting with modified principal component analysis to distinguish unique single molecular break junction trajectories.” arXiv:1705.06161 [cond-mat.mes-hall]

Quantum Logic Spectroscopy for Single Trapped Molecular Ions

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The application of quantum techniques to the spectroscopy of single trapped particles has enabled the determination of atomic properties at unprecedented levels of precision. “Quantum-logic spectroscopy” (QLS) has enabled the next generation of atomic clocks and new precision tests of fundamental physical theories[1]. Thus, we wish to extend the scope of quantum techniques to spectroscopically probe the properties of single isolated molecular ions[2]. We also intend to establish a quantum toolbox for the non-destructive interrogation of single molecules by coupling to a single atom. These developments will pave the way for molecular precision spectroscopic measurements to study, e.g., a possible time variation of particle masses[3-5] with N_2^+ which has been identified as a promising candidate system[3]. We will report our recent progress towards these goals.

[1] P. O. Schmidt *et. al.*, *Science* **309** (2005), 749.
[2] M. Germann *et al.*, *Nature Physics* **10** (2014), 820.
[3] M. Kajita *et. al.*, *Phys. Rev. A* **89** (2014), 032509.
[4] S. Willitsch, *Int. Rev. Phys. Chem.* **31** (2012), 175.
[5] S. Schiller *et. al.*, *Phys. Rev. Lett.* **113** (2014), 023004.

Unravelling the Atomic-level Structure of Calcium Silicate Hydrate

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Calcium silicate hydrate (CSH) is one of the most versatile and widely used substances worldwide. The main use of CSH is as primary binding component in concrete, where it forms about 50-60% by volume of the dried cement paste [1]. With cement being the most widely used construction material, so abundant that its production is the leading industrial source of greenhouse gases, contributing to about 8% of global emissions, a deep knowledge of the structure of CSH is of global priority.

Other emerging applications of CSH range from usage in dental fillings and bone repair, requiring biocompatibility, to waste water treatment, requiring a high specific surface area, to encasement of nuclear waste, requiring high structural integrity. Despite the versatile and frequent usage of CSH it is surprising that the full atomic-level structure of CSH remains unknown [2,3].

The main reasons for the unresolved atomic-level structure of CSH arise from the fact that CSH always is slightly disordered, that it occurs in nature in conjunction with other materials phases, and that previously synthetic CSH could only be produced with Ca:Si ratios below 1.6, whereas the industrially relevant ratio is greater than 1.75 [4]. Here we present a novel method which achieves the synthesis of uniform CSH phases with Ca:Si ratios between 1.0 and 2.0. We then solve the three-dimensional atomic-level structure using an approach combining dynamic nuclear polarization (DNP) enhanced solid state nuclear magnetic resonance (ssNMR) experiments, molecular dynamics (MD) simulations and chemical shift calculations based on first principle.

To solve the atomic-level structure of CSH we first determine structural constraints through one- and two- dimensional ^{29}Si DNP cross polarization ssNMR experiments, employing magic angle spinning (MAS) of the sample. These constraints, in combination with force-field based MD simulations, are then used to generate an ensemble of possible short range building blocks for the CSH structure. By combining these building blocks we then generate a set of medium to long range structural motifs, which we optimize using density functional theory (DFT). We then compare the DFT calculated ^{1}H chemical shifts of these motifs with experimentally measured two-dimensional $\{^{1}H\}^{29}$Si DNP HETCOR chemical shifts to determine the subset of structures that best describe the CSH structure. This subset in combination with additional structural constraints, resulting from the ^{29}Si chemical shift experiments, and MD simulations then allow us to propose a full atomic-level structure of CSH.

[1] Scrivener, K. L.; Nonat, A. *Cem. Concr. Res.* **2011**, *41* (7), 651.
[2] Lothenbach, B.; Nonat, A. *Cem. Concr. Res.* **2015**, *78*, *Part A*, 57–70.
[3] Richardson, I. G. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* **2014**, *70* (6), 903–923.
[4] Allen, A. J.; Thomas, J. J. *Cem. Concr. Res.* **2007**, *37* (3), 319.

Light induced conformational isomerisation of helical photoswitchable S-peptide and perturbation of S-protein/S-peptide complex

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Transient infrared spectroscopy is a promising technique for time-resolved investigation of proteins' conformational changes induced by e.g. peptide binding. Model system that we are currently interested in is ribonuclease S (RNase S), a non-covalent complex composed of S-protein and S-peptide. RNase S is produced by subtilisin cleavage of ribonuclease A at specific position and consists of tightly associated S-peptide (residues 1-20) and S-protein (residues 21-124) which possess full enzymatic activity. Dissociated S-peptide has predominantly random coil conformation in solution, whereas alpha helical conformation is favored in the bound state to folded S-protein[1]. Our main aim is to gain further insights in mechanism of S-peptide – S-protein binding by using different modified forms of S-peptide. By covalently modifying S-peptide, we managed to introduce a bridging photoswitchable water soluble azobenzene molecule which allows us to perturb the structure in a controlled manner.This perturbation should be large enough to lead to dissociation of the S-peptide from the complex, which would allow us to monitor time-resolved changes of S-peptide and S-protein conformation upon ligand unbinding. Furthermore, incorporation of site-specific and sensitive infrared labels, either in S-peptide or S-protein, would provide even more specific and detailed information on conformational changes that occur[2].

[1] Annett Bachmann, et al. *Proceedings of the National Academy of Sciences*, **2011,** 108, 3952-3957.

[2] Robert Bloem, et al. *Journal of Physical Chemistry B,* **2012,** 116, 13705–13712.

$Au_{38}Cu_1(SC_2H_4Ph)_{24}$ Nanoclusters: Synthesis, Enantioseparation and Luminescence

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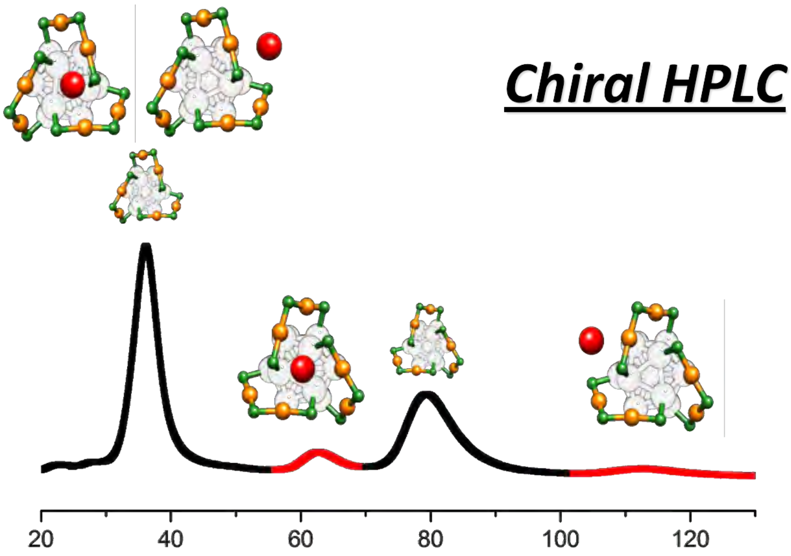
Gold alloy nanoparticles have recently triggered much research interest for their various applications in several fields such as catalysis and imaging. [1] Nonetheless, preparing alloy nanoparticles with atomic monodispersity has long been a major challenge, and until now only few have been attained with atomic precision and molecular purity. [2] In this study, a $CuAu_{38}$ bimetallic nanocluster was synthesized by adding a single copper atom to the Au_{38}(2-PET)$_{24}$ nanocluster. The absence of Cu_xAu_{38}(2-PET)$_{24}$ doped species was demonstrated by MALDI-TOF mass spectrometry. A separation of bimetallic clusters was attained for the first time where isomers of the E2 enantiomer of the $Au_{38}Cu_1$ adduct were successfully isolated from their parent cluster using chiral HPLC. The CD of the isolated isomers revealed a change in their electronic structure upon copper addition. The luminescence of the $Au_{38}Cu_1$ adduct is significantly enhanced in comparison with the parent Au_{38} nanocluster. The stability of the newly formed adduct is strongly dependent on the coexistence of the Au_{38} nanoclusters.



[1] C. Yao, J. Chen, M. B. Li, L. Liu, J. Yang and Z. Wu, Nano Letters, **2015**, 15, 1281-1287.
[2] S. Wang, Y. Song, S. Jin, X. Liu, J. Zhang, Y. Pei, X. Meng, M. Chen, P. Li and M. Zhu, Journal of American Chemical Society, **2015**, 137, 4018-4021.

Mechanistic studies of conformationally controlled ionic cycloadditions and state selective reactions

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Despite their significance in organic synthesis, the mechanistic details of Diels-Alder cycloadditions, in which a diene and a dienophile react to form a cyclic product, still remain an unsolved and extensively discussed question. It has proven difficult to determine whether only the s-cis conformer (concerted mechanism) or both conformers (stepwise mechanism) of the involved diene react to form the cyclic product. Due to their high stereo- and regioselectivity, a concerted mechanism is generally assumed [1]. For polar Diels-Alder reactions, however, where one of the reactants contains a charge, the reaction may instead favor a stepwise mechanism [2].

In order to shed light on these questions we investigate the reactivities of individual conformers by employing molecular beam technology [3]. Owing to their different dipole moments, conformers can be spatially separated in an inhomogeneous electric field. Directing a molecular beam of spatially separated conformers into a cloud of sympathetically cooled molecular ions in an ion trap allows us to study highly conformationally selective reactions such as Diels-Alder cycloadditions. Previously, this method has been successfully applied to study reactive collisions of 3-aminophenol with a Coulomb crystal of Ca^+ ions [4][5]. As a representative example, we want to study the conformationally resolved ionic cycloaddition reaction of 2,3-dibromo-1,3-butadiene which exhibits two different conformers, s-cis and s-trans, with ionic maleic anhydride. The products of the reactive collisions are analyzed by an integrated high-resolution time-of-flight mass-spectrometer. The performance of the setup was recently confirmed by measuring the rate constant of the reaction between laser cooled Ca^+ ions with N_2O [6]. This advancement will enable us to trace the complex mechanistic pathways of Diels-Alder reactions.

Besides conformers, our setup also enables us to study state selective reactions. In the presence of a strong inhomogeneous electric field, water molecules in a molecular beam can be separated into their two nuclear spin isomers ortho and para which correlate with different rotational states [7]. Currently we are investigating the reaction of rotational state selected H_2O molecules with N_2^+ and N_2H^+ ions. The flexibility of our setup allows us to access the individual spin isomers and study their reactivities.

[1] M. Eberlin, *Int. Journal of Mass Spectrometry*, **2004**, 235, 263.
[2] U. Rivero et. al., *Chem. Phys. Lett.*, **2017**, dx.doi.org/10.1016/j.cplett.2017.03.063.
[3] F. Filsinger et al., *Phys. Rev. Lett.*, **2008**, 100, 133003.
[4] Y.-P. Chang et al., *Science*, **2013**, 342, 98.
[5] D. Rösch et al., *JCP*, **2014**, 140, 124202).
[6] D. Rösch et. al., *EPJ techniques and instrumentation*, **2016**, 3:5.
[7] D. A. Horke et al., *Angew. Chem. Int. Ed.*, **2014**, 53, 11965- 11968.

THz Emission Spectroscopy on organic semiconductors

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In the terahertz emission spectroscopy (TES) sample systems are investigated on an ultrashort timescale. With optical excitation of the material with a light pulse on the order of tens of femtoseconds and subsequent acceleration of photoexcited carriers, we create electric fields in the THz frequency range. Using free space electro optic sampling (FSEOS) these fields are recorded and a full waveform is reconstructed. From that waveform we extract material properties and obtain information on the generation and recombination rates of photoexcited carriers through comparison with simulations. Assumptions for the simulations are justified with additional experiments using THz-Time domain spectroscopy (THz-TDS). Here we present a proof of concept and first measurements to show the feasibility and versatility of this novel technique.

Correlation Between Charge Carrier Lifetimes and Cation Dynamics in Mixed Double A-Cation Lead Halide Perovskites Revealed by Solid-state NMR

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Mixed cation organic lead halide perovskites emerged as an attractive alternative to silicon-based solar cells. Currently, one of the best performing materials contains 4 cations and provides power conversion efficiencies up to around 22 %.[1] Here, we report the first quantitative, cation-specific data on cation rotational dynamics in hybrid double-cation formamidinium (FA)/methylammonium (MA) lead iodide perovskites using ^{14}N and ^{2}H MAS NMR. Our findings suggest that the excellent photovoltaic properties of perovskite materials are directly correlated to cation reorientation dynamics, and corroborate the polaronic nature of charge carriers in these materials.

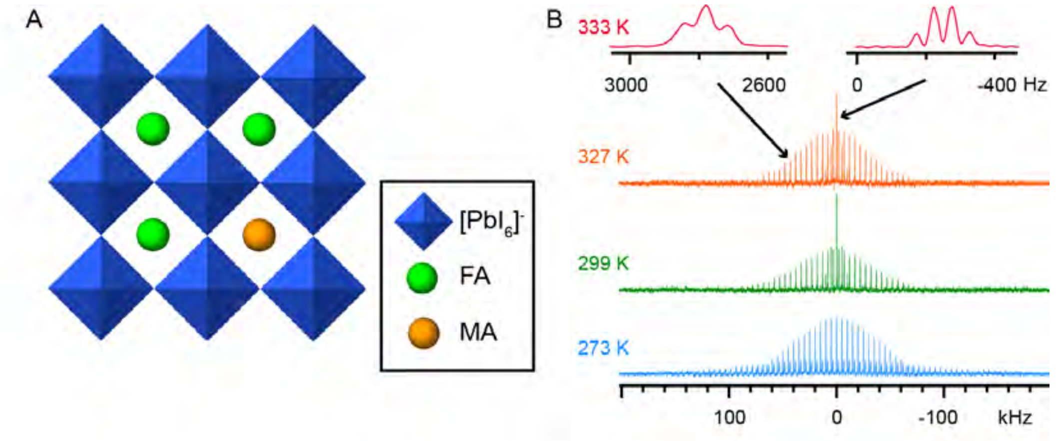

Fig. 1. A) A cartoon showing the structure of the double-cation three-dimensional perovskite phase of $FA_{0.67}MA_{0.33}PbI_3$, B) and the corresponding solid-state ^{14}N echo-detected variable-temperature 5 kHz MAS NMR spectra. The top insets (red) show a close-up of the isotropic peak at 333 K and 20 kHz MAS, conditions under which a characteristic splitting due to the *J*-coupling between the nitrogen and the proton is resolved, making the signal assignment straightforward. The arrows indicate the corresponding SSB manifolds.

[1] Saliba, M.; Matsui, T.; Domanski, K.; Seo, J. Y.; Ummadisingu, A.; Zakeeruddin, S. M.; Correa-Baena, J. P.; Tress, W. R.; Abate, A.; Hagfeldt, A.; Gratzel, M., *Science* 2016**, 354**, 206.

An Excited-State Proton Transfer Disentangled by fs Broadband Spectroscopies

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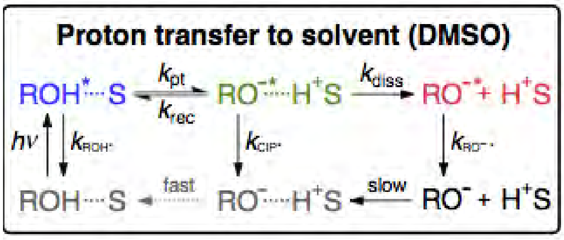
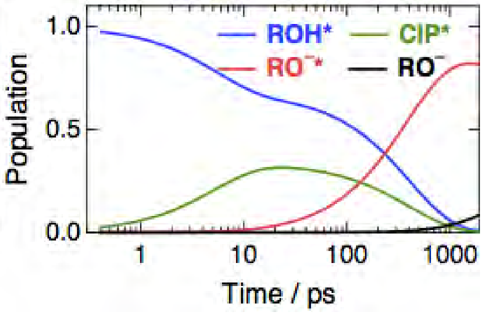
Proton transfer is undoubtedly one of the most significant reactions in chemistry and biology. The discovery of excited-state acids, also known as photoacids, has enabled detailed time-resolved investigations on the mechanism and kinetics of the dissociation process.[1] Despite the wealth of investigations on excited-state proton-transfer (ESPT) reactions, some aspects are still under discussion. For example, the influence of solvent environment on ESPT is recognized both from experimental and theoretical viewpoints but only a few studies have explicitly accounted for the dynamic solvent relaxation in the excited-state. Second, ESPT reactions are usually modeled according to the Eigen-Weller scheme which consists of an initial short-range proton-transfer step producing contact ion pairs followed by a diffusion-controlled separation into free ions (**Figure**). However, the model is often discussed only qualitatively and detailed investigations resolving all microscopic rate constants and relaxation pathways are scarce. Lastly, data obtained using different spectroscopic techniques have sometimes resulted in differing interpretations of the studied processes.





In our communication, we report on the ESPT from a 1,8-naphthalimide-derived "super" photoacid[2] to solvent (DMSO) investigated using three fs broadband techniques: visible and IR transient absorptions, in addition to fluorescence up–conversion. We will demonstrate how a combination of these techniques gives much deeper insight into the overall photocycle including both ground- and excited-state species. Broadband fluorescence up–conversion gives us direct access to the solvent relaxation reported by the dynamic Stokes shift of the fluorescence band which is modeled using a recently developed global analysis scheme based on time-dependent band-shape functions.[3] Transient absorption, on the other hand, yields valuable information about the additional decay channels to the ground-state species. Lastly, the use of a target model based on the reaction scheme (**Figure**) enables recovery of all the individual rate constants and concentrations of the different intermediates.

[1] N. Agmon, *J. Phys. Chem A*, **2005**, 109, 13-35.
[2] T. Kumpulainen, B. H. Bakker, M. Hilbers, A. M. Brouwer, *J. Phys. Chem. B*, **2015**, 119, 2515-2524.
[3] T. Kumpulainen, A. Rosspeintner, E. Vauthey, *Phys. Chem. Chem. Phys.*, **2017**, 19, 8815-8825.

The Study of Electrolytes for Li-Air Batteries

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Rechargeable lithium-air batteries potentially provide higher energy densities than the conventional rechargeable batteries due to the redox combination of light lithium metal anode and oxygen cathode. However, the redox reversible reactions and cyclability of those batteries remain a challenge. Among the possible set-ups of Li-air batteries, using an aqueous electrolyte provides a higher efficiency and cyclability due to the high ionic mobility and the solubility of discharge products [1]. However, water must not contact the lithium metal anode to avoid a violent reaction, producing heat and gas evolution. Thus, we apply an organic electrolyte on the lithium anode to protect the metal and an aqueous electrolyte on the cathode side to allow reversible electrochemical reactions. Another scientific issue is that during discharging, the value of pH increases due to the formation of LiOH, which damages the membranes [2,3] and leads upon saturation to LiOH precipitation [4]. Therefore, suppressing high pH in an aqueous electrolyte is a key parameter to improve the redox reversible reactions.

The solubility of O_2 in a mild pH of the aqueous solution was studied by adding H_3PO_4 in a half cell Li-air system. Fig. 1 shows the comparison of redox reactions in aqueous and organic electrolytes using different salts in Ar and O2 atmosphere. In case of using organic electrolyte, the oxidation current intensity was affected by the lower limit voltage. The further discussion will be presented in the conference.

[1] X. Wang, Y. Hou, Y. Zhu, Y. Wu, R. Holze, Nature **2013**, 3, 1401.
[2] D.J. Lee, O. Yamamoto, D.-M. Im, Y. Takeda, N. Imanishi, **2012**, Patent Application No. 13/191769.
[3] J. Christensen, P. Albertus, R. S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, A. Kojic, *J. Electrochem. Soc.* **2012**, *159*, R1-R30.
[4] Y. Wang, H. Zhou, *J. Power Sources* **2010**, *195*, 358-361.

A Mechanosensitive Dye as Surface Second Harmonic Generation Probe of Biomimetic Interfaces

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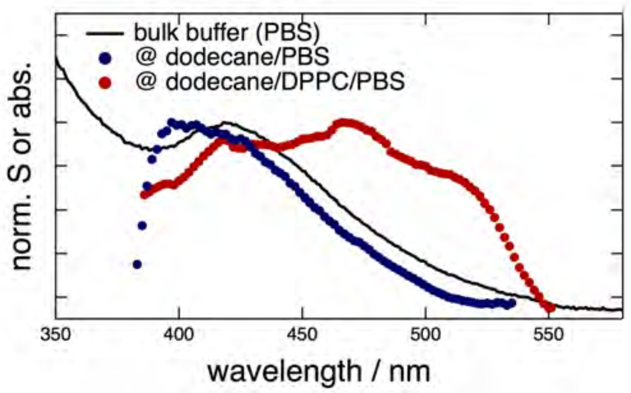
The development of well-designed fluorescent probes has enabled the visualization of various natural processes, particularly in biology, with improved detection limits and high specificity. However, for environments such as interfaces where the response is hidden by the bulk, the fluorescence technique is not adequate and more specific methods need to be employed. Here, a stationary and ultrafast time-resolved Surface Second Harmonic Generation (SSHG) technique,[1,2] which provides the required interface specificity, is applied.
A new dithienothiophene derivative, the best mechanosensitive membrane probe so far,[3] is investigated at different interfaces using SSHG. For example, the figure demonstrates that the interfacial spectrum of this compound is shifted to lower energy in the presence of the ordered phospholipid monolayer, revealing the sensitivity to membrane pressure.

The present work shows the remarkable performance of this dye as a SSHG probe and, for instance, the possibility to use it in SHG microscopy, which could in the future give a deeper insight into biologically relevant questions.



[1] K. B. Eisenthal, *Chemical Reviews,* **1996**, *96*, 1343-1360.
[2] G. Licari, P.-F. Brevet, E. Vauthey, *Physical Chemistry Chemical Physics,* **2016**, *18*, 2981-2992.
[3] S. Soleimanpour, A. Colom, E. Derivery, M. Gonzalez-Gaitan, A. Roux, N. Sakai, S Matile, *Chemical Communications.,* **2016**, *52*, 14450-14453.

Carbon coating for nano-rattle Sn@C composite anode material for alkali metal ion batteries

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Tin based alloy anode material undergoes huge volume expansion upon lithium ion insertion (up to 360%) which causes cracking of the active material, consequently leading to capacity fading. This greatly hinders the practical application of Sn as anode material in lithium ion batteries[1]. ‘Nano-rattle’ type Sn nanoparticles (NPs) encapsulated in a carbon shell are proposed here as they feature a buffer volume (void) to cope with the volume expansion problem.

Carbon coating: A reverse micelle micro emulsion technique has been adopted to form SiO_2 NPs in the first step[2], followed by hydrothermal carbonization to form carbon coating on silica NPs. The nano-rattle morphology is however difficult to obtain if the intermediate hydrothermal carbonization step does not yield a uniform carbon coating on the silica surface. This is why this study emphasizes on the variation of the pH, the concentration and the respective surface polarity values which influence the wettability, adsorption and aggregation properties[3].

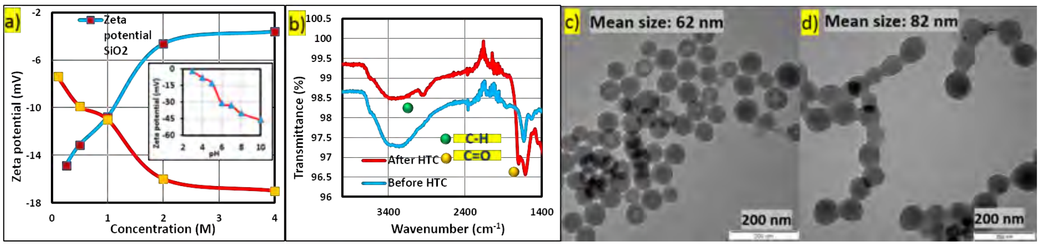

Figure 1: Graphs showing Zeta potential analysis (a) and FTIR (b), TEM images showing SiO2 NPs before (c) and after (d) hydrothermal carbonization Figure 1a shows the zeta potential measurements as a function of the concentration of silica and sucrose, which was used as carbon source. The inset graph shows that the silica suspension is more stable at high pH. The FTIR graph in figure 1b shows the presence of C=O and C-H bands after coating of sucrose on the surface of silica. The TEM images 1c and 1d show the as-formed silica NPs before and after hydrothermal carbonization, respectively. The particle size increased after the hydrothermal process, probably due to formation of a porous, spongy carbon shell.

Conclusion and perspectives: A thin and homogeneous carbon coating on the surface of single silica sphere can be formed by controlling silica surface and a well-dispersed suspension. Further steps are on-going to obtain Sn@C nano-rattles after the substrate etching process and Sn impregnation process. Finally, the electrochemical properties of the nano-rattle Sn@C composite electrode will be analysed by cycling at different C-rates.

[1] Besenhard, J. O.; Yang, J.; Winter, M.,*Journal of Power Sources* **1997**, *68* (1), 87-90.
[2]Priebe, M.; Fromm, K. M., *Particle & Particle Systems Characterization* **2014**, *31* (6), 645-651.
[3]Yu, L.; Falco, C.; Weber, J.; White, R. J.; Howe, J. Y.; Titirici, M.-M., *Langmuir* **2012,** *28* (33), 12373-12383.

Bimolecular Photoinduced Electron Transfer: the effect of the reorganization energy

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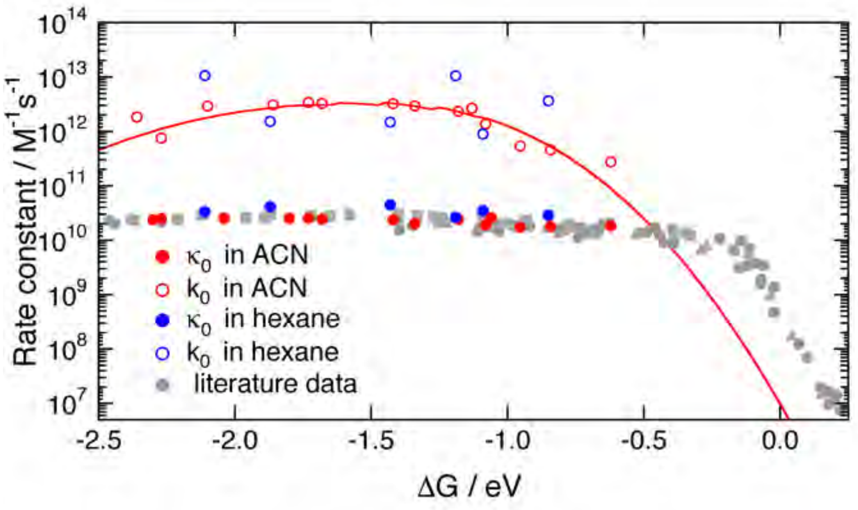
Electron transfer (ET) is one of the simplest chemical reactions, as it does not require the formation or the breaking of a chemical bond. Moreover, photoinduced ET it is one of the most investigated photochemical reactions.[1] ET processes are usually described theoretically in terms of the Marcus model, which connects the driving force of the reaction with its rate constant.[2] The latter depends on several additional parameters such as the temperature, the reorganization energy and the electronic coupling between the initial and final states.

We will present a study focussing on the reorganization energy, which is composed of the contribution from the solvent, λ_s, and from intramolecular modes, λ_i. The effect of λ_s was investigated by measuring the dynamics of bimolecular photoinduced ET reactions in an apolar solvent and by comparison with previous results in a polar solvent.[3] The effect of λ_i was studied by performing measurements with perdeuterated compounds.



The above figure illustrates the driving force dependence of the ET rate constant in hexane and in acetonitrile (ACN). Here, k_0 is the intrinsic, diffusion-free, bimolecular ET rate constant, whereas k_0 is the diffusion-controlled rate constant. Surprisingly, the observed ET dynamics does not exhibit a significant dependence on the solvent polarity, despite very different λ_s. This result suggests that the intramolecular modes play a predominant role in the ET dynamics.

[1] Tatu Kumpulainen, Bernhard Lang, Arnulf Rosspeintner, Eric Vauthey, *Chemical Reviews,* **2017**, DOI: 10.1021/acs.chemrev.6b00491

[2] R. A. Marcus, *The Journal of Chemical Physics.* **1956,** 24, 966-78.

[3] Arnulf Rosspeintner, Gonzalo Angulo, Eric Vauthey, *Journal of the American Chemical Society,* **2014,** 136, 2026-2032.

Molecular Insights on the 3D Lipid Monolayers of Lipid Droplet Organelle

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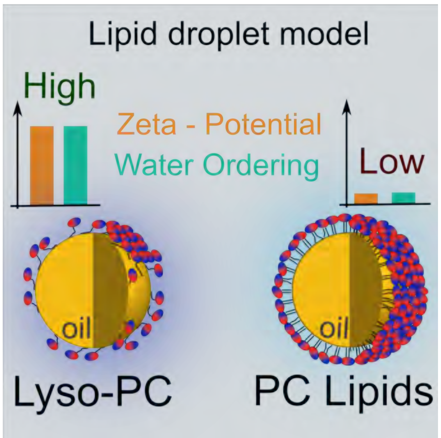
Three-dimensional (3D) phospholipid monolayers at hydrophobic surfaces are omnipresent in nature as adiposome organelle, also known as lipid droplets, or in man-made materials such as drug delivery systems. Nevertheless, the molecular level understanding of such monolayers remains elusive. We investigate the molecular structure of phosphatidylcholine (PC) lipids forming 3D monolayers on the surface of hexadecane nanodroplets. The influences of acyl chain length, saturation, and number of acyl tails per lipid were studied with vibrational sum frequency, and second harmonic scattering, interface sensitive non-linear optical techniques. We find that 1,2-dihexadecanoyl-sn-glycero-3-phosphocholine (DPPC; 16:0) lipids form tightly packed, liquid-condensed-like monolayers.[1] Upon shortening the tail length to 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC; 14:0) and 1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC; 12:0), more gauche defects in the lipid tails are observed. Monolayers of unsaturated 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC; 18:1) and single acyl tailed 1-palmitoyl-2-hydroxy-sn-glycero-3-phosphocholine (lyso-PC; 16:0) contain more disorder. Despite these variations in the packing of the tail region, the headgroup orientation remains approximately parallel to the nanodroplet interface. Remarkably, the lyso-PC lipids uniquely form more diluted and “patchy” 3D monolayers.[2] These results are supported by zeta-potential measurements and fluorometric analysis of Nile-red dye adsorption to these 3D phospholipid monolayers. Our findings suggest a vital role for the presence of single-tailed lipids on the lipid droplet organelles. Specifically, these lipids enhance the accessibility of the hydrophobic non-polar core by the water soluble enzymes; i.e. lipases, present in the cytosol.



[1] Yixing Chen, Kailash C. Jena, Cornelis Luetgebaucks, Halil I. Okur, Sylvie Roke, Nano Lett., **2015**, 15, 5558-5563.
[2] Halil I. Okur, Yixing Chen, Nikolay Smolentsev, Evangelia Zdrali, and Sylvie Roke, J. Phys. Chem. B, **2017**, 121, 2808-2813.

Application of Reactive Molecular Dynamics on Astrochemical interest systems.

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The combination of quantum and classical methodologies is a winning strategy for studying astrochemical phenomena, making possible to explain telescopic observations. In this work two reactive events are studied in this way, using Reactive dynamics performed using MS-ARMD (Multi-Surface Reactive Dynamics) [1] module present in CHARMM[2].

The first study regards the formation of O2 in the Interstellar Media (ISM): this species is considered the first reservoir of atomic Oxygen, but there are only few observations that support this hypothesis. Mass-spectrometric observations of comet colas suggest that O2 is highly correlated with water ice grains[3]. After characterizing the ice structure at ISM temperature regime, 50 K, reactive simulations are performed inside the ice bulk and on top of its surface, using a MRCI Potential Energy Curve to describe O2. The majority of the reactions are observed within the first 5 ps of simulation, showing the ability of the ice morphology to catalyze the reaction. The scarce interaction between O2-H2O has as consequence a slow relaxation of the new formed molecule that is estimated on the 100 ns time scale., in the meanwhile it acts as a heat source for the bulky ice increasing the temperature of 15 K during a 5 ns time scale.

The second example investigates the interaction of fullerene cations with hydrogen ($C60H^+$ and $C60H2^+$). It results of particular interest in both astrochemical (as can be used to trace the fullerene contributions to the Carbon abundance in the Universe) and technological (due high capacity of these species of storing Hydrogen) fields. The energetic profiles are characterized via B3LYP/6-31g(d) calculations. The chemisorption of one hydrogen atom on fullerene results in 85.87 kcal/mol stabilization, and consequent possibility of diffusion on top of the adsorbate specie (barrier of 29.45 kcal/mol). Nanosecond MD simulations shows the equivalence between the different adsorption sites. In agreement with previous studies on Carbon Nanotubes [4], H2 bond is broken during the chemisorption.

In both example the use of MS-ARMD techniques shows up to be important: Ab-Inito levels results can be easily reproduced at cost of a classical simulations. The inclusion of possibles diabatic crosses between PES is planned as further improvement of this module, opening the possibility to study more complicated photochemical processes.

[1] T. Nagy, J. Y. Reyes and M. Meuwly, J. Chem. Theo. Comp, 2014, 10, 1366-1375;
[2] B.R. Brooks and al, J. Comput. Chem., 2009,30,1545-1614 ;
[3] A. Bieler and al , Nature, 2015,526,7575,678-681;
[4] G Chen and al, Phys. Rev. B, 2005, 72, 045444.

Using puled EPR dipolar spectroscopy for the coarse-grained localisation of a residue in the intrinsically disordered domain of hnRNP A1

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The regulatory function of the human protein hnRNP A1 in splicing is believed to be mediated by multimerisation of individual hnRNP A1 units on long RNAs via an intrinsically disordered C-terminal domain [1]. The two N-terminal domains of hnRNP A1 are known to fold in a well-defined structure, which has been solved by X-ray crystallography, and more recently by solution NMR (pdb: 2LYV). The high degree of flexibility of the C-terminal domain, however, makes it inaccessible for both structural techniques. Using site-directed spin labelling, we determine distance distributions from residues in the structured domains, termed beacon sites, to individual residues in the disordered domain using the DEER pulsed EPR technique [2]. Together with a set of distances measured between the beacon sites themselves, it is then possible to calculate a spa-tial distribution of the position of a given residue in the disordered domain, which can be visualised as an isosurface of the probability density [3]. This analysis approach is included in the current version of the modelling software MMM [4].

Figure 1. NMR sub-ensemble structure (2LYV) of hnRNP A1 with visualisation of spin label rotamer clouds (purple) at the beacon sites and the 50% probability density isosurface (green and red) of finding residue 231. The distances between all possible pairs were measured using the DEER pulsed EPR experiment on samples of doubly labelled (MTSL) hnRNP A1.

Support: This work is supported by SNF grant 200020 157034.

[1] H. L. Okunola, A. R. Krainer, Cooperative-Binding and Splicing-Repressive Properties of hnRNP A1, *Molecular and Cellular Biology*, **2009**, 29, 5620–5631
[2] G. Jeschke, DEER Distance Measurements on Proteins, *Annual Review of Physical Chemistry*, **2012**, 63, 419–446
[3] G. Jeschke, Ensemble models of proteins and protein domains based on distance distribution restraints, *Proteins*, **2016**, 84, 544–560
[4] G. Jeschke, Y. Polyhach, E. Bordignon, Multiscale Modeling of Macromolecules—MMM, **2010**, ETH Zurich (*http://www.epr.ethz.ch/software.html*)

How good is the generalized Langevin equation to describe the dynamics of photo-induced electron transfer in fluid solution?

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The dynamics of unimolecular photo-triggered reactions can be strongly affected by the surrounding medium for which a large number of theoretical descriptions have been used in the past. An accurate description of these reactions requires knowing the potential energy surface and the friction felt by the reactants. Most of these theories start from the Langevin equation to derive the dynamics, but there are few examples comparing it with experiments.[1]

Here we explore the applicability of a Generalized Langevin Equation (GLE) with an arbitrary potential and a non-markovian friction.[2] To this end we have performed broadband fluorescence measurements[3] with sub-picosecond time resolution of a covalently linked organic electron donor-acceptor system in solvents of changing viscosity and dielectric permittivity. The free energy surface (FES) of the reaction is established using stationary electronic spectroscopy, while the dynamics of a non-reacting reference provide the calibrating tool for the non-markovian friction over the FES. In addition, the simpler and computationally faster Generalized Smoluchowski Equation (GSE) is also applied for comparison.[4]

While both approaches reproduce the measurements in most of the solvents reasonably well, the GSE shows larger discrepancies whenever the dynamics become slow. At long times some differences arise from the intrinsic shortcomings of the solvatochromic model and at short times from the excess excitation energy.

The here applied method can be used to predict the dynamics of any other reacting system, given the FES parameters and solvent dynamics are provided. Thus **no fitting parameters** enter the simulations, within the applicability limits found for the model in this work.

[1] K. Tominaga, G.C. Walker, T.J. Kang, P.F. Barbara, T. Fonseca, *J. Phys. Chem.*, **1991**, 95, 10485-10492.
[2] R.F. Grote, J.T. Hynes, *J. Chem. Phys.*, **1980**, 73, 2715-2732.
[3] L. Zhao, L. Perez Lustres, V. Farztdinov, N.P. Ernsting, *PCCP*, **2005**, 7, 1716-1725.
[4] J.T. Hynes, *J. Phys. Chem.*, **1986**, 90, 3701–3706.

The interfacial structure of water droplets in a hydrophobic liquid

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Nanoscopic and microscopic water droplets and ice crystals embedded in liquid hydrophobic surroundings are key components of aerosols, rocks, oil fields and the human body. The chemical properties of such droplets critically depend on the interfacial structure of the water droplet. Here, we report the surface structure of 200 nm sized water droplets in mixtures of hydrophobic oils and surfactants as obtained from vibrational sum frequency scattering measurements. The interface of a water droplet shows significantly stronger hydrogen bonds than the air/water or hexane/water interface and previously reported planar liquid hydrophobic/water interfaces at room temperature. The observed spectral difference is similar to that of a planar air/water surface at ~50 K lower temperature. Supercooling the droplets to 263 K does not change the surface structure. Below the homogeneous ice nucleation temperature a single vibrational mode is present with a similar mean hydrogen bond strength as for a planar ice/air interface.

[1] Nikolay Smolentsev, Wilbert J. Smit, Huib J. Bakker, Sylvie Roke, *Nature Communications*, **2017**, 8, 15548.

Investigating Excited-State Symmetry Breaking in Quadrupolar Compounds using Time-resolved Infrared spectroscopy.

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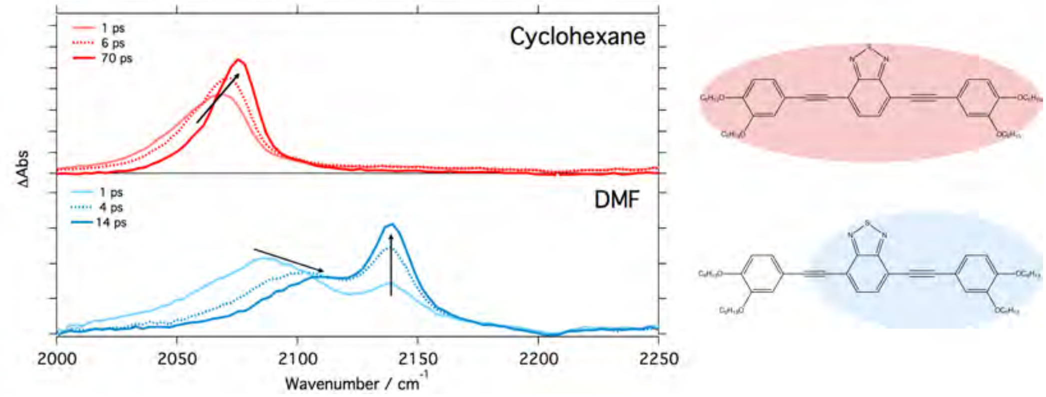
Quadrupolar molecules, comprising of D-π-A-π-D or A-π-D-π-A motifs, are mostly studied for to their strong two-photon absorption cross section. These compounds show almost no solvatochromism in their electronic absorption spectra but fluorescence reveals that the emitting state is greatly affected by the solvent. This phenomenon has been ascribed to excited-state symmetry breaking, i.e. to the unbalanced distribution of the excitation over the molecule due to fluctuations of the solvent or of the geometry of the molecule [1]. Whereas time-resolved electronic spectroscopic techniques do not provide much insight into the dynamics of the symmetry breaking of these compounds, time-resolved infrared spectroscopy constitutes an excellent tool to study this phenomenom. We are currently studying different quadrupolar compounds consisting of alkoxybenzenes as weakly donating groups and either benzothiadiazoles or anthracene moieties as central acceptors [2]. The D and A moieties are linked together with a carbon triple bond, which serves as an excellent IR active probe. We will discuss whether the solvation is the dominant factor determining the extent of symmetry breaking or whether conformational changes alone can induce symmetry breaking in these compounds.



[1] Bogdan Dereka, Arnulf Rosspeintner, Zhiquan Li, Robert Liska, and Eric Vauthey, J. Am. Chem. Soc., **2016**, 138, 4643-4649.
[2] Federica Ricci, Fausto Elisei, Paolo Foggi, Assunta Marrocchi, Anna Spalletti, and Benedetta Carlotti, J. Phys. Chem. C, **2016**, 120, 23726-23739.

On the Photoelectron Spectrum and Heat of Formation of the meta-Xylylene Biradical

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[1]Paul Scherrer Institute, [2]ETH Zürich, [3]University of Wollongong, [4]University of Melbourne

The meta-xylylene biradical *m*-C8H8 represents a prototypical organic triplet that serves as a model compound for the test and refinement of quantum theoretical calculations and is a promising building block for organic molecule-based magnets. We used flash vacuum pyrolysis of 1,3-bisiodomethyl-benzene (*m*-C8H8I2) to produce *m*-C8H8 in the gas phase and photoelectron spectroscopy to probe the first two electronic states of the radical cation. The ionization energy was found to be (7.27±0.01) eV. From that, the heat of formation of the biradical is derived indirectly by investigating the C-I bond dissociation behavior of the precursor ion. We obtain $\Delta H_{f;298K}$ = (321.3±10) kJ/mol, which is slightly below the value of a previous study applying a different experimental approach.

Radical geometry: a key to efficient Dynamic Nuclear Polarization.

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Dynamic nuclear polarization (DNP) is becoming an essential tool to dramatically improve the sensitivity of numerous experiments in nuclear magnetic resonance (NMR) including those involving the elucidation of surface structure of advanced materials[1] and the characterisation of polymorphs in organic solids[2]. The method is based on the transfer of polarization from electron to nuclear spins by saturation of the electron spin transitions. The upper limit of transferable polarization, at equilibrium, is dictated by the ratio of the gyromagnetic values of electron and nuclear spins: about 660 for ^{1}H and even more for other low abundant nuclei such as ^{13}C, ^{15}N. The primary parameter to perform an efficient DNP experiment remains by far the choice of the radical[3]. Several factors have been identified to affect the efficiency of the polarising agent: rigidity, bulkiness, relaxation properties to name a few.

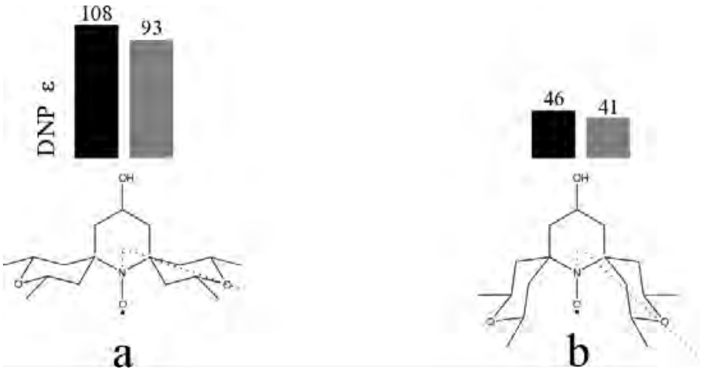

Fig. 1: *Nitroxide monoradicals used as polarizing agents for MAS ssDNP experiments at 9.4T, ~100 K, MAS=8000 Hz. The displacement of the cyclohexane sidearms from the nitroxide axis is larger for the open than for the closed configuration (panel a) and b) respectively). The rectangles indicate the MAS ssDNP enhancement obtained via ^{1}H-^{13}C cross polarization when the solvent used is glycerol-d_8:D_2O:H_2O (black) and TCE (grey).*

Here we show for a set of nitroxide mono- and bi-radicals how the local geometric conformation, especially in the vicinity of the unpaired electron spin, leads to considerably different enhancement factors for MAS ssDNP (Magic Angle Spinning solid state DNP) experiments conducted at 9.4 T and ~100K in 1,1,2,2-tetrachloroethane (TCE), glycerol-d_8:D_2O:H_2O, and DMSO-d_6:D_2O:H_2O. Given the impact on the experimental enhancement factor we include the local geometry among the set of important variables to consider in the design of new polarising species. The *open* configuration (Fig 1a) leads always to a better DNP enhancement either for the nitroxides mono- and bi-radicals irrespective of the solvent used. The different DNP performance between *open* and *closed* is currently accounted for by postulating a difference in solvent accessibility to the unpaired electron caused by the bulky substituents.

[1] A. J. Rossini, A. Zagdoun, M. Lelli, A. Lesage, and C. Cop, **2013**,
[2]A. C. Pinon, A. J. Rossini, C. M. Widdifield, D. Gajan, and L. Emsley, *Mol. Pharm.*, **2015**, 12, 4146–4153.
[3] D. J. Kubicki, A. J. Rossini, A. Purea, A. Zagdoun, O. Ouari, P. Tordo, F. Engelke, A. Lesage, and L. Emsley, *J. Am. Chem. Soc.*, **2014**, 136, 15711–15718.

Conformational effects in radical reactions

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Revealing the dynamics of hydrocarbons reacting with free radicals is of major relevance for understanding atmospheric processes and combustion chemistry [1]. Despite their significance demonstrated by the vast body of literature, the conformational dependence of radical reactions still remains largely unexplored. Only a few studies demonstrate conformational effects in these reactions [2, 3]

To gain detailed insights into reaction dynamics, a crossed-molecular-beam apparatus with integrated conformer-selector is being built. The molecular beam technique allows us to study single-collision events under well controlled initial conditions. Due to different dipole moments, conformers can be spatially separated in a molecular beam using an inhomogeneous electric field. This technique of separation has been previously successfully implemented to study conformationally resolved reactions of 3-aminophenol with Ca^+ ions [4].

We are now extending this approach to neutral reactions. Our first target is the reaction of conformationally selected 1,2-bis(trifluorosilyl)ethane with chlorine radicals [5]. Calculations of the potential energy surface suggest that the abstraction of hydrogen by chlorine is more favourable from the gauche-conformer because of the sterical hinderance exerted by the SiF_3 groups. In a first stage, we aim to measure conformer-specific reaction rates which yield information about the activation energies of different conformational reaction pathways. At a later stage, the experiments will be extended for measurements of product state and angular distributions and different radical species, e.g., fluorine.

[1] R. I. Kaiser, A. M. Mebel, *Int. Rev. Phys. Chem.,* **2002**, 21, 307-356.
[2] V. L. Orkin et al., *J. Phys. Chem.* A, **2011**, 115, 6568-6574.
[3] C. A. Taatjes et al., *Science*, **2013**, 340, 177-180.
[4] D. Rösch et al., *Science*, **2013**, 342, 98-101.
[5] P. Klaeboe et al., *J. Raman Spectrosc.*, **2009**, 40, 2111-2122.

Computational modeling of band gaps in perovskites

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Finding new semiconductor materials with specific band gaps, in particular within the class of perovskite compounds, is essential for the development of optoelectronic and photovoltaic applications. The screening of a wide compositional range of potentially suitable candidates requires elaboration of an accurate and fast computational methodology for the band gap evaluation. In this work, the band gaps in a series of doped perovskite materials are computed within the Density Functional theory. The impact of spin-orbit coupling, temperature and excitonic effects (BSE calculations) on the band gap value is analyzed as a function of dopant type and concentration. The applied methodology is iteratively assessed by dint of comparison with the experimental data for these systems. This approach is demonstrated to provide a close estimate of band gaps in doped perovskite compounds.

Characterization of the Platinum/liquid (gas) Catalytic Interface

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Hydrogen Evolution Reaction (HER) taking place at Pt electrodes is among the most studied electrochemical processes regarding its importance for the hydrogen economy and fundamental understanding of the heterogeneous catalysis.[1] Surface sensitive spectroscopy, such as Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy proved to be useful in characterization of the chemical species present at interfaces.[2] Regarding the HER at the Pt electrode, adsorbed hydrogen atom is the primary intermediate and it is known to have vibrational bands (Pt-H) between 2000-2100 cm^{-1}.[3] However CO, which poisons Pt surfaces, is also known to have IR bands in the same spectral region.[4] Such overlap makes the unambiguous assignment of the Pt-H band a non-trivial task.

Thin films (< 5nm) of Pt were sputter coated on right-angle prism substrates. The experiments involve either (1) adsorption from gas phase or (2) electrochemical adsorption in solution phase: (1) Gas phase adsorption is induced by admission of high purity H_2 and D_2 gases into the sample cell. Effect of H_2/D_2 and CO adsorption alone, as well as coadsorption of H_2/D_2 to CO covered Pt surface were examined. (2) Spectro-electrochemical measurements have been performed both in 0.5 M H_2SO_4 (in H_2O) and D_2SO_4 (in D_2O) at potentials where HER takes place.

ATR-FTIR results from both set of experiments indicate appearance of bands, which are assigned to adsorbed CO, whose spectroscopic appearance is affected by hydrogen. Previous FTIR experiments have attributed these bands to Pt-H, excluding the possibility of CO formation.[3] 2D ATR IR spectroscopy shows similar lineshapes for all the bands, even though higher anharmonicity is expected from the Pt-H vibration in comparison to that of Pt-CO. Finding the source of CO affected by hydrogen is an important step towards the unambiguous assignment of the Pt-H vibrational band.

[1] R. J. Nichols and A. Bewick, *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry,* **1988,** 243, 445-453.
[2] J. P. Kraack, et al., *The Journal of Physical Chemistry Letters* , **2014,** 5 (13), 2325-2329.
[3] K. Kunimatsu, et al., *Electrochimica Acta,* **2007,** 52, 5715-5724.
[4] K. Kunimatsu, et al., *Langmuir* , **1986,** 2 (4), 464-468.

DNP Jelly

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Dynamic Nuclear Polarization (DNP) is a hyperpolarization method that can deliver an increase in NMR signal intensity by up to 2 orders of magnitude, thereby permitting unprecedented atomic-level characterization of systems that were previously inaccessible such as cements or nanoparticles.[1] Dynamic nuclear polarization (DNP) experiments usually rely on the transfer of polarization from a radical containing matrix to a target of interest. Today, the matrix is either a glycerol-*d*8/D_2O/H_2O (6/3/1 v/v) mixture, so-called “DNP Juice"[2] or an organic liquid such as 1,1,2,2- tetrachloroethane[3] or *ortho*-terphenyl.[4] While these matrices work well, they present limitations in many cases, where solubility is partial, aggregation occurs at low temperatures, or if the substrate reacts with the matrix. Expanding the water based formulations range of matrices that can be used for DNP experiments is of considerable interest.

We present water based acrylamide gels as polarizing matrices for DNP. We observe that an increase in cross linker ratio combined with low concentration of biradical provides high enhancements comparable (ε = 200 for DNP Jelly) to the popular matrices available today, “DNP Juice”. The aqueous acrylamide gel allows the characterization of core-type CdTe-COOH quantum-dots using surface-enhanced NMR spectroscopy methods. The gels introduced here prevent aggregation while maintaining high enhancements, and Cd-113 spectra are acquired in minutes.

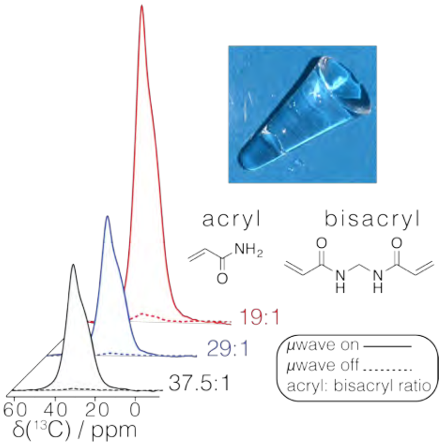

Figure 1. DNP enhancements in polyacrylamide water based gels as a function of pore size which decreases with the acryl: bisacryl ratio (given on the right).

[1] a) Rossini, A. J. ; Zagdoun, A. ; Lelli, M. ; Lesage, A. ; Copéret, C. ; Emsley, L. *Acc. Chem. Res.* **2013**, (46), 1942-1951; b) Piveteau, L. ; Ong, T.-C. ; Rossini, A. J. ; Emsley, L. ; Copéret, C. ; Kovalenko, M. V. *J. Am. Chem. Soc.* **2015**, (137), 13964-13971. [2] van der Wel, P. C. A.; Hu, K.-N.; Lewandowski, J.; Griffin, R. G., *J. Am. Chem. Soc.* **2006,** (128) , 10840-10846. [3] Zagdoun, A.; Rossini, A. J.; Gajan, D.; Bourdolle, A.; Ouari, O.; Rosay, M.; Maas, W. E.; Tordo, P.; Lelli, M.; Emsley, L.; Lesage, A.; Coperet, C., *Chem. Commun.* **2012,** (48), 654-656. [4] a) Ong, T.-C.; Mak-Jurkauskas, M. L.; Walish, J. J.; Michaelis, V. K.; Corzilius, B.; Smith, A. A.; Clausen, A. M.; Cheetham, J. C.; Swager, T. M.; Griffin R. G. *J. Phys. Chem. B.* **2013** (117), 3040-3046; b) Lelli, M.; Chaudhari, S. R.; Gajan, D.; Casano, G.; Rossini, A. J.; Ouari, O.; Tordo, P.; Lesage, A.; Emsley, L., *J. Am. Chem. Soc.* **2015** (137), 14558-14561.

Cold ion-molecule collisions in a cryogenic hybrid trap

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In recent years, collisions of cold atoms with atomic and molecular ions have been studied intensively [1]. The development of “hybrid traps” which allow for the simultaneous trapping of cold neutral atoms and ions have paved the way for gaining insights into the nature of ion-atom collisional processes at very low temperatures [2].

We are currently developing a cryogenic trap for the simultaneous confinement of cold neutral molecules and cold molecular ions. Translationally cold neutral molecules are produced by Stark deceleration and loaded into a magnetic trap [3]. The magnetic trap’s center can be mechanically displaced and superimposed with the center of an RF ion trap. The interaction of room temperature black body radiation (BBR) results in rotational excitation of the OH leading to trap loss after few seconds. To alleviate this effect, the hybrid trap is cooled down to 15 K to be shielded from room temperature BBR, which is increases the lifetime of the trapped molecules by several orders of magnitude, commensurate with the trap lifetime of the ions.

This new setup will allow for the first time studies of ion-molecule collisions in the millikelvin regime. We will present a detailed characterization of the experiment and first results.

[1] S. Willitsch, *Int. Rev. Phys. Chem*., 31, 175-199 **(2012)**
[2] S. Willitsch, *Proc. Int. Sch. Phys. Enrico Fermi*, 189, 255 **(2015)**
[3] B. Stuhl, M. Yeo, M. T. Hummon and J. Ye, *Mol. Phys*, 111, 1798-1804 **(2013)**

In-situ studies on the early stages of calcium carbonate nucleation from supersaturated micro droplets.

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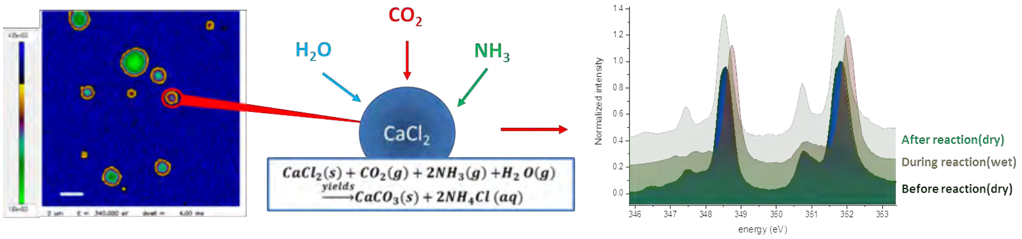
Calcium carbonate is one of the largest reservoirs of the earths CO_2 which forms in nature through the reaction of calcium ions and carbon dioxide. Although biominerals have mastered the art of utilizing calcium carbonate to form functional materials ranging from eye lenses to protective shells through the careful control of the early stages of nucleation, a full understanding of these processes still pose a challenge to scientists despite years of research. Recent studies have shown that the nucleation process of calcium carbonate follows a multistep process involving formation of amorphous calcium carbonate (ACC) as intermediate[1][2]. However, stability of ACC and their subsequent transformation to more stable crystalline phases is still an open question. In particular the pathway of ACC dehydration, which is the critical route of transformation from ACC to crystalline materials is not well understood.

By utilizing a well-designed *in-situ* cell for probing microdroplets, the early stages of nucleation of calcium carbonate and subsequent dehydration of ACC were studied through the diffusion controlled reaction of calcium chloride with gas phase water, carbon dioxide and ammonia[3]. The structural changes occurring during the reaction were monitored *in-situ* using synchrotron based STXM (scanning transmission X-ray microscopy) and infrared spectroscopy. The results obtained confirmed the formation of ACC[4] as an intermediate step and further structural changes were observed in the formed ACC during dehydration under different relative humidity conditions.



[1] M. H. Nielsen, S. Aloni, and J. J. De Yoreo, “In situ TEM imaging of CaCO 3 nucleation reveals coexistence of direct and indirect pathways,” *science*, vol. 218, no. April, pp. 213–218, 2014.
[2] D. Gebauer and H. Cölfen, “Prenucleation Clusters and Non- classical Nucleation,” *Nano Today*, vol. 6, no. 564–584, pp. 2–59, 2011.
[3] J. Ihli, P. Bots, A. Kulak, L. G. Benning, and F. C. Meldrum, “Elucidating Mechanisms of Diffusion-Based Calcium Carbonate Synthesis Leads to Controlled Mesocrystal Formation,” *Adv. Funct. Mater.*, pp. 1–9, 2012.
[4] J. Ihli *et al.*, “Dehydration and crystallization of amorphous calcium carbonate in solution and in air.,” *Nat. Commun.*, vol. 5, p. 3169, 2014.

Ionic Liquids based on Crown Ethers as electrolytes additives for batteries

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Room temperature ionic liquids (RTILs) are salts that are liquid at room temperature and that are usually composed of an asymmetrical organic cation and a large charge-delocalized anion which is poorly coordinated. They are non-flammable, and thermally as well as electrochemically stable. These properties make them very interesting for many applications including green solvents for synthesis, catalysis, and electrolytes for ionic and electronic devices

Crown ethers are able to strongly interact with alkali metal cations (Li^+, Na^+, K^+) and have been used as additives in battery electrolytes in order to increase the ionic conductivity of the latter and to prevent electrolyte decomposition[2-3]. However, few studies have been done on crown ethers in the field of electrolytes.

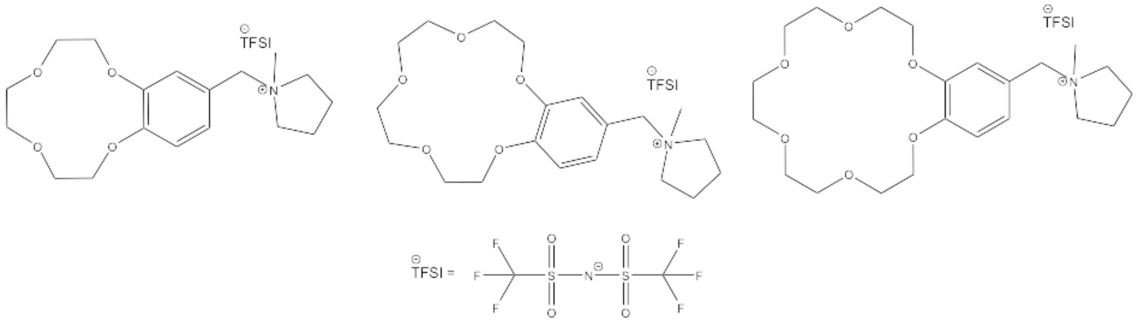

Figure 1:New Ionic liquids based on crown ether building blocks

This is why we propose to integrate them covalently as an alkali cation carrier [4-5] in the ionic liquid system. The aim of the project is thus to design and synthesize new Room Temperature Ionic Liquids (RTILs) based on crown ether moieties, to investigate their properties (flammability, thermal and electrochemical stability, conductivity, Li/Na-ion diffusion) and then to use them as electrolytes for rechargeable batteries. We will present their synthesis, structures and properties in this contribution.

[1] H. Ohno, *Electrochemical aspects of Ionics liquids*, John Whiley & sons, **2005**
[2] Abouimrane, A.; Alarco. P J., *Journal of power source*, **2007**, 174, 1193-1196
[3] Danil de Namor, Margot. A.; Abu Lebdeh. Y.; Davidson. I.; Armand. M., *Journal of Physical Chemistry*, **1994**, 98, 11796-11802
[4] Shu, Z.X.; McMillan. R S.; Murray. J J., *Journal of the Electrochemical Society*, **1993**, 140, 101-103
[5] Assuma, C.D.; Crochet. A.; Cheremond.Y. ; Giese. B.; Fromm. K M., *Angewandte Chemie International Edition*, **2013**, 52, 4682-4685

Studying Synthetic DNA using Molecular Dynamics Simulations

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Recently, the creation and stable growth of a semisynthetic organism (SSO) originating from *E. Coli* was reported [1]. Besides the natural guanine-cytosine (G-C) and adenine-thymine (A-T) base pairs, its DNA also contains an unnatural base pair (UBP), X-Y. The bases used in the UBP are named NaM (X) and 5SICS/TPT3 (Y) respectively [1], [2], [3]. The X-Y base pair is hydrophobic, and the two bases are stabilized via packing interactions instead of hydrogen bonds. In the present work, the conformational dynamics of a large DNA fragment (39 base pairs) containing a X-Y base pair is investigated using classical molecular dynamics simulations. Both NaM-5SICS (moderate SSO growth, only under restricted conditions [1]) and NaM-TPT3 (robust SSO growth [1]) UBPs have been considered. Two different simulations were ran for each UBP, placing it in an A-T rich and a G-C rich region of the DNA fragment, respectively. Preliminary analysis (UBP in the A-T rich region) indicates that both UBPs adopt a configuration that resembles the natural Watson-Crick base pairing, and each base is stabilized via packing interactions with its neighboring bases. This finding is in agreement with a recent computational study of a DNA 11mer containing a NaM-5SICS pair [4].

[1] Yorke Zhang, Brian M. Lamb, Aaron W. Feldman, Anne Xiaozhou, Thomas Lavergne, Lingjun Li, Floyd E. Romesberg, *PNAS*, **2017**, 114(6), 1317-1322.
[2] Karin Betz, Denis A. Malyshev, Thomas Lavergne, Wolfram Welte, Kay Diederichs, Floyd E. Romesberg, Andreas Marx, *J. Am. Chem. Soc.*, **2013**, 135, 18637-18643.
[3] Denis A. Malyshev, Floyd E. Romesberg, *Angew. Chemie Int. Ed.*, **2015**, 54, 11930-11944.
[4] Sk Jahiruddin, Ayan Datta, *J. Phys. Chem. B*, **2015**, 119, 5839-5845.

Electronic structure calculations of Br-based halide perovskites

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Halide perovskites have gained large interest during the last years due to their rapidly growing solar cell photoconversion efficiency. However, it is still challenging to find a perovskite compound which provides high efficiency and good stability at the same time. In this work we investigate the electronic structure of several perovskites which are not much studied so far: perovskites with FA, Cs and Rb cations in combination with Br anions. For all of the compounds, we calculate band gaps with a PBE functional, both with and without spin-orbit interactions. We also calculate band gaps using GW calculations, which are shown to give band gaps closest to the experimental values. Additionally, we compare the electronic structures of FASnBr3 and FAPbBr3 and comment on the possible origins of the unusual gap inversion observed for these compounds.

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Ultrafast electroabsorption spectroscopy study of carrier dynamics within hybrid lead halide perovskites

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Since their first advent, hybrid lead-halide perovskite solar cells (PSCs) have kept their promises and proven to be a valid alternative to current solar cell technologies, with power conversion efficiencies rising above 20%. At this point, however, further improvements require a more fundamental understanding of some key features inherent to PSCs, such as their interfacial properties. Indeed, on top of travelling smoothly across the perovskite layer, the photocarriers must be injected efficiently into their respective extracting layers, for optimized devices.

Herein, we aim at unravelling the origin of performance inhomogeneity in PSCs by probing three essential properties : (i) the transmission of carriers across various heterojunctions, namely perovskite-*spiro*-MeOTAD and perovskite-SnO_2, (ii) the carrier recombination in the bulk material, and (iii) the carrier transport across the perovskite layer. In this respect, time-resolved electroabsorption spectroscopy (TREAS) appears as a method of choice. This technique relies on the ultrafast monitoring of the electroabsorption signal and allows to probe field-induced phenomena such as the dynamics of field screening and charge accumulation at interfaces. As a consequence, the three abovementioned properties can be successfully accessed when using this technique in combination with transient absorption spectroscopy (TAS).

In this study, two different perovskite materials ($MAPbI_3$ and $(MA, FA)PbI_{3-x}Br_x$) within four PSCs architecture exhibiting different interfacial structures have been studied by TREAS and TA spectroscopy techniques. We report a significantly more efficient electron injection at the $SnO_2/(MA, FA)PbI_{3-x}Br_x$ interface, together with a decreased bulk recombination for the latter material, compared with the standard $MAPbI_3$. This accounts for the reported higer V_{OC} and alltogether better performance of $(MA, FA)PbI_{3-x}Br_x$-based PSCs. At the material level, we assign this to the presence of nano-domains of various compositions favouring charge separation.

Unraveling the electronic states of the copper dimer using nonlinear optical spectroscopy

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High-resolution optical spectra of transition metal containing molecules and clusters are characterized by dense-lying rotational lines, originating from many overlapping vibrational and electronic bands. The copper dimer is considered to be one of the simplest transition metal systems. However, despite its hydrogen-like ground state, the electronic excited states give rise to complex spectra that are difficult to assign. As a consequence, even for the better characterized high-lying states, fundamental spectroscopic properties like molecular constants and electronic term symbols are missing.

We use Two-Color Resonant Four-Wave Mixing (TC-RFWM) methods to assign the lines of such complex absorption bands. TC-RFWM produces a spatially separated, background-free signal beam from the non-linear interaction of three input beams that overlap within the common focal point in the probe region. In the optically thin environment of a molecular beam, observable TC-RFWM signal generation requires resonance-enhancement by two transitions that share a common level. Therefore, selection rules for optical-optical double resonances apply and reduce the complex spectra to just a few rotational lines which are often assigned in a straightforward manner.

The laser ablation-based cluster source used to prepare the copper dimers in gas phase and the optical setup is described in [1]. Figure 1 shows a selected set of spectra containing rotationally resolved transitions obtained by TC-RFWM. For one isotopologue, extra lines where found and assigned to a perturbing state that is crossing the potential curve of the J-state. Some of these extra lines have already been seen before, but could not be assigned at that time. In the ongoing work, by measuring and assigning unambiguously over 600 lines in the energy range of the I-X and the J-X transitions, a rich network of perturbing states could be identified for several vibronic levels and their molecular constants could be determined. The investigations reveal a detailed picture of the complex bonding structure of this transition metal dimer. This can be used as a benchmark for prospective quantum chemical *ab initio* methods, but is also basis for future studies of heteronuclear transition metal systems.

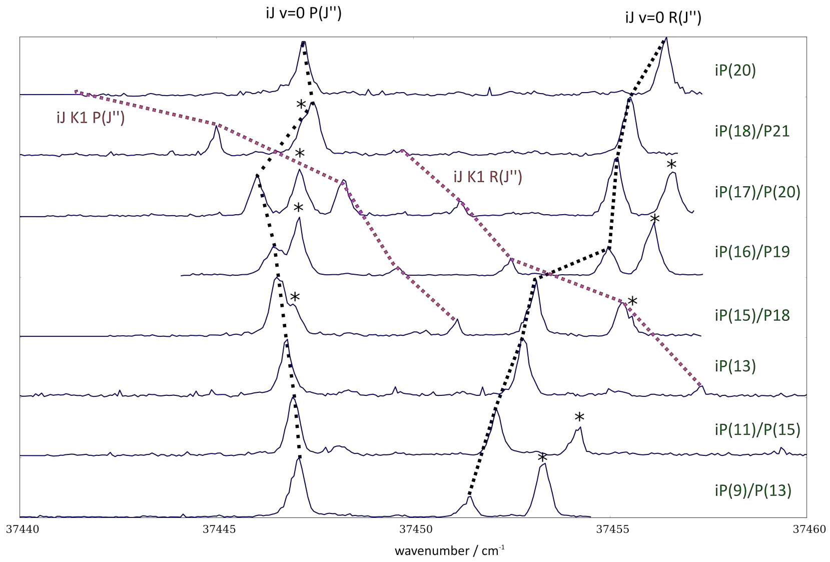

Figure 1: TC-RFWM spectra of $^{63}Cu^{65}Cu$ J-X (0-0). Single rotational lines where made visible by intermediate state labeling, pumping individual lines in the B-X (1-0) band (green labels). "i" indicates transitions in the $^{63}Cu^{65}Cu$ isotopologue, while the plain labels indicate overlapping transitions in the $^{63}Cu_2$ isotopologue. Spectral features contributed by the latter are marked with an asterisk. Within the rotational series that is pumped in $^{63}Cu^{65}Cu$, a not yet fully assigned perturbing state "K1" mixes with J, causing line shifts but also gains intensity itself.

[1] B. Visser et al., *J. Raman Spectrosc.*, **2016**, 47, 425-431.

Protein-nucleotide interactions studied by magnetic resonance

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In this contribution we present strategies to characterize protein-nucleotide interactions in large biological assemblies using the example of the (double-) hexameric DnaB helicase from *Helicobacter pylori* with a molecular weight of 672 kDa. The binding of nucleotides (ATP-analogues and single-stranded DNA, ssDNA) to the helicase is monitored by ^{31}P,^{1}H cross-polarization experiments. The observed ^{31}P chemical-shift values allow a clear discrimination between the different nucleotides used in this work and reveal that two nucleotides of bound ssDNA can be structurally distinguished. ^{15}N,^{13}C correlation experiments highlight the role of arginine sidechains in binding to single-stranded DNA.

We further present dipolar-coupling based polarization transfer experiments from ^{31}P spins of bound nucleotides to ^{13}C or ^{15}N spins of the protein (or vice versa) to describe nucleotide binding on a molecular level (see Figure 1). Residues involved in protein-nucleotide interactions are identified in CHHP and NHHP correlation experiments.

While conventional NMR experiments on such large protein assemblies typically suffer from low signal-to-noise ratios and thus long experimental measurements times, we used Dynamic Nuclear Polarization (DNP) enhanced MAS experiments to increase the sensitivity. The samples for DNP were prepared in the absence of glycerol which results in the highest sensitivity for DnaB. The obtained spectra allow to identify spin systems of the helicase in the neighborhood of ^{31}P spins of the nucleotides. The extensive line-broadening at cryogenic temperatures is not a severe issue in this case due to the sparsity of the obtained spectra.

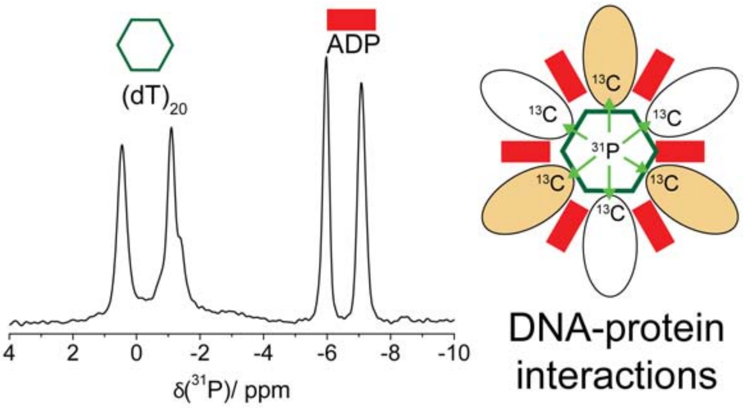

Figure 1: ^{31}P spins of bound nucleotides can be used in solid-state NMR experiments to identify helicase-nucleotide interactions.

Electrolytes induce long-range orientational order and free energy changes in the H-bond network of bulk water

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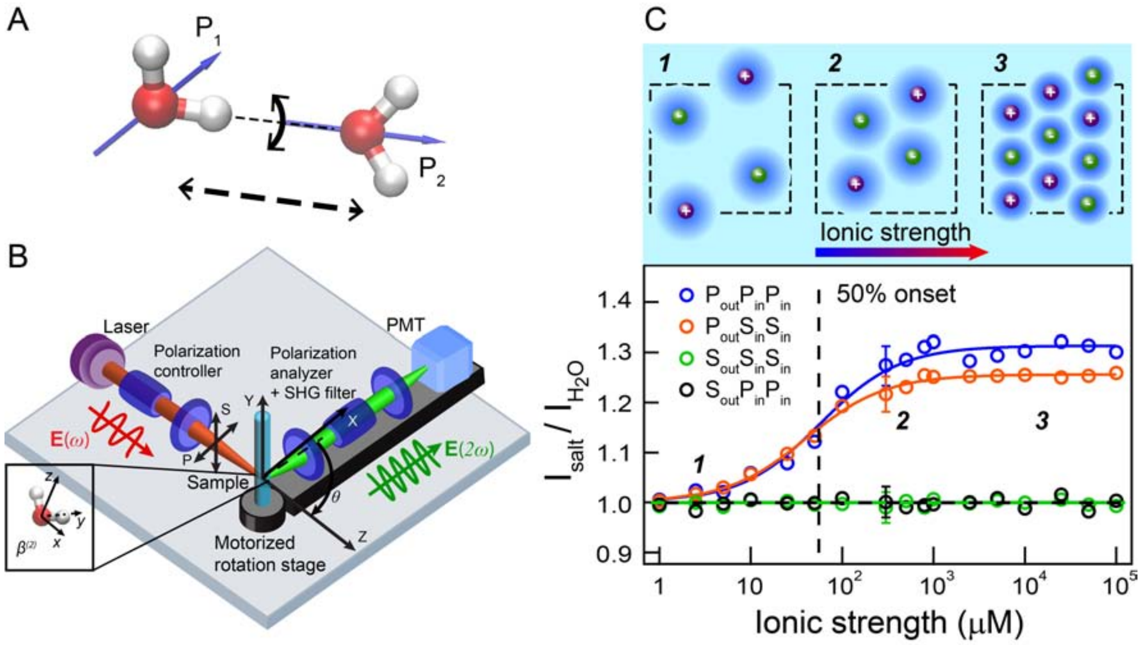
Electrolytes interact with water in many ways: changing dipole orientation, inducing charge transfer, and distorting the hydrogen-bond network in the bulk and at interfaces. Numerous experiments and computations have detected short-range perturbations that extend up to three hydration shells around individual ions. We report a multiscale investigation of the bulk and surface of aqueous electrolyte solutions that extends from the atomic scale (using atomistic modeling) to nanoscopic length scales (using bulk and interfacial femtosecond second harmonic measurements) to the macroscopic scale (using surface tension experiments). Electrolytes induce orientational order at concentrations starting at 10 μM that causes nonspecific changes in the surface tension of dilute electrolyte solutions. Aside from ion-dipole interactions, collective hydrogen-bond interactions are crucial and explain the observed difference of a factor of 6 between light water and heavy water.



[1] Yixing Chen *et al.*, Science Advances, **2016**, 2, 4, e1501891.

High resolution analysis and quantum dynamics of fluoroform $^{12,13}CHF_3$

I. Bolotova[1], S. Albert[1], S. Bauerecker[2], E. Bekhtereva[3,1], Z. Chen[1], C. Fabri[1], H. Hollenstein[1], M. Quack[1]*, O. Ulenikov[3,1]

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The spectroscopy of $^{12}CHF_3$ has been the basis for the study of time independent and time dependent quantum dynamics for a long time [1-9]. There have also been substantial efforts concerning the *ab initio* potential hypersurface ([10, 11] and references cited therein). We present a survey of our recent analyses ranging from the Terahertz (Far infrared) spectral range to about 3000 cm^{-1}, with particular emphasis on the pure rotational (FIR) spectra measured at the infrared beamline of the Swiss synchrotron Light Source (SLS), ν_3 fundamental (700 cm^{-1} range), the ν_2, ν_5, $\nu_3+\nu_6$ polyad (1200 cm^{-1} range), the $\nu_4/2\nu_3$ dyad (1400 cm^{-1}), the $2\nu_4$ (A_1 and E) dyad and results on the $^{13}CHF_3$ isotopomer including the ν_1 fundamental. The implications for the study of intramolecular vibrational energy redistribution (IVR) will be outlined with particular emphasis on ^{13}C isotope effects.

[1] a) S. Albert, K. Keppler Albert, H. Hollenstein, C. Manca-Tanner, and M. Quack Fundamentals of Rotation-Vibration Spectra, Vol. 1, pp. 117-173; b) S. Albert, K. Keppler Albert, and M. Quack High-Resolution Fourier Transform Infrared Spectroscopy, Vol. 2, pp. 965-1019; c) M. Quack Fundamental Symmetries and Symmetry Violations from High-Resolution Spectroscopy, Vol. 1, pp. 659-722 in Handbook of High Resolution Spectroscopy, M. Quack and F. Merkt eds., Wiley Chichester (2011).
[2] H.-R. Dübal, M. Quack, *Chemical Physics Letters,* **1981**, 80, 439; H.-R. Dübal, M. Quack, *Journal of Chemical Physics*, **1984**, 81, 3779.
[3] R. Marquardt, M. Quack, J. Stohner, E. Sutcliffe, *J. Chem. Soc., Faraday Transac.*, **1986**, 82, 1173.
[4] A. S. Pine, J. M. Pliva, Journal of Molecular Spectroscopy, **1988**, 130, 431.
[5] J. Segall, R. N. Zare, H.-R. Dübal, M. Lewerenz, M. Quack, *Journal of Chemical Physics*, **1986**, 86, 634.
[6] A. Amrein, M. Quack, U. Schmitt, *Molecular Physics*, **1987**, 60, 237.
[7] A. Amrein, M. Quack, U. Schmitt, *Journal of Physical Chemistry*, **1988**, 92, 5455.
[8] M. Quack, *Annual Review of Physical Chemistry*, **1990**, 41, 839.
[9] T. Carrington Jr., L. Halonen, M. Quack, *Chemical Physics Letters*, **1987**, 140, 512.
[10] T. K. Ha, M. Lewerenz, R. Marquardt, M. Quack, *Journal of Chemical Physics*, **1990**, 93, 7097.
[11] R. Marquardt, M. Quack Global Analytical Potential Energy Surfaces for High-Resolution Molecular Spectroscopy and Reaction Dynamics, Vol. 1, pp. 511-550 in [1].

Spectroscopic behavior of a water-soluble conjugated polyelectrolyte in biological environment

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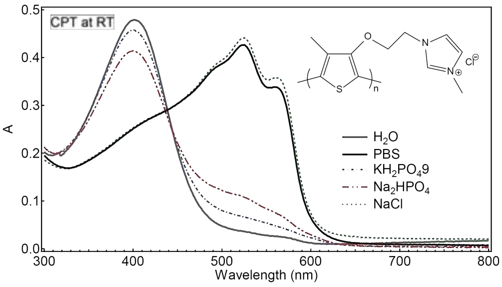
Here we present a spectroscopic study of a conjugated polyelectrolyte, which consists in a polythiophene derivative with cationic side chains that has been used as a biological sensor[1]. This work is an effort to understand the changes of photophysical properties of polyelectrolytes, depending on their conformation, which is usually linked also to the biosensing mechanism. In pure water, the polymer adopts a random-coil conformation at room temperature. On the other hand, when dissolved in an aqueous biological environment (phosphate buffered saline, PBS), the polymer chains are ordering due to the favorable interactions with the buffer ions. These different degrees of ordering in the polymer lead to color changes of the solution, with an important red-shift in the absorption spectrum in PBS. Additionally, the ratio of ordered to random-coiled polymer chains in PBS can be varied by tuning the temperature. Using resonance Raman spectroscopy combined with density functional calculations, it was shown that the ordering is linked to planarization of the polymer backbone. The excited-state behavior of the polymer in different conformations was investigated with femtosecond transient absorption spectroscopy. In the random-coil conformations, triplet state formation occurs, while in the ordered chains, a small fraction of polarons is formed, probably favored by interchain interactions.



[1] H. A. Ho, M. Boissinot, M. G. Bergeron, G. Corbeil, K. Dore, D. Boudreau, M. Leclerc, *Angew. Chem. Int. Ed.* **2002**, *41*, 1548-1551.

Direct Local Solvent Probing by Transient Infrared Reveals the Mechanism of H-Bond Induced Nonradiative Deactivation

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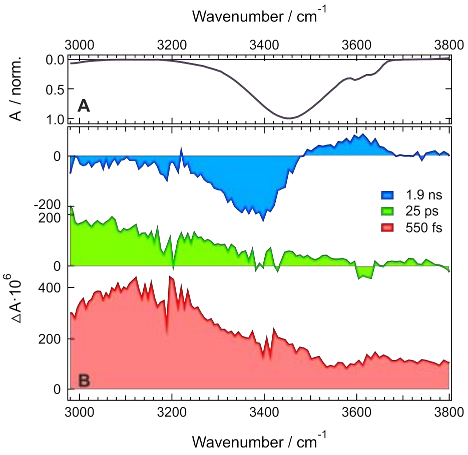
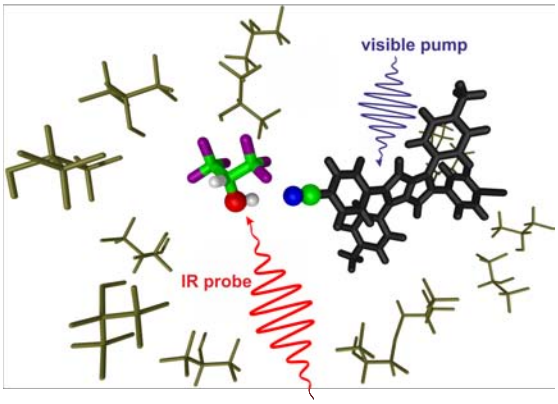
Many organic molecules undergo a substantial quenching of their charge-transfer electronic excited state in protic solvents without occurrence of excited-state proton transfer or proton-coupled electron transfer reactions. The mechanism of this H-Bond Induced Nonradiative Deactivation (HBIND) phenomenon has been elusive for a long time. By using ultrafast transient infrared spectroscopy, we show that it can be unambiguously elucidated by probing the local vibrational modes of solvent molecules coupled to the chromophore. Using such ‘solute-pump/solvent-probe’ approach reveals all relevant molecular steps, such as high initial coupling to the H-bonded solvent molecules, symmetry breaking, H-bond strengthening, and excitation energy dissipation to the solvent molecules. Our data reveal the key role of both solute-solvent H-bond strength and solvent-solvent intermolecular coupling for the efficient HBIND. Polarization-resolved experiments give an additional insight into the structure of a reactive intermediate.





Reaction monitoring using multiple NMR receivers

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Conventional NMR spectrometer require three main components: the superconducting magnet generating the strong magnetic field, the sensor (or probe) acting as send and receive antenna and the spectrometer console hosting the electronics required to perform the NMR experiment. The recently introduced AVANCE NEO console electronics is based on a fully modular and highly integrated RF transmit and receive (so-called transceiver) concept. Hence, each NMR channel consists of a fully autonomous and independent pulse sequence programmer, transmitter and receiver. This opens up new possibilities acquiring multi-receiver NMR experiments[1] since every AVANCE NEO console is inherently multi-receive capable with any available nucleus and probe combination. With the general availability of multi-receive capable NMR spectrometers attractive new combinations of experiments[2] will experience a fast increase in development. Multi-receive experiments are thus expected to substantially contribute in increasing the throughput of NMR spectrometer and hence pushing back one of its strongest limitations, the comparative low sensitivity.

The impact of acquiring several NMR experiments in a single shot is illustrated with an example in the field of reaction monitoring. The protodeboronation reaction of fluorinated aryl boronic acids under basic conditions allows monitoring three suitable isotopes for NMR in the course of the reaction: ^{1}H, ^{19}F and ^{11}B. Simultaneous acquisition schemes with multiple-receivers then allow obtaining kinetic data with a higher temporal resolution as compared to using a conventional acquisition with sequential data collection.

[1] E. Kupce, R. Freeman, B. K. John, *JACS*, **2006**, 128, 9606-9607.
[2] A. Viegas, T. Viennet, T.Y. Yu, F. Schumann, W. Bermel, G. Wagner, M. Etzkorn*J Biomol NMR*, **2016** , 64, 9-15.

Metal centres in EPR Spectroscopy

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Unpaired electrons are the basis of Electron Paramagnetic Resonance (EPR) spectroscopy. Electron pairing is usually energetically favorable and thus only a small fraction of systems contain native paramagnetic centres or can be put into paramagnetic states to exhibit an intrinsic EPR signal. On the other hand, it allows to use EPR spectroscopy in combination with so called site-directed spin labeling (SDSL) under a wide range of conditions.[1]

In this contribution we want to give a brief overview of the use of metal ions in EPR spectroscopy in biological systems and then focus on two examples using Mn^{2+} or Gd^{3+} as spin probes. In the first case we demonstrate, what insights can be obtained from EPR by the substitution of diamagnetic Mg^{2+} to paramagnetic Mn^{2+} in a DnaB helicase.[2] In the second example we want to demonstrate advantages and disadvantages of using high spin Gd^{3+} ions for distance measurements.[3,4]

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[1] G. Jeschke, *Annu Rev Phys Chem.*, **2012**; 63:419-46.
[2] T. Wiegand, D. Lacabanne, K. Keller, R. Cadalbert, L. Lecoq, M. Yulikov, L. Terradot, G. Jeschke, B. Meier, A. Böckmann, *Angew. Chem*., **2017**, 56, 3369 –3373
[3] D. Goldfarb, *Phys. Chem. Chem. Phys.*, **2014**, 16, 9685–9699.
[4] M. Yulikov, *Electron Paramagn. Reson.*, **2015**, 24, 1–31.

High Resolution ^{1}H NMR in Organic Solids at Natural Abundance

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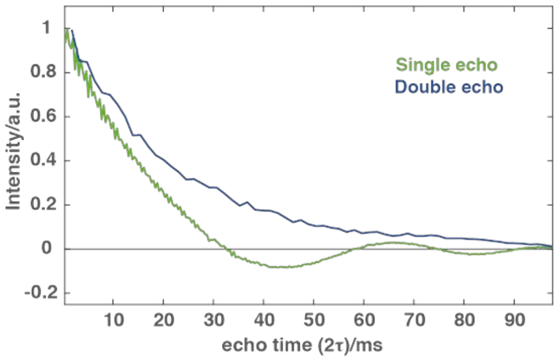
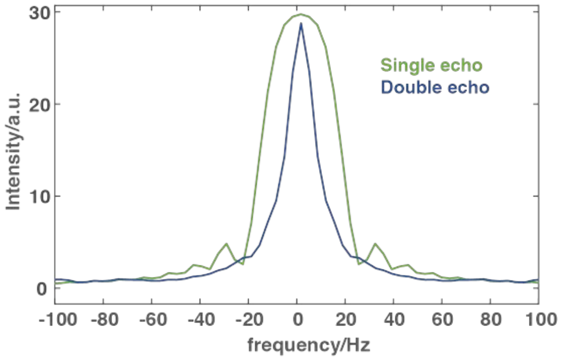
High resolution ^{1}H NMR spectra have transformed molecular chemistry over the last 60 years. However, due to the absence of molecular tumbling, in solid samples proton spectra usually have linewidths of more than 50 ppm, obscuring all chemical information. To obtain high resolution ^{1}H spectra in solids would provide a key tool for the atomic-level characterization of modern materials, especially since NMR does not require long range order.

^{1}H line broadening is primarily due to strong ^{1}H homonuclear dipolar couplings. It is possible to improve the resolution with the application of techniques such as magic angle spinning (MAS)[1] and multi-pulse sequences specifically designed to lead to homonuclear dipolar decoupling. The best results achievable today are obtained using these two techniques simultaneously, in the so-called combined rotation and multi-pulse spectroscopy (CRAMPS) approaches,[2] but linewidths are still on the order of 150 Hz.[3,4] The underlying reasons for this apparent limit on ^{1}H resolution are not understood.

Here we discover one of the limiting factors of resolution: an undecoupled residual anisotropic interaction that leads to a residual splitting. The mechanisms of line broadening were evaluated by measuring transverse dephasing times T'_2, which are indicators of the presence of non-refocusable interactions[5,6]. We have discovered an unexpected oscillating component, present in the spin-echo dephasing curves for BR-24, eDUMBO-1_{22}, LG4 and even WAHUHA. The Fourier transforms of these curves show that the oscillations correspond to an anisotropic splitting of up to 80 Hz. We also show that this residual interaction, which is one of the limiting factors on the lifetime of the decay, can be removed by the application of a double echo. As a result, the dephasing curves have slower decay, characterized by T'_2 of up to 22 ms, which corresponds to a refocused linewidth of 14 Hz.





[1] Andrew, E., Bradbury, A. & Eades, R, *Nature*, **1959**, 183(4678), 1802-1803.
[2] Gerstein, B., Pembleton, R., Wilson, R. & Ryan, L.,*The Journal of Chemical Physics*, **1977**, 66, 361-362.
[3] Halse, M. E. & Emsley, L., *The Journal of Physical Chemistry A* , **2013**, 117, 5280-5290.
[4] Salager, E., Stein, R. S., Steuernagel, S., Lesage, A., Elena, B. & Emsley, L., *Chemical Physics Letters*, **2009**, 469, 336-341.
[5] Lesage, A., Bardet, M. & Emsley, L. *Journal of the American Chemical Society*, **1999**, 121, 10987-10993.
[6] Lesage, A., Duma, L., Sakellariou, D. & Emsley, L., *Journal of the American Chemical Society*, **2001**, 123, 5747-5752.

Detecting structure and conformation of single DNA and RNA molecules by Escape-Time Electrometry

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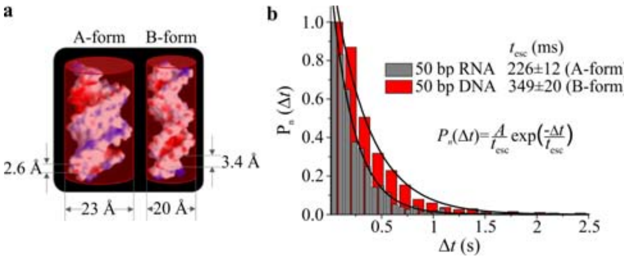
Fundamental functions of biological macromolecules, such as proteins and nucleic acids, in all living organisms strongly depend on the molecules' 3D structures, which are of great scientific interest. However, currently existing methods are bulk measurements, and further require high concentrations. We recently reported a measurement principle – escape-time electrometry (ETe) [1] – that offers a new approach to measuring the effective electrical charge, q_m of a single molecule in solution, in real time. Since the effective charge of a molecule in solution is a strong function of its 3D conformation [2], we have demonstrated the ability to directly link a high precision measurement of electrical charge with the 3D conformation of a charged molecule. The ETe approach exploits the spatial confinement of single molecules in an electrostatic fluidic trap. The trap is based on the spatial modulation of the electrostatic interaction energy created in a topographically-tailored fluidic nanoslit [3]. Measurement of the average escape time of single molecules from a trap of known depth allows us to determine the effective electrical charge of a molecular species with high precision.

We have performed ETe on double-stranded (ds) nucleic acids with identical base sequences, but different helical structures: A-form (dsRNA) and B-form (dsDNA). Modelling these molecules as uniformly-charged cylinders of different dimensions we also determine theoretically expected values for the effective charge, q_c (Fig. a, c). Our measured values of effective charge are in good agreement with the theoretical predictions, and uniquely permit the detection of important structural features of nucleic acids at the level of the single molecule (Fig. b, c).



c

50 bp	q_m (-e)	q_c (-e)
A-form (RNA)	37.7±0.7	34.4±1.7
B-form (DNA)	41.2±0.5	40.2±2.0

Furthermore, we are currently performing measurements on single-stranded (ss) RNA and DNA molecules of effectively identical sequence. In contrast to ssDNA, ssRNA is well known to form stable and varied secondary structures, which are in fact critical to biological function. While our preliminary measurements yield a single escape timescale for ssDNA, interestingly they reveal a spectrum of timescales for the equivalent ssRNA species, indicating a variety of folded states. Our results illustrate that ETe will likely enjoy broad relevance in 3D conformation determination in biology.

[1] F. Ruggeri, F. Zosel, N. Mutter, M. Różycka, M. Wojtas, A. Ożyhar, B. Schuler, and M. Krishnan, *Nature Nanotechnology,* **2017,** advance online publication.
[2] M. Krishnan, *Journal of Chemical Physics*, to appear.
[3] M. Krishnan, N. Mojarad, P. Kukura, and V. Sandoghdar, *Nature,* **2010**, 467, 692-695.

Fluorophore guided RNA modeling

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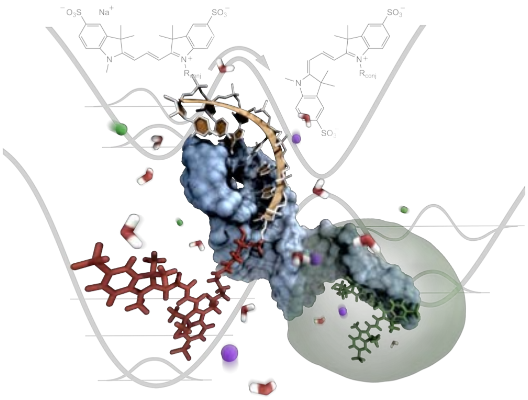
Non-coding RNAs engage in numerous cellular processes at various stages of gene expression. As a spectroscopic ruler [1] single-molecule FRET is a versatile tool to investigate the folding of RNA [2]. Yet, interconversion of transfer efficiencies and absolute distances between a donor and an acceptor fluorophore requires thorough control over both the dyes' photophysics as well as their orientation within the macromolecule [3]. We make use of the photoisomerization propensity of carbocyanines [4] to sense perturbations in their local environment. Changes to the torsional flexibility of the polymethine scaffold are probed by time-resolved fluorescence anisotropy and RNA-induced fluorescence enhancement (RIFE) [5]. The constrained dye mobility due to entrapment on the RNA surface is evaluated by means of all-atom molecular dynamics simulations using the exon and intron binding site (EBS1/IBS1) of a group II intron [6] as a model of an RNA tertiary contact [5]. These atomistic simulations give access to the dye-linker dynamics which are key to defining the volume accessible to the fluorophore in the context of the RNA.



Building on a refined description of the dyes, a set of *de novo* modeled RNA structures is then filtered against experimentally derived distance distributions of one or multiple FRET pairs. Imposing such restraints on different parts of the RNA confines the search space while at the same time pinpointing regions of increased flexibility. We validate this integrative modeling approach by reconstituting the solution structure of the EBS1 hairpin motif *in silico*. After all, the combination of smFRET and molecular modeling will open up new avenues to explore the world of long non-coding RNAs whose three-dimensional fold is yet to be discovered.

[1] Lubert Stryer, Richard. P. Haugland, *Proc. Natl. Acad. Sci. USA*, **1967**, 58, 719-726.
[2] Richard Börner, Danny Kowerko, Helena Guiset-Miserachs, Michelle F. Schaffer, Roland K.O. Sigel, *Coord. Chem. Rev.,* **2016**, 327-328, 123-142.
[3] Benjamin Schuler, Everett A. Lipman, Peter J. Steinbach, Michael Kumke, William A. Eaton, *Proc. Natl. Acad. Sci.*, **2005**, 102, 2754-2759.
[4] Marcia Levitus, Suman Ranjit, *Q. Rev. Biophys*, **2011**, 44, 123-151.
[5] Fabio D. Steffen, Roland K.O. Sigel, Richard Börner, *Phys. Chem. Chem. Phys.*, **2016**, 18, 29045-29055.
[6] Danny Kowerko, Sebastian L.B. König, Miriam Skilandat, Daniela Kruschel, Mélodie C.A.S. Hadzic, Lucia Cardo, Roland K.O. Sigel, *Proc. Natl. Acad. Sci.,* **2015**, 112, 3403-3408.

A Proof-of-Concept for a Photoinitiated Single-Molecule Circuit

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The ‘holy-grail’ of molecular electronics is the ability to develop fully-integrated molecular circuitry, and by extension, single-molecule circuitry.[1,2] The design principles for a molecular wire have already been well established,[3] but a molecular circuit represents a far greater challenge. A molecular wire must have charge transfer between two stations/electrodes, whereas a molecular circuit must have charge travel unidirectionally in a complete circuit and recombine at the origin. A molecular circuit also requires a controllable external field to initiate the flow of charge.

This presentation shall cover the design principles and spectroscopic characterisation of an electron donor-acceptor-acceptor (D-A-A) triad as a proof-of-concept photoinitiated molecular circuit (**Figure 1**), with a conservatively estimated quantum efficiency of 7.8%. This is achieved through three sequential charge-transfer processes, and the exploitation of geometric rearrangement in the excited state.

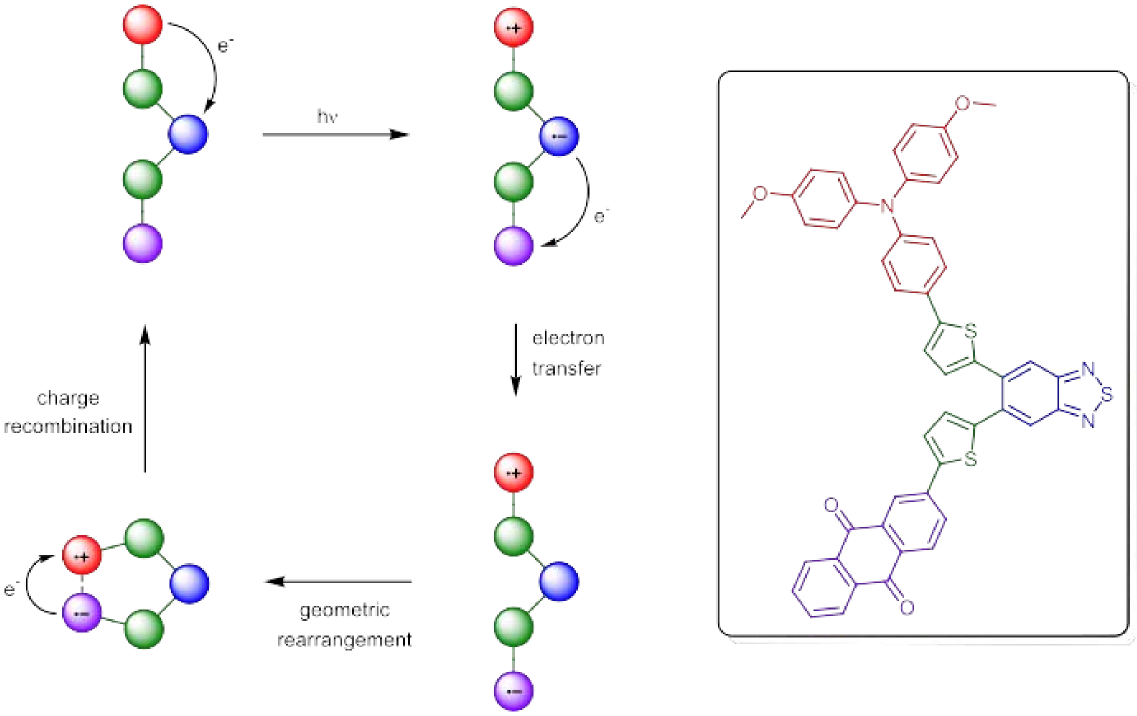

Figure 1. Proposed mechanism for the photoinitiated molecular circuit. Red = Donor, Blue = Acceptor 1, Purple = Acceptor 2, Green = Bridge.

[1] Sriharsha V. Aradhya, Latha Venkataraman, *Nature Nanotechnology*, **2013**, 8, 399-410
[2] Timothy A. Su, Madhav Neupane, Michasel L. Steigerwald, Latha Venkataraman, Colin Nuckolls, *Natrue Review Materials*, **2016**, 1, 1-15
[3] Annie Butler Ricks, Kristen E. Brown, Matthias Wenninger, Steven D. Karlen, Yuri A. Berlin, Dick T. Co, Michael R. Wasielewski, *Journal of the American Chemical Society*, **2012**, 134, 4581-4588