# Doctoral School of Chemistry

## Panel A

### Retreat 2021: Stift Seitenstetten

## Contents

# 1   General information

Google map of Seitenstetten



Check-In and Check-Out

The check-in will be on Wednesday at 10:45 - 11:45 am.
The check-out is on Friday, 8:00 - 9:00 am.
The luggage can be stored in the conference room until the departure of the bus.

Breakfast, Lunch, Dinner

Breakfast, lunch and dinner will be served at the "Großer Gästespeisesaal"
at the basement floor regardless of the location of your rooms.

## Erdgeschoss und Untergeschoss

Untergeschoss: Großer Gästespeisesaal

Untergeschoss: Theatersaal

Abgang Untergeschoss

Gästezimmer 1-5

Aufgang 1. und 2. OG

Gästestüberl

Raum Scholastika

Raum Udiskalk

Zimmer 6

Raum Benediktus

Abteistiege

**WC**

Gästebüro Rezeption

**i**

Klosterladen

Stiftsportal
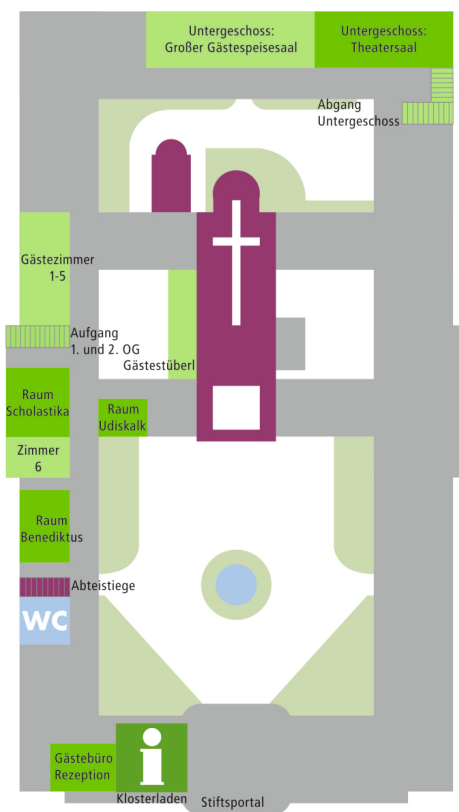
Gästebereich
Seminarräume

## 1. Obergeschoss

Neue Galerie

Gäste-stiege

Kammer-diener-zimmer

Matura-saal

Aufgang Galerie

**WC**

Stiftsgalerie

Promulgations-saal
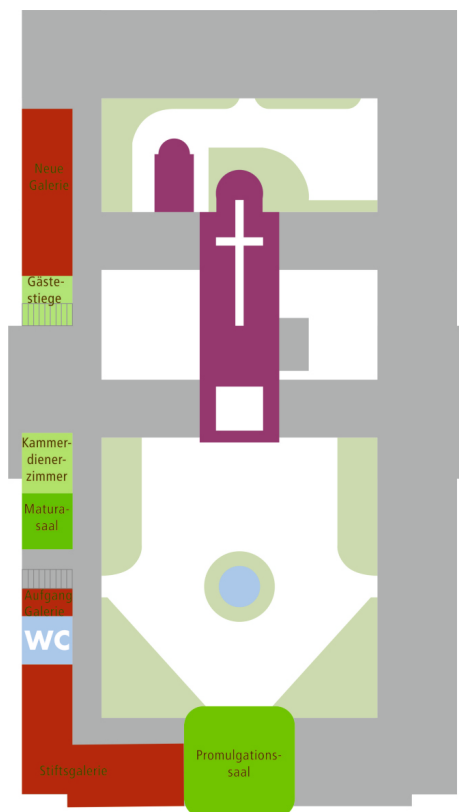
mit Eintrittskarte besichtigbar
Stiftskirche und Ritterkapelle

## 2. Obergeschoss

Haus Gennesaret Gästezimmer

↓   ↑

Zugang Zimmer 201-212

Galerie
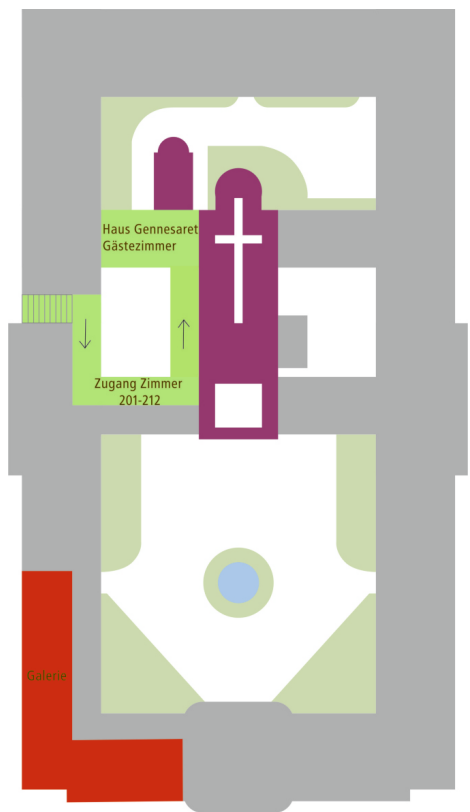
## WICHTIGE TELEFONNUMMERN

Rettung St. Peter: 059 144-51800
Polizei St. Peter: 059 133  3112-100
Ärzte Notdienst: 141

Gästebüro: 07477 42300-223
Gastmeister: 07477 42300-232
Klosterladen: 07477 42300-277

Tischreservierungen Stiftsmeierhof:
07477 43070

## ÖFFNUNGSZEITEN

**Gästebüro**
Mo - Fr 08.00-12.00 Uhr
        13.00-16.00 Uhr

**Klosterladen**
täglich
von 09.00 -12.00 Uhr
und 13.00 -17.00 Uhr
von Ostermontag bis Ende Oktober geöffnet

Stift

Spielplatz

Meierhof

Glashaus

Hofgarten

Pflanzenverkauf
Selbstbedienung

Linz
(ca. 50 km)
Abfahrt Enns/Steyr
Abfahrt Haag
Abfahrt Oed
Abfahrt Amstetten-West
A1
Wien
(ca. 150 km)
Bahnhof St. Valentin
Haltestelle St. Peter/Seitenstetten
Bahnhof Amstetten
Westbahn-strecke
Steyr
Stift Seitenstetten
Basilika Sonntagberg
Waidhofen/Y.
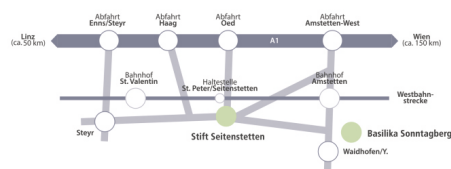
GARTEN SOMMER NIEDERÖSTERREICH

top Niederösterreich Ausflugsziele

Most Straße

KLÖSTERREICH

Stift
Seitenstetten

## KOMMT UND SEHT !
Besucherinformation

| Wednesday, November 17th | |
|---|---|
| 8:00 | Meeting at Boltzmanngasse |
| 8:00 - 8:30 | Checking of 2G rule |
| 8:30 - 10:45 | Bus transport to Seitenstetten |
| 10:45 - 11:45 | Check - in |
| 11:45 - 13:00 | Lunch |
| 13:00 - 13:20 | Opening remarks (Ellen Backus) |
| 13:20 - 14:20 | Speed dating (1,2,3) |
| 14:20 - 14:40 | Coffee break |
| 14:40 - 15:40 | Speed dating (4,5,6) |
| 15:40 - 16:00 | Coffee break |
| 16:00 - 17:30 | Digital talk Marcel van der Heiden |
| 17:30 - 18:00 | Upload of presentations |
| 18:00 - 19:00 | Dinner |
| 19:00 - 22:00 | Poster session |

| Thursday, November 18th | |
|---|---|
| 8:30 - 9:30 | Karin Föttinger |
| 9:30 - 9:50 | Wisnu Sudjarwo |
| 9:50 - 10:10 | Mirela Encheva |
| 10:10 - 10:40 | Coffee break |
| 10:40 - 11:40 | Markus Valtiner |
| 11:40 - 12:00 | Birgit Bräuer |
| 12:00 - 13:00 | Lunch |
| 13:00 - 14:00 | Maren Podewitz |
| 14:00 - 14:20 | Ludwig Schwiedrzik |
| 14:20 - 14:40 | Martin Werner |
| 14:40 - 15:00 | Coffee break |
| 15:00 - 18:00 | Hiking |
| 18:00 - 19:00 | Dinner |
| 19:00 - 22:00 | Board games |

| Friday, November 19th | |
|---|---|
| 8:00 - 9:00 | Check-out |
| 9:00 - 10:00 | Philipp Marquetand |
| 10:00 - 10:20 | Maria Waldl |
| 10:20 - 10:40 | Claudia Iriate Mesa |
| 10:40 - 11:10 | Coffee break |
| 11:10 - 12:30 | Digital talk Boehringer-Ingelheim |
| 12:30 - 13:30 | Lunch |
| 13:30 - 13:50 | Veronika Wank |
| 13:50 - 14:10 | Kathrin Weiland |
| 14:10 - 14:30 | Best poster and best talk awards |
| 14:30 - 15:00 | Closure remarks |
| 15:00 | Departure |

# 2   Invited speakers

16:00 - 17:30    Marcel van der Heyden
*"Research Integrity"*

8:30 - 9:30      Karin Föttinger
*"Operando studies of metal and oxide catalysts: Mechanistic insights and structural dynamics"*

10:40 - 11:40    Markus Valtiner
*"Complementing theory and experiment: Examples and challanges from (electrochemical) interface science"*

13:00 - 14:00    Maren Podewitz
*"Predicting reactivity and selectivity - towards in-silico design of catalysts"*

9:00 - 10:00    Philipp Marquetand
*"Excited-state machine learning molecular dynamics"*

11:10 - 12:30    Julian Fuchs & Lorenz Herdeis
*"Boehringer-Ingelheim"*

# OPERANDO STUDIES OF METAL AND OXIDE CATALYSTS: MECHANISTIC INSIGHTS AND SRUCTURAL DYNAMICS
## Föttinger K.[1]

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A fundamental understanding of the properties and composition of catalysts under working conditions and of the chemical processes on catalyst surfaces is important for a rational improvement. The aim of my work is obtaining fundamental insights into the catalysis occurring at the molecular level on oxides and metal nanoparticles by applying operando spectroscopic techniques. As key methods, we combine reaction kinetics, vibrational and X-ray based spectroscopy (X-ray absorption and photoelectron spectroscopy).

In this contribution, I will discuss our studies on bimetallic Au and Pd catalysts supported on active oxides and their reactivity in methanol and ethanol conversions. Pd-alloys have been applied for $H_2$ generation by methanol steam reforming, a promising compound to chemically store $H_2$. The major challenges in the process are selectivity, avoiding production of the unwanted byproduct CO, and stability. A detailed understanding of the chemical processes occurring at the surface of ZnO and $Ga_2O_3$ supported Pd nanoparticles was obtained, and the key factors determining selectivity and stability were identified. Furthermore, the clean-up of $H_2$ by the preferential oxidation of CO impurities has been studied on $Co_3O_4$ materials, again focusing on structure, surface chemistry and oxidation states under reactions conditions. Au bimetallics have attracted much interest for selective oxidation reactions, as they offer a wide range of possibilities to tune the catalytic properties by the choice of the second metal component. We have investigated the selective oxidation of ethanol on $AuAg/TiO_2$ by our operando approach to understand the role of each component in the mechanism, the origin of synergistic effects, and address questions such as segregation, alloy formation, (surface) oxide formation, etc. under reaction conditions.

$$E_b = h\upsilon - E_{kin} - \phi$$

**X-rays** **XPS** **GC, MS**

**IR** $\ln I_0/I$ **EXAFS** $\ln I_0/I$
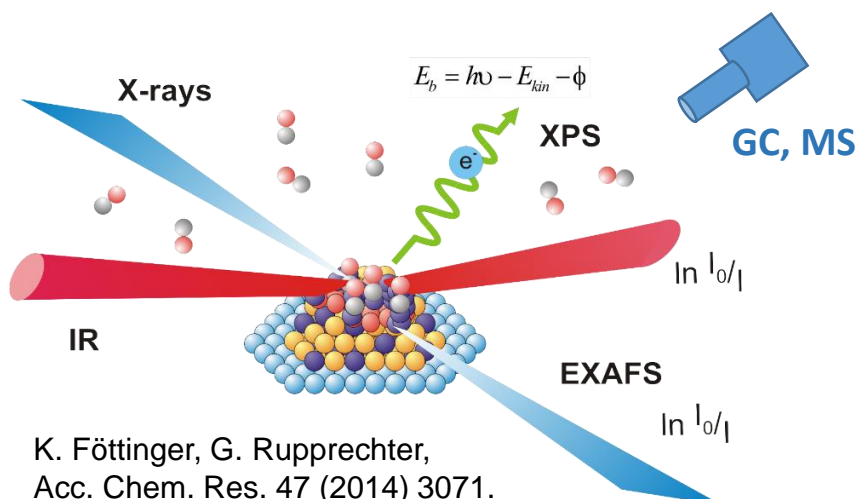
K. Föttinger, G. Rupprechter,
Acc. Chem. Res. 47 (2014) 3071.

# COMPLEMENTING THEORY AND EXPERIMENT: EXAMPLES AND CHALLANGES FROM (ELECTROCHEMICAL) INTERFACE SCIENCE

## VALTINER M.[1]

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*Abstract:*

In this presentation I will show selected examples of our work on highly resolved experimental studies of solid/liquid interfaces that are complemented by theory, and will show experimental data that will still require theoretical input for extracting molecular level information.

Examples include, a combined experimental−simulation approach to directly measure and quantify the sequence dependence and additivity of hydrophobic interactions (HIs) in peptide systems at the single-molecule scale.[1] We combine dynamic single-molecule force spectroscopy on nonequilibrium, molecular dynamics (MD) simulations of the same systems. Specifically, we mutate a flexible $(GS)_5$ peptide scaffold with increasing numbers of hydrophobic leucine monomers and measure the peptides' desorption from hydrophobic self-assembled monolayer surfaces. Based on the analysis of nonequilibrium work-trajectories, we measure an interaction free energy that scales linearly with 3.0−3.4 $k_B$T per leucine. In good agreement, simulations indicate a similar trend with 2.1 $k_B$T per leucine, while also providing a detailed molecular view into HIs.

A second example [2] will focus on thestudy of the dissolution of zinc oxide single crystals with (0001) and (10$\bar{1}$0) orientations. A significant influence of the UV radiation and the pH of the electrolyte was observed. The observed dissolution behavior agrees well with the surface chemistry and stabilization mechanism of ZnO surfaces. In particular, polar ZnO(0001) shows ideal stability at low potentials and under hydrogen evolution conditions. Whereas ZnO(10$\bar{1}$0) sustains higher dissolution rates, while it is inactive for water splitting. These results will be discussed in terms of ab initio surface phase diagrams.

I will end with a few examples of highly resolved experimental data, where we lack complementing theoretical approaches.

*References:*

[1] P. Stock et al. in ACS Nano 2017, 11, 2586−2597

[2] D. Dworschak et al. in ACS Appl. Mater. Interfaces 2020, 12, 51530−51536

# PREDICTING REACTIVITY AND SELECTIVITY – TOWARDS IN-SILICO DESIGN OF CATALYSTS

## Podewitz M.[1]

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### Abstract:

Quantum chemistry has emerged as a toolbox to describe chemical reactions by explicitly accounting for changes in the valence electrons upon bond formation and cleavage. Such investigations not only yield a reaction profile but also provide atomistic insights and information about intermediates and transition states that are not directly accessible in experiment. The reliability of such investigations and the potential to predict reactivity and selectivity crucially depends on the accuracy of the chemical model and computational methodology.

However, current computational studies base their investigations on available x-ray crystal data, considering only one specific conformation and describing only implicit solvation. In contrast, most chemical reactions take place in the liquid phase. Relevant conformations may differ from the solid state and specific solute-solvent interactions might impact reactivity. This may particularly be the case for highly flexible transition-metal catalysts that can adjust their geometries to perturbations by the environment. Yet, a systematic conformational search and inclusion of explicit solute-solvent interactions at low computational cost are not performed on a routinely basis. In this talk, we will present multiscale strategies to tackle conformational diversity and explicit solvation to arrive at an improved description of reactivity and selectivity as a prerequisite for in-silico design.

As different metals and different ligand types require different treatment, we developed tailored multilevel protocols to assess the conformational diversity in Mo-based olefin metathesis catalysts [1] and in supramolecular Cu-based C-N coupling catalysts. These strategies proved to be crucial for a reliable prediction of the reaction free energy profiles and the selectivity. [1] In addition, we will present a physics-based approach to quantum chemical microsolvation, where the number and position of explicitly treated solvent molecules are rigorously defined. [2]

### References:

[1] M. Podewitz, S. Sen, M. R. Buchmeiser, *Organometallics*, **40** (2021), 2478–2488.

[2] M. Steiner, T. Holzknecht, M. Schauperl, M. Podewitz, *Molecules* **26** (2021), 1793.

# EXCITED-STATE MACHINE LEARNING MOLECULAR DYNAMICS

## Marquetand P.[1,2,3]

[1] Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Str. 17, 1090 Vienna, Austria

[2] Research Platform on Accelerating Photoreaction Discovery, University of Vienna, Währinger Str. 17, 1090 Vienna, Austria

[3] Data Science @ Uni Vienna, University of Vienna, Währinger Str. 29, 1090 Vienna,

*E-mail*: philipp.marquetand@univie.ac.at

*Abstract:*

Deep learning models are presented to advance the field of photochemistry by learning all important properties—multiple energies, forces, and different couplings [1,2]. We use different variants of deep neural networks for photodynamics simulations up to nanosecond time scales [3,4]. Furthermore, transition dipole moments can be learned for the prediction of UV absorption spectra [5]. Also kernel-ridge regression models can be extended for multiple outputs in order to treat excited states [6]. The different machine learning models are combined with the molecular dynamics program SHARC (surface hopping including arbitrary couplings) [7] for efficient nonadiabatic excited-state simulations of polyatomic molecules.

*References:*

[1] J. Westermayr, P. Marquetand, *Chem. Rev.* **2021**, 121, 9873–9926.

[2] J. Westermayr, P. Marquetand*, Mach. Learn.: Sci. Technol.* **2020**, 1, 043001.

[3] J. Westermayr, M. Gastegger, M. Menger, S. Mai, L. González, P. Marquetand, *Chem. Sci.* **2019**,10, 8100–8107.

[4] J. Westermayr, M. Gastegger, P. Marquetand, *J. Phys. Chem. Lett.* **2020**, 11, 3828-3834.

[5] J. Westermayr, P. Marquetand, *J. Chem. Phys.* **2020**, 153, 154112.

[6] J. Westermayr, F. A. Faber, A. S. Christensen, O. A. von Lilienfeld, P. Marquetand, *Mach. Learn.: Sci. Technol.* **2020**, 1, 025009.

[7] S. Mai, P. Marquetand, L. González, *WIREs Comput. Mol. Sci.* **2018**, 8, e1370.

# 3   Student talks

Please prepare your presentation that it will take approximately 12 min and leave 8 min for discussion and short feedback. The chairs of your session will take time and start to play Waltz music if you extend your time slot.

Please make sure that your slides are correctly displayed on screen using our computer equipment at Wednesday, November 17th, 5:30 - 6:00 pm. You will receive written feedback from several PIs via email after the conference.

| Thursday, November 18th | | Feedback |
|---|---|---|
| 9:30 - 9:50 | Wisnu Sudjarwo | Woodward, Mezger-Backus, Konrat, Mautner |
| 9:50 - 10:10 | Mirela Encheva | Mautner, Lieberzeit, Zagrovic, Konrat |
| 11:40 - 12:00 | Birgit Bräuer | Woodward, Mezger-Backus, Hofacker, Marquetand |
| 14:00 - 14:20 | Ludwig Schwiedrzik | Schröder, Gonzalez, Flamm, Marquetand |
| 14:20 - 14:40 | Martin Werner | Flandorfer, Woodward, Mezger-Backus, Hofacker, Mautner |

| Friday, November 19th | | Feedback |
|---|---|---|
| 10:00 - 10:20 | Maria Waldl | Zagrovic, Gonzalez, Flamm, Marquetand |
| 10:20 - 10:40 | Claudia Iriate Mesa | Schröder, Richter, Flandorfer, Hofacker |
| 13:30 - 13:50 | Veronika Wank | Schröder, Richter, Konrat, Gonzalez |
| 13:50 - 14:10 | Kathrin Weiland | Richter, Flandorfer, Hofacker, Zagrovic |

# THE IMPLEMENTATION OF QCM-BASED SENSOR COMBINED WITH PLASTIC NANO-BODIES FOR THE RECEPTOR OF IN SITU ASSAY FOR HUMAN SERUM ALBUMIN DETECTION

## Wisnu Arfian A. Sudjarwo[1], Peter A. Lieberzeit[1]

[1] University of Vienna, Faculty for Chemistry, Department of Physical Chemistry
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*Abstract:*

The promising potential of synthesizing Molecularly Imprinted Polymers (MIPs) using Solid Phase Imprinting was first demonstrated by the group of S. Piletsky[1], which described plastic nano-bodies for small and complex molecules. Herein, we adapted and optimized the method to generate MIP nanoparticles for Human Serum Albumin (HSA) recognition combined with Quartz Crystal microbalance (QCM) assay. Commencing with anchoring HSA on silica surface, polymerization took place in the presence of HSA to define the cavity which corresponds to the shape and size of the template after removing it from the matrix. We fabricated organic polymer nano-MIPs with diameter of 53±19 nm, core-shell silica nano-MIPs with diameter of 150-200 nm and silica nano-MIPs with diameter of 250-300 nm according to Dynamic Light Scattering (DLS) measurements and confirmed using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The corresponding nano-NIPs as a reference have dimensions of 191±96 nm. Fluorescence assays lead to Stern-Volmer plots revealing selective binding to HSA with selectivity factors of 1.9-2.7 compared to lysozyme, 1.8-2.1 for trypsin and 4.1 for pepsin. One can confirm both affinities and selectivities using QCM measurements: MIPs are 10 times more sensitive than nano-NIPs, whilst 1.7-2.7 times more selective for HSA toward lysozyme, and 30 times more sensitive and even bigger for HSA toward pepsin. This study thus demonstrates a feasible method to develop assay formats for protein recognition and to overcome the limitations of natural antibodies, particularly in terms of cost and stability.

Keywords: MIP, nanoparticle, HSA recognition, QCM

*References:*

[1] Canfarotta F, Poma A, Guerreiro A, Piletsky S (2016) Solid-phase synthesis of molecularly imprinted nanoparticles. Nat Protoc 11:443–455. https://doi.org/10.1038/nprot.2016.030

# WATER INDUCED POLYMER REORIENTATION AT A POLYSTYRENE/POLYACRYLIC ACID SURFACE

**Encheva M.[1], Li X.[2], Berger R.[2], Backus E.H.G[1]**

[1] Department of Physical Chemistry, Faculty of Chemistry, University of Vienna, Vienna, Austria
[2] Department of Physics at Interfaces, Max Planck Institute for Polymer Research, Mainz, Germany

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## Abstract:

Certain polymer surfaces undergo an adaptation process after being exposed to liquids due to side chains movements. This reorientation often leads to a preferential exposure of certain polymer groups on the liquid interface, modifying consequently the observed features in surface experiments such as contact angle measurements. This behavior is even more accentuated in block copolymers, where the elements that are most compatible with the liquid are reoriented in order to be in contact with the liquid phase.

In this project, we focus on the reorientation of a copolymer made out of polystyrene and polyacrylic acid (PS/PAA) after water exposure. Previous studies [1] involving advancing and receding contact angle measurements suggest a possible reorientation of the different copolymer segments after being in contact with water. Our objective is to corroborate such reorientation by means of sum-frequency generation spectroscopy (SFG).

In our experiments, we evaluated and compared the vibrational SFG spectra of the samples before and after being in contact with water, to determine whether this exposure resulted in a reorientation of the copolymer. In addition, the reversibility of the reorientation by sample annealing was also tested.

Due to the intensity change observed in a marker band of the PS polymer in the vibrational SFG spectrum, we were able to confirm a reorientation of the copolymer. Furthermore, we proved that the intensity of this band can be recovered after annealing the samples, proving the reversibility of the process.

## References:

[1] X. Li, S. Silge, A. Saal, G. Kircher, K. Koynov, R. Berger, H.-J. Butt, *Langmuir.* **2021** *37*, 1571–1577.

# Surface studies of *Escherichia coli*-imprinted polymers using Confocal Raman Microscopy and Partial Least Squares Discriminant Analysis

**Bräuer B.**[1], Thier F.[1], Baurecht D.[1], Lieberzeit P.[1]

[1] Department of Physical Chemistry, University of Vienna, Vienna, Austria

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*Abstract:*

Previously established detection and quantification methods for *E.coli* - a food and water hygiene indicator - include flow cytometry[1], polymerase chain reaction[2] and enzyme-linked immunosorbent assay[3]. These standard techniques require trained personnel, bacteria growth and/or enrichment, or offer unsatisfactory sensitivity or selectivity[4]. To circumvent these challenges, sensors aiming at direct *E.coli* detection in water have been developed based on molecularly imprinted polymers (MIPs) as receptor layers on Quartz Crystal Microbalances. Characterizing MIP surfaces is crucial to ensure reproducibility of the polymer synthesis and confirm imprinting success.

Conventional methods such as Atomic Force Microscopy (AFM) provide topographical information on the MIP surface, but give no information on its chemical composition. Thus, this project aims at utilizing Confocal Raman Microscopy as a method to characterize the surfaces of *E.coli*-imprinted polymers synthesized via a covalent stamp-imprinting approach. Overlaying Raman Image Scans (visualizing the spatial intensity distribution of the aliphatic CH-stretching signal at 2908 cm$^{-1}$) with the corresponding light microscopy images constitutes a straightforward technique to differentiate *E.coli*-imprints, bacteria and polymer surface from each other. AFM imaging confirms the accuracy of this correlation. Furthermore, we were able to demonstrate that Confocal Raman Microscopy in combination with Partial Least Squares Discriminant Analysis (PLS-DA) serves to distinguish different bacteria strains on *E.coli*-imprinted polymers based on their respective Raman spectra. With PLS-DA, this is possible despite their spectral similarity and intense Raman signals originating from the polymers. This provides the basis for establishing a Raman-based technique to assess selectivity of the *E.coli*-imprinted polymers towards the target analyte, when it is directly competing for binding to the MIP surface with other bacteria strains. Additionally, using PLS-DA, Raman spectra of imprints of two different bacteria strains, *E.coli* and *B.cereus,* were successfully differentiated, providing first hints towards differences in surface chemistry between imprints of different species and the surrounding polymer.

*References:*

[1] Kempf, V. A. J.; Mändle, T.; Schumacher, U.; Schäfer, A.; Autenrieth, I. B. International Journal of Medical Microbiology **2005**, 295 (1).

[2] Belgrader, P.; Benett, W.; Hadley, D.; Richards, J.; Stratton, P.; Mariella, R.; Milanovich, F. Science. **1999**.

[3] Dylla, B. L.; Vetter, E. A.; Hughes, J. G.; Cockerill, F. R. Journal of Clinical Microbiology. **1995**, 222-224

[4] Zhou, H.; Yang, D.; Ivleva, N. P.; Mircescu, N. E.; Niessner, R.; Haisch, C., Analytical Chemistry **2014**, 86 (3).

# STRETCH TO GET ACTIVE: REDOX ISOMERISM AND JAHN-TELLER EFFECTS IN A MANGANESE-OXO WATER OXIDATION CATALYST
## Schwiedrzik L.[1]

[1] Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Straße 17, 1090 Vienna, Austria.

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## *Abstract:*

In nature, photosystem II catalyzes water splitting as part of photosynthesis to fuel cell growth and produce the oxygen all aerobic life depends on. Within photosystem II, the water oxidation half-reaction is catalyzed by the oxygen-evolving complex (OEC), a highly efficient $Mn_4CaO_x$ cluster that has inspired attempts to develop synthetic catalysts of similar structure.[1] We propose a catalytic cycle for the highly active synthetic water oxidation catalyst (WOC) $[Mn_4V_4O_{17}(OAc)_3]^{3-}$ (**1**),[2] a model system for the OEC. Comparison among multiple pathways shows that the pre-catalyst **1** is activated by oxidation and ligand exchange;[3] water oxidation then proceeds through a series of proton-coupled electron transfer steps, with a predicted thermodynamic overpotential of 0.71 V.[4] In-depth investigations of the ligand exchange, O-O bond formation, and $O_2$ evolution steps reveals the highly dynamic interplay between redox isomerism and Jahn-Teller effects in the catalytic cycle: both serve to enhance catalytic reactivity by redistributing electrons between mixed-valence metal centers and weakening key bonds through Jahn-Teller distortions, introducing flexibility to the otherwise-rigid cubane core of **1**. These results are of general importance both for understanding water oxidation on molecular catalysts as well as advancing the design of Mn-containing homogeneous and heterogeneous WOCs.

## *References:*

[1] Lubitz, W.; Reijerse, E. J.; Messinger, J. Solar Water-Splitting into H2 and O2: Design Principles of Photosystem II and Hydrogenases. *Energy Environ. Sci.* **2008**, 1 (1), 15–31. https://doi.org/10.1039/B808792J

[2] Schwarz, B.; Forster, J.; Goetz, M. K.; Yücel, D.; Berger, C.; Jacob, T.; Streb, C. Visible-Light-Driven Water Oxidation by a Molecular Manganese Vanadium Oxide Cluster. *Angew. Chem. Int. Ed.* **2016**, 55 (21), 6329–6333. https://doi.org/10.1002/anie.201601799

[3] Cárdenas, G.; Trentin, I.; Schwiedrzik, L.; Hernández-Castillo, D.; Lowe, G. A.; Kund, J.; Kranz, C.; Klingler, S.; Stach, R.; Mizaikoff, B.; Marquetand, P.; Nogueira, J. J.; Streb, C.; González, L. Activation by Oxidation and Ligand Exchange in a Molecular Manganese Vanadium Oxide Water Oxidation Catalyst. *Chem. Sci.* **2021**. https://doi.org/10.1039/D1SC03239A

[4] Schwiedrzik, L.; Brieskorn, V.; González, L. Flexibility Enhances Reactivity in a Bioinspired Mn4O4 Cubane Water Oxidation Catalyst: Interplay between Redox Isomerism and Jahn-Teller Effects. *ACS Catal.* **2021**, in press.

# AFM Investigations on Sub-Structures of Surface-Imprinted Polymers

**Werner M.**[1], **Glück M.S.**[1], **Lieberzeit P.A.**[1]

[1] University of Vienna, Faculty for Chemistry, Department of Physical Chemistry, Währingerstraße 42, 1090 Vienna, Austria

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*Abstract:*

Fabrication of surface-imprinted polymers (SIPs), as a sub-discipline of molecular imprinting, follows different strategies [1]. While stamp imprinting is widely used to generate polymer thin films as recognition layers for chemical sensing [2-3], Pickering emulsion polymerization can be used to generate SIP on polymer beads [4]. Investigation on lithographic differences and presence of deposited biomolecules on SIP surfaces are of interest, as both are known to influence cell adhesion properties [5-6].

This study utilizes atomic force microscopy (AFM) to map structural sub-components within surface imprints of *E. coli* bacteria cells, synthesized via stamp imprinting or Pickering emulsion polymerization in poly(styrene-co-divinylbenzene). Additionally, differences in adhesion properties on SIP layers were mapped with functionalized AFM-tips using Peak Force Quantitative Nano Mechanics (PF-QNM).

Investigations on SIP thin-film revealed structures that resemble the negative pattern of flagella or pili within the imprints, which indicates that the method is feasible to pattern cell sub-structures to the nanometer scale. While the imprints on thin films reveal low surface roughness at $R_q$ 3.3 nm $\pm$ 1.0 nm, the imprints formed during Pickering emulsion polymerization show $R_q$ 6.1 nm $\pm$ 1.6nm, i.e. higher surface roughness. This results from globular nano-structures accumulated within the imprints. One can also observe such structures on *E. coli* cells after Pickering emulsion polymerization. PF-QNM reveales differences in adhesion properties between imprints and surrounding polymer on SIPs synthesized via Pickering emulsion polymerization. In contrast, stamp imprinting in thin films does not lead to such differences. This indicates that the observed globular nano-structures are biomolecule residues on the surface.

Hence, the two surface imprinting approaches result in imprints with fundamentally different properties: while stamp imprinting leads to low surface roughness within the cavities, Pickering emulsion polymerization resulted in imprints that contain substantial amount of biomolecule residues.

*References:*

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# MODELING THE KINETICS OF RNA-RNA INTERACTION FORMATION

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*Abstract:*

Interactions between RNAs are an essential mechanism in gene regulation. State-of-the-art computational genome-wide screens predict targets of regulatory RNAs based on thermodynamic stability but largely neglect kinetic effects. To overcome this limitation, we propose novel models of RNA-RNA interaction dynamics. On this basis we can improve our understanding of general principles that govern RNA-RNA interaction formation and improve target prediction tools.

While the dynamics of secondary structure formation of single RNAs have been successfully modeled using transition systems between conformations, analogous approaches for RNA-RNA interaction quickly lead to infeasibly large systems. Therefore, we propose reducing the interaction system to the direct trajectories (shortest paths) from possible first contacts to full hybridization. This key idea enables studying general principles and relevant features of the interaction formation as well as model details; e.g. the relative speed of intra- and intermolecular folding. Specifically, we isolate kinetic effects by comparing experimentally confirmed interactions from Salmonella and E. coli to a randomized background with similar thermodynamic properties. These experiments show that kinetics often look remarkably different depending on the site of the initial contact. Moreover, they indicate that native interactions are kinetically favored, which can be exploited to filter target predictions.

Due to the design of our RNA kinetics model, features like energy barriers can be computed efficiently. This enables refining genome-wide target predictions through kinetic criteria. Beyond these immediate practical improvements, we shed light on general principles like the long-debated influence of the accessibility of the initial contact site.

# FUNCTIONAL MESOPOROUS SILICA NANOPARTICLES FOR THE IMPROVED ORAL DELIVERY OF INSULIN

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Despite more than a century of research to achieve oral delivery insulin, the current clinical reality remains unchanged in terms of therapeutic administration, due to the challenge of overcoming gastrointestinal barriers.[1] It has been recently reported by our group that with the use of dendritic mesoporous silica nanoparticles (DMSNs) together with a protein-based excipient, succinylated $\beta$-lactoglobulin (BL), pH-responsive tablets could prevent the premature gastric release and degradation of encapsulated insulin.[2] However, there are still open issues related to colloidal stability, control of release rate, permeation enhancement and mucoadhesion, which need to be addressed before reaching in vivo tests. To this aim, we focus our studies on the examination of the influence of surface chemistry/charge and colloidal stability of DMSNs on the loading efficiency and insulin release performances. For this, DMSNs (130 nm; pore size: 7.0 nm) were functionalized with polyethylene glycol (PEG, 2 kDa) and a phosphonate-silane, trihydroxysilylpropyl methylphosphonate (THMP), introduced through different post-grafting strategies.[3,4] The functionalized DMSNs (DMSNs-PEG and DMSNs-$PO_3$) exhibited an enhanced colloidal stability in aqueous and saline media (PBS) over a wide pH range. Different formulations for oral administration were prepared by mixing BL with pure and functionalized DMSNs containing insulin (20 % w/w) and preliminary release tests were performed with simulated body fluids.[2] Compared to a DMSNs-free formulation, encapsulated insulin was even more protected and the release was lowered down to acceptable threshold (less than 10 %) at pH 1.2, while at pH 7.4 controlled release could be reached for 24 h. The analysis of the released insulin confirmed that drug confinement into the pores of the hybrid DMSNs did not affect the peptide structure. The ability of DMSNs to be internalized by intestinal cells was tested using non transformed human epithelial colon cells (HCEC) through live cell imaging and benchmarking the biological activity of insulin uptake with respective cell metabolic status.

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# SPECTROSCOPIC INVESTIGATION OF THE ORIENTATION OF PYRUVIC ACID AT AN AQUEOUS INTERFACE AS FUNCTION OF PH

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*Abstract:*

Pyruvic acid (PA) is not only a relevant carboxylic acid for metabolic processes, it is also very important in the environment. Its acid/base behavior, in particular at interfaces, is pivotal for understanding the chemical interaction of organic matter in oceans and atmospheric aerosols, where reaction rates and product distributions change due to different conditions. [1]

At the interface of aerosols, the behavior of atmospherically relevant molecules is a major topic, as the surface is the first area where chemical processes take place and thus determines the main reactivity.
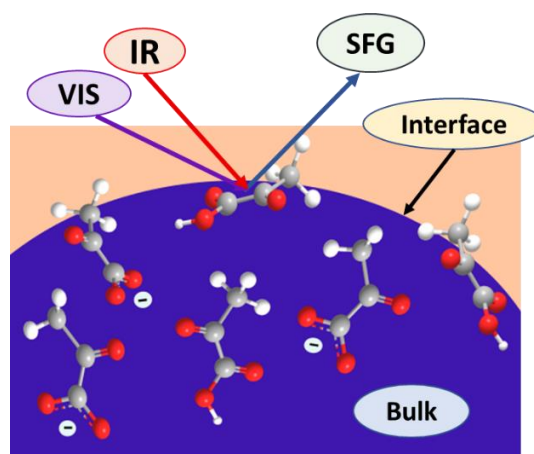
This motivates us to study the interfacial orientation of PA in aqueous solution as a function of pH using the surface specific spectroscopic technique, phase-resolved sum frequency generation spectroscopy (PR-SFG). In this way, the protonation state of PA could be determined from the vibrational signatures of the carboxylic acid groups at the interface: at low pH the protonated (COOH) and at higher pH the deprotonated species (COO$^-$) are present. In addition, the interaction of PA with water was investigated.

We observe that PA at the air/water interface during ionization is on average not significantly changing its orientation. It also shows that the $CH_3$ group points mostly upwards to the air, while the COO(H) group points downwards to the water, indicating $CH_3$ as the first possible interfacial reaction group to the environment water/air. Moreover, our results indicate that the deprotonated species tends to move into the bulk due to the larger amount of solvation. It is also evident from the SFG intensity spectra that at higher pH, the water molecules on the surface are displaced by PA molecules. This is an indication that different protonation states can affect the conformation and function of molecules on aqueous surfaces and have possible effects on the environment and biologically relevant reaction processes.

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# Poop and Prejudice: Upcycling of manure into value added products

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## Abstract:

Increasing consumption of animal-based food and products, caused by a growing human population, results in the inevitable problem of higher waste generation, in particular faeces produced by the high number of animals farmed.[1] Although manure does not have a high commercial value in itself, it causes a high environmental impact by being one of the main contributors to the emission of greenhouse gases in the agricultural sector and potentially threatening the safety of drinking water sources by leakage of nitrates and pathogens.[2] Even though its use in the production of biogas by anaerobic digestion is one way to mitigate this environmental burden, this process is incomplete and wastes valuable resources. Thus, another approach for the utilisation of animal manure is highly desirable, for instance in the pulp and paper industry. Traditional processing of lignocellulosic material into paper products is chemical and energy intensive,[3] however, bio-pulping utilising white rot fungi poses a sustainable pathway for the separation of lignin from cellulose and hemicellulose, in particular for animal manure as initial substrate.[4] Confronting traditional stigma of utilising animal manure and limitations of bio-pulping processes, we demonstrate the benefits of utilizing *P. ostreatus* and *T. versicolor* fungal growth on animal waste derived lignocellulosic material, stretching well beyond merely delignification to the hybridisation of lignocellulosic and chitinous fibres. Ultimately composite papers with improved mechanical and surface properties were produced. Considerably more hydrophobic paper surfaces were obtained already after 4 weeks. Longer growth periods, spanning several weeks, resulted in interfacing of cellulose microfibrils with nanoscale fungal chitin-β-glucan networks, through which considerable improvements in tensile strength and elastic modulus were achieved. This highlights the missed opportunities in traditional delignification-based bioprocessing and demonstrates the tremendous potential of the fungal biorefinery and animal waste as raw material.

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# 4    Student posters

Poster walls will be present in the lecture hall from Wednesday to Friday. We ask you to be present at your poster during the Poster session as the poster jury will only award posters after discussion with the authors. Remember please take your posters down on Friday after the award session. This gives you plenty of time to discuss your results with others at all conference days.

| Poster session, Wednesday, November 17th, 7 -10 pm | |
|---|---|
| Mahdieh Bagheri | Multi object optimization of MIP NPsFOR specific detection of penicillin V potassium |
| Martin Buessler | Photocatalytic Water Splitting, Chemical characterization of Strontium titanate (SrTiO3)Water-Solid interface |
| Ricardo Cruz Meyrelles | HFIP mediation of aza-Morita-Baylis-Hillman reactions |
| Lukas Fischer | Liquid and semi-liquid metal anodes for Li-ion batteries: Constitution and thermodynamics of respective intermetallic systems |
| Daniel Garstenauer | Developing the Vapour-Solid Synthesis of Intermetallic Nanoparticles and Investigation regarding their Catalytic Performance |
| Patrick Guggenberger | Boosting the electrocatalytic activity of the ordered mesoporous Ni/Co-based spinel oxides toward OER by incorporating of Fe/Mn and altering the mesostructure |
| Florian Jörg | Proton transfer in the protic ionic liquid 1-methylimidazolium acetate |
| Johannes Karwounopoulos | Transformato – a tool for free energy simulations using the common core/ serialatom insertion method |
| Gianvito Romano | In situ electropolymerisation for electrochromic high-contrast irreversible smart labels |
| Andràs Szabadi | Arrhenian temperature dependence of the dielectric spectra of ionic liquids |
| Moritz Zelenka | Influence of flow on the MgO-water interface |

# MULTI OBJECT OPTIMIZATION OF MIP NPs FOR SPECIFIC DETECTION OF PENICILLIN V POTASSIUM

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**Abstract:**

Herein we present optimization of the binding properties of molecularly imprinted polymer nanoparticles (MIP NPs) which specifically bind Penicillin V potassium (target molecule) [1]. The effect of using co-monomer and co-crosslinker system on sensing properties approach were studied. Six different polymeric nanoparticles were synthesized. By varying molar equivalent of Methacrylic acid (MAA): Acrylic acid (AA) (0%, 11%, 25% of AA) as monomers [2] and Trimethylpropanerimethyl acrylate (TRIM: Ethylene glycol dimethacrylate (EGDMA) (0%, 50%, 100% of EGDMA) as crosslinker via precipitation polymerization in Acetonitrile Figure 1, shows an example of synthesized NPs shape which are uniform and spherical in the range of 300-400 nm diameter.
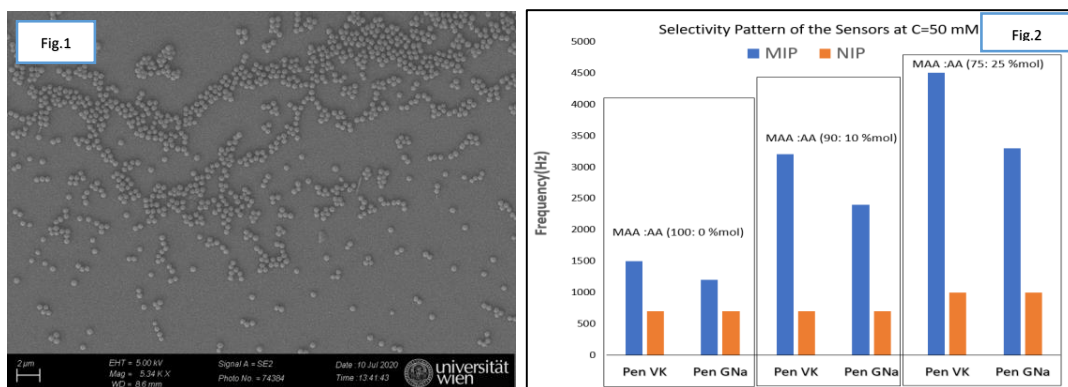
*Figure 1. SEM image illustrate uniform spherical MIP NPs, Figure 2.Selectivity and sensitivity results of NIP and MIP NPs for samples 1-3 against Pen v (50 mM) and Pen G(50mM)*

Furthermore, figure 2 shows the QCM sensor responses for different compositions of co-polymer MIP with MAA and AA (blue column) in comparison with relative NIP (orang column) which acted as reference. As a result, frequency signals of MIP NPs to Pen VK at 50 mM is in the range of 1500-4500 Hz. With increasing the AA molar equivalent to 25 (mol%), it gave rise to sensor signal as high as -4500 Hz. Additionally, using both MAA and AA as monomers for nanoparticle synthesis has huge influence on reducing nonspecific adsorption. The MIP NPs recipe with MAA: AA (75:25 mol%) turned out optimal: it leads to the highest selectivity factor (SF= 1.36) versus Penicillin G molecule which has similar structure to Pen V (see Fig.2). In terms of crosslinker type, having TRIM and EGDMA (50:50%mol) in polymer system increases sensitivity of the sensor from -500 Hz to -1400 Hz in comparison with using only TRIM or EGDMA. Finally, the QCM sensors reveal a limit of detection of LoD=1 mM.

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# Photocatalytic Water Splitting,
## Chemical characterization of Strontium titanate (SrTiO₃)
## Water-Solid interface

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*Abstract:*

The direct conversion of solar energy to hydrogen is considered as a promising method to produce carbon neutral hydrogen fuel. The mechanism of water splitting involves the chemical breakdown of water into hydrogen and oxygen by photonic energy. In 1972 Fujishima and Honda described a first photo electrochemical system capable of generating $H_2$ and $O_2$ using a thin-film of $TiO_2$. Currently, the major goal is to improve the solar to hydrogen conversion efficiency by doping, coupling and modifying the catalysts. The selection rules of a suitable material are well established and the major challenge is to understand the interfacial reactions driving the water oxidation and reduction.

Using the surface specific vibrational spectroscopy sum frequency generation (SFG), our final goal is to describe the water splitting process by observing the oxygen-hydrogen bonds conformation along the reaction. In this spectroscopic method an infrared beam in resonance with a molecular vibration and a visible laser beam are combined at the interface from where the sum frequency is generated. As no SFG signal is generated in centrosymmetric media like bulk water, this method provides information about the water alignment at the interface. Moreover, the frequency of the resonance reports on the hydrogen bonding strength.

We have over the last month intensively studied the interface between water and the photocatalyst Strontium titanate (SrTiO₃) known to photodissociate water. By studying the conformation of the water molecules at the strontium-water interface, we have been able to describe the water orientation at the interface, to identify the different water species present and to observe changes of the hydrogen bonding strength as a function of pH.

This study shows a first chemical characterization of the Strontium-water interface by SFG spectroscopy and it is a first step to dynamically study the water splitting mechanism.
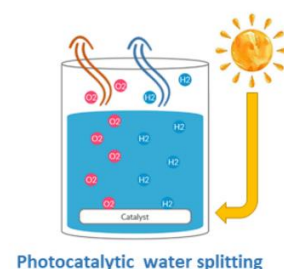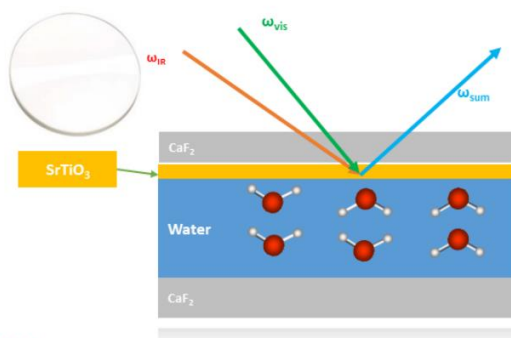
# HFIP mediation of aza-Morita-Baylis-Hillman reactions

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The Morita–Baylis–Hillman (MBH) reaction has become a privileged tool for C–C bond formation, attracting considerable interest and generating numerous variations[1]. The aza-version of the MBH reaction, which employs imine derivatives as electrophiles, is of particular interest for synthesizing β-amino carbonyls[2]. While the vast majority of aza-MBH reactions require the use of imines bearing electron-withdrawing substituents, the use of *N*-dialkyl iminium ions is scarce. We developed a catalyst-free, hexafluoroisopropanol (HFIP)-mediated α-aminomethylation of Michael acceptors[3]. The role of HIFP was studied with DFT methods, revealing the importance of this solvent in the mediation of key proton transfer steps of the reaction mechanism and in the dissociation of the iminium salt in the reaction media.
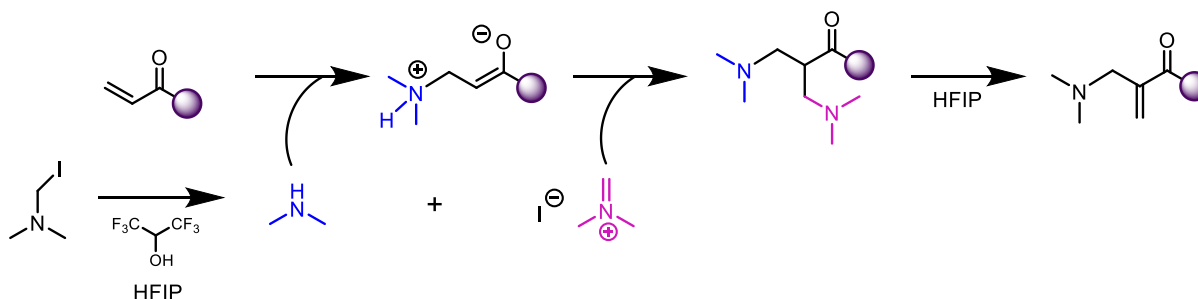
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# Liquid and semi-liquid metal anodes for Li-ion batteries: Constitution and thermodynamics of respective intermetallic systems

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***Abstract:***

Steadily increasing energy demands of today's society generates severe challenges such as a strong dependency on fossil fuels coupled with high $CO_2$ and other greenhouse gas emissions. Consequently, there is an increasing requirement for sustainable and renewable energy and a necessity of energy storage devices for electric mobility and load-leveling of energy sources which are only temporally available.

Among batteries one promising cell type is the Li-ion battery that shows several advantages. However, high power performance characteristics can only be satisfied based on new electrode and electrolyte materials. Conventional carbon-based anodes like graphite are abundant, cheap and persistent but suffer on poor specific capacities (372 mAh/g). Alternatives among others are intermetallic formation anodes like Sn. Sn is an excellent electron conductor and shows a high theoretical capacity of 994 mAh/g when lithiated (up to $Li_{4.4}Sn$). A major disadvantage, however, is crack formation on repeated charge and discharge cycles caused by large volume changes during lithiation leading to rather fast degradation of the electrode material and thus low cyclability.

Self-healing based on liquid and semi-liquid electrode materials is one solution for this problem. The base idea is lowering of the melting point of Sn by addition of further elements like Bi, Ga, In and Zn. Phase diagram investigations based on XRD, thermal analysis and SEM-EDX are performed at the moment to understand the related electrode alloys and their lithiation. This re-assessments of intermetallic systems also includes thermochemical measurements, e.g., calorimetry. All results can be introduced into the optimization of thermodynamic modelling (CALPHAD). Our investigations started with the systems Li-Zn, the only binary which is not yet fully clarified.

The electrochemical performance of selected alloys will be tested (CV, GCPL, GITT) as half cells against Li. Additionally, wetting experiments and preparation of diffusion couples of electrode material/solid electrolyte pairs are planned.

***Keywords:*** Li-ion batteries, liquid anode active materials, phase diagram investigation, thermodynamics

**Developing the Vapour-Solid Synthesis of Intermetallic Nanoparticles and Investigation regarding their Catalytic Performance.**
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*Abstract:*

The steadily increasing demand for energy and the associated effects on the climate and the environment require the development and research of sustainable alternatives for energy harvesting. Hence, the optimization and development of catalyst materials for respective key-reactions play a vital role in current research.

Intermetallic compounds possess unique chemical and physical properties, which make them particularly interesting for catalytic applications. The utilization and synthesis optimization for nanoparticulate intermetallic compounds gained increased attention in recent years. The adjustability of intermetallic materials promises high potential in a variety of heterogeneous catalysed reactions.

Intermetallic nanoparticles are usually synthesized by solvent-based (co-)reduction or impregnation approaches which have to be developed individually for each product. Also, precise composition control is not accessible by these methods, hindering the broad application of intermetallic nanoparticles in catalysis. A very promising alternative method is the direct vapour-solid synthesis of intermetallic nanoparticles by interaction of a metal with high vapour pressure in the gaseous phase with solid metal nanoparticles. In principle, the reaction is driven through the equilibration of a solid component with the vapour of a volatile element. The thermodynamic activity, vapour pressure and thus the product composition are controlled by the reaction temperatures in a temperature gradient.

In a present approach, we performed the vapour-solid method to prepare Nickel-Zinc bulk alloys as well as supported Palladium-Zinc nanoparticles. Investigation of the samples was carried out by SEM-EDX; powder-XRD and BET. The synthesis method was suitable for producing homogeneous intermetallic compounds of precise and predictable composition.

The vapour-solid synthesis is a promising method for the preparation of nanoparticulate intermetallic catalysts. Further metal reactants of interest are the volatile elements Tellurium, Selenium and Antimony in combination with Nickel, Cobalt, Iron, Gold, Iridium, Platinum, Palladium, Ruthenium and Rhodium. The optimization of the reaction parameters for a generally applicable synthesis strategy will be the key of a successful project. Characterization will include testing of the synthesized nanoparticles in various (electro-)catalytic reactions.

*Keywords:*

Vapour-solid Synthesis, Intermetallics, Nanoparticles, Catalysis

# Boosting the electrocatalytic activity of the ordered mesoporous Ni/Co-based spinel oxides toward OER by incorporating of Fe/Mn and altering the mesostructure

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## Abstract:

The development of new low-cost water splitting electrocatalysts to replace the expensive and scarce established noble metal Pt and $RuO_2/IrO_2$ catalysts is a major challenge on the way to green hydrogen production. Ordered mesoporous transition metal oxides, and especially the $Co_3O_4$ derived ones, were hence studied extensively owing to their good performance and stability in alkaline electrolytes for the oxygen evolution reaction (OER).[1] The preparation of bimetallic transition metal oxides like $NiCo_2O_4$, but also the incorporation of small amounts of transition metals – as cation substitutions - led to improved electrocatalysts due to synergistic effects between the metal oxide species.[2, 3] In this work, we synthesized Mn and Fe-substituted ordered mesoporous nickel cobalt oxides via one-step impregnation using KIT-6 aged at 40°C as a hard template to obtain electrocatalysts exhibiting high porosity and surface area. By implementation of a low-temperature calcination approach, the temperature necessary to obtain spinel-type transition metal oxides could be significantly reduced from typically 500°C to 200°C. This was achieved by exploiting the 'container effect' described by Sun et al.[4] Wide-angle XRD revealed phase pure spinel structure for $Co_3O_4$, $Ni_{0.5}Co_{2.5}O_4$, and the Fe and Mn-substituted samples. XPS and HR-EDX allowed us to compare the surface chemistry of the catalysts and prove the homogeneous elemental distribution of the transition metals. HR-TEM, low-angle XRD, and nitrogen physisorption confirmed the high textural quality of the replicas, exhibiting pronounced mesopore ordering, a bimodal pore size distribution (typical for KIT-6-40 replicas), high BET surface area around 130 m²/g, and a total pore volume of approximately 0.3 cm³/g. Further, the electrocatalytic performance was ascertained for the OER in 1M KOH electrolyte. The incorporation of Fe and/or Mn was shown to substantially improve the electrocatalytic performance of the catalysts. With a low overpotential of only 359 mV (@10 mA/cm²) and a high current density of 279 mA/cm² @1,7 V vs. RHE, the $Mn_{0.1}Fe_{0.1}Ni_{0.3}Co_{2.5}O_x$ composition exhibited the best OER performance. Galvanostatic polarization experiments were performed to benchmark the stability of the catalysts. Their high stability was not only confirmed for lab conditions (1M KOH, room temperature) but also at demanding conditions typically employed in water electrolyzers (6M KOH, 80°C).

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# PROTON TRANSFER IN THE PROTIC IONIC LIQUID 1-METHYLIMIDAZOLIUM ACETATE

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*Abstract:*

Ionic liquids are promising candidates in applications such as electrochemistry, synthesis, catalysis, extraction or solvation, due to their specific and tuneable properties. The subclass of protic ionic liquids, distinguished by the possibility of proton transfers, is especially interesting in the field of electrochemistry. Having usually higher conductivities than aprotic ionic liquids, while being non-flammable and having high electrochemical windows, they can be used as alternatives to classical electrolytes in new battery and fuel-cell generations. Many effort is put into computer calculations of these substances to gain insight in underlying processes.

Molecular dynamics are especially useful, since large systems can be simulated for relatively long times. By deducing certain properties up to a molecular or even atomar level, important information can be obtained. However, classical force fields cannot account for bond breaking or formation, which is crucial to protic ionic liquids. Hence, we develop a new method to allow for proton transfer between the molecules during the simulation and investigate the ionic liquid on a deeper level than ever before.

A representative is the protic ionic liquid 1-methylimidazolium acetate and the neutral form 1-methylimidazole and acetic acid, respectively. Introducing proton transfer to the simulation, different transport mechanisms can be investigated, as well as the influence to important dynamic properties and spectroscopic data explored.

# Transformato – a tool for free energy simulations using the common core/ serial atom insertion method

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*Abstract:*

Molecular Dynamics (MD) simulations are an important method for understanding (bio-) chemical systems, including large molecules like proteins. For pharmaceutical applications ligand-protein interactions are of great interest to improve the binding affinity between drug and protein. Hereby, Free Energy Simulations (FES) play a major role. With the help of an alchemical pathway between two molecules the free energy difference between them can be calculated and their relative binding affinities can be estimated.[1] With increasing computational power in recent years, FES has become more and more popular and can be performed relatively routinely using set-up tools like CHARMM-GUI and analysis protocols like the python library pymbar.[2] As for MD simulations in general, the principal sources of error are shortcomings of the force field and/or insufficient sampling.

Setting up such simulations correctly can be still very challenging and time consuming. Most of the available code for FES so far is only designed for specific engines and sometimes lack the GPU support (e.g. PERT in CHARMM). Hence, a pipline for setting up such FES making use of the common core/ serial atom insertion method was developed in our group. Tests on small solute-water systems already showed excellent accordance between free energies obtained by a traditional setup (the PERT module in CHARMM) and our approach. For further applications, the free energy between a protein and different ligands is of great interest which is why our pipline was extended on protein-ligand systems. Here, first tests show good accordance between our results and already published approaches.[3]

After the tests are completed successfully, our goal is to provide non-expert users an easily usable framework for reliable calculating free energies making use of the common core/serial atom insertion method.

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[2] S. Jo, T. Kim, V.G. Iyer, W. Im, *J. Comput. Chem. **2008**, 29, 1859-1865.*

[3] L. Wang et. al., *J. Am. Chem. Soc.* **2015**, 137, 2695-2703

# IN SITU ELECTROPOLYMERISATION FOR ELECTROCHROMIC HIGH-CONTRAST IRREVERSIBLE SMART LABELS
## <u>Gianvito Romano</u>

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### *Abstract:*

Electrochromic (EC) labels are electrochemical cells based on materials which change colour upon an applied potential[1]. Most of the prototypes currently available work with reversible technology, switching multiple times between distinct redox states, each characterised by a specific absorption. Irreversible EC labels, especially interesting for anti-counterfeiting applications (*e.g.*, impossibility of modifying their redox state/colour after first transition), are instead very limited, and characterised by slow switching, low contrast and poor stability.

In this contribution, challenges and achievements in the development of novel, fast, easily processable, accessible and most importantly sustainable irreversible EC materials based on small naturally-occurring organic molecules will be presented. Upon application of a low voltage (< 1.5 V), the irreversible transformation of a transparent monomer into a dark polymeric film, characterised by a high ΔT, speed and long stability, is achieved. Its application as an irreversible electrochromic display combined with temperature detection probes is further assessed, indicating the possibility of commercial exploitation.
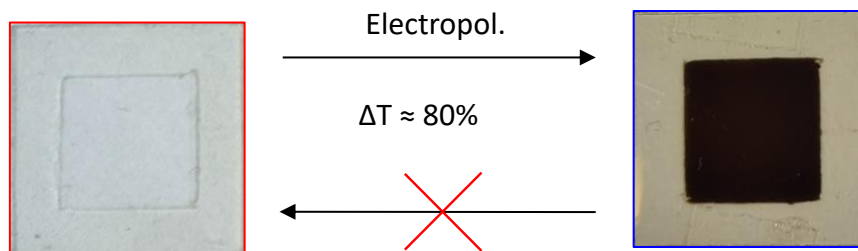
Illustration of a smart label immortalized before and after the electropolymerisation process through the application of an external voltage (ΔT ≈ 80 %)

[1] P. Chen, C. Chang, T. Ko, S. Hsu, K. Li, J. Wu, *Scientific Reports* **2020**, 10, 8430

# ARRHENIAN TEMPERATURE DEPENDENCE OF THE DIELECTRIC SPECTRA OF IONIC LIQUIDS
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*Abstract:*

The dielectric spectra of ionic liquids are known to be temperature-dependent, but a thorough interpretation can be difficult due to the large number of underlying physical processes. By computing decomposed dielectric relaxation spectra of polarizable molecular dynamics trajectories, contributions from collective translation and rotation can be investigated separately. Fitting the resulting correlation functions reveals that the slower relaxation modes adhere to Arrhenius' law, while the fast ones (in the extreme case) do not depend on temperature at all.

This behavior in turn leads to a blue-shift in the low-frequency domain of the spectra at increased temperatures, while the high-frequency region remains unchanged.

A more rigorous interrogation of both structural and dynamic parameters, e.g. coordination numbers, PMF, conductivity and diffusion, coupled with Voronoi tessellation reveals that for ionic liquids the classical picture of a central ion surrounded by a spherical layer of oppositely charged ions cannot always hold true.

Furthermore, calculating the activation energies of said processes shows that the properties of a shared cation depend on the chosen anion, contrary to the idea of "innocent" ions barely interacting with each other.

# Influence of flow on the MgO-water interface
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***Abstract:***

Understanding the dissolution and surface adsorption processes of magnesium oxide (MgO) in aqueous solutions has motivated various studies in the past. However, the underlying molecular processes and interfacial water structure with a macroscopic amount of water, either static or flowing along the solid, has still to be elucidated.

With sum frequency generation spectroscopy, it is possible to obtain interface specific vibrational information. Therefore, we employ this technique to perform a kinetic study of the MgO-water interface at pH 3-11 under static and flowing conditions.

The sum frequency generated signal of flowing water was higher for lower pH values, decreasing strongly from pH 3 to pH 7. Furthermore, when changing from flowing to static water the signal was decreasing as well.

As the sum frequency signal is proportional to a net interfacial orientation of molecules, it can be concluded that at low pH values the surface is positively charged and therefore the water molecules orient with their oxygen atom towards the interface. The decreasing signal, when changing from flowing to static water, can be explained by the dissolution of MgO, which reduces the surface charge. Under static conditions the dissolution effectively drains the $H^+$ concentration near the interface, making it diffusion controlled. Contrary, under flowing conditions $H^+$ is steadily supplied and the dissolution is controlled by the surface reaction.

In conclusion, the water structure and dissolution kinetics of the MgO-water interface were investigated with sum frequency generation spectroscopy. At pH values below pH 4 water molecules are strongly oriented with their oxygen atoms towards the interface. The dissolution rate of MgO is controlled by $H^+$ diffusion under static conditions and by the surface reaction with flowing water.

***Graphical abstract:***
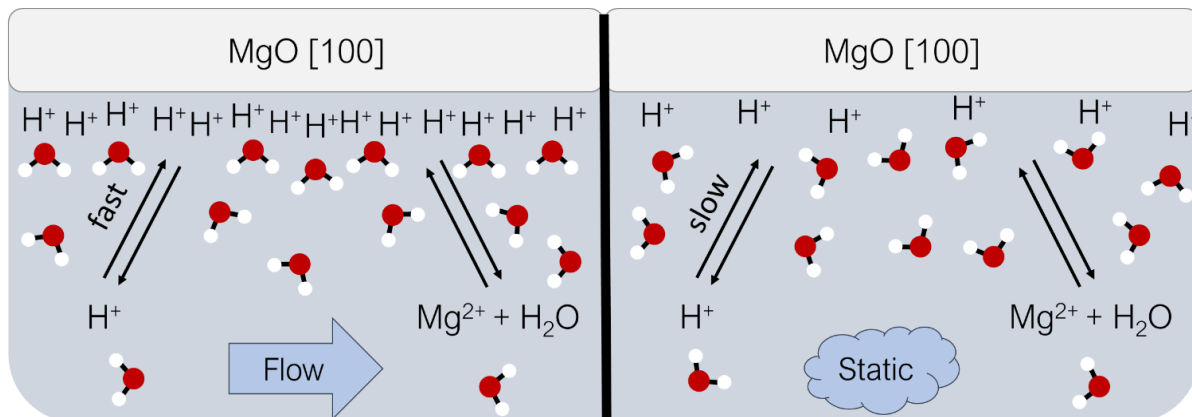
# 5   Information on our PIs

## 5.1   Computational Biological Chemistry

Experimental spectroscopy yields complex spectra characterized by the superposition of various aspects of molecular motion. Therefore, it is left to computer simulation to evaluate individual components and thus disentangle the complex information for meaningful interpretation. As the computational spectra cover frequencies from MHz to THz, our molecular dynamics simulations are based on classical mechanics. However, electronic degrees of freedom may be modeled by polarizable forces. This is, in particular, useful for systems with strong Coulombic interactions such as ionic liquids. These salts are liquid at room temperature and are applied as catalytic solvents, for the extraction of valuable ingredients from biomass, or non-flammable electrolytes in electrochemical applications.

Christian Schröder

## 5.2   Inorganic Chemistry / Functional materials

He is interested in different aspects of structure and properties of intermetallic compounds, experimental determination of phase equilibria in complex multi-component systems and thermodynamic characterization of metal systems, including thermodynamic modelling. Development of new synthesis strategies for intermetallic bulk- and nano-materials. Experimental studies focus on materials systems with high potential for application as well as on fundamental investigations of structure-property relations in nonstoichiometric intermetallics. A variety of methods like thermal analyses, X-ray diffraction, electron microscopy and vapor pressure methods are used.

Klaus Richter

His research activities mainly focus on application-oriented basic research. This comprises the thermodynamic investigation of intermetallic systems as fundamental for new materials' theory-based, target-oriented computational design. Under investigation are phase equilibria, intermetallic phases, and their structure as well as thermochemical properties like, e.g., enthalpies of formation, chemical potentials, and heat capacities.

Hans Flandorfer

## 5.3  Materials Chemistry



Robert Woodward

His research focus is the design and production of new porous organic polymers and carbons for a variety of separation and storage applications. These include water purification, fractionation of complex mixtures, gas separation and storage, energy storage, and catalysis. By exploiting low-cost Friedel-Crafts chemistry he designs hypercrosslinked polymers, the simple and robust synthesis of which allow a vast array of aromatic compounds to be used as monomeric building blocks in adsorbent design.



Andreas Mautner

Andreas is leading the Core Facility "Interface Characterisation'. This facility seeks to deepen the understanding of phenomena occurring at interfaces between phases, thus explaining the macroscopic properties of materials, particularly composites and polymers. We perform research into the interfaces between various classes of materials, particularly polymer and composite materials but are open to any class of material, and provide measurements to members of the Faculty of Chemistry of the University of Vienna. Furthermore, Andreas is involved in the research of sustainable materials, mostly polysaccharide nanomaterials, i.e. cellulose and chitin nanofibrils as well as mycelium materials, and their application in water treatment and composite materials.

## 5.4   Physical Chemistry

Ellen Mezger-Backus

The current focus of the research group is on understanding the structure and dynamics of interfacial water. Amongst others, the properties of water adjacent to hard and soft interfaces are relevant for applications in electrochemistry, folding of macromolecules, and catalysis. To study water molecules selectively at interfaces, we use nonlinear optical spectroscopic techniques. In these methods, no signal is generated from centrosymmetric media. At interfaces, the bulk symmetry is broken. Therefore, selectively interfacial molecules can be studied. In my group, we predominantly use the nonlinear method sum frequency generation (SFG) spectroscopy. Besides our primary research focus on water at interfaces, we are also interested in the structure, orientation, and dynamics of molecules like surfactants, peptides, and organic acids. We are currently building up a lab to study dynamics on ultrafast timescales (sub-picoseconds) in bulk as well.

Peter Lieberzeit

Research of the group of chemical sensing and rapid analysis mainly relies on intermolecular interactions: its primary goal is to implement bioanalogous recognition in artificial matrices and utilize them for analysis of target species ranging from small molecules to entire cells. Several techniques and experimental approaches serve that purpose, namely mainly molecular imprinting into polymer thin films and particles as well as self-assembling monolayers on device surfaces In terms of sensor measurements, the group has built an international reputation in mass-sensitive sensing, mainly based on quartz crystal microbalances (QCMs). We produce those in-house, which allows for maximum possible flexibility and versatility of the systems. Other techniques complement those measurements: Currently, those are mainly surface plasmon resonance (SPR), surface-enhanced Raman spectroscopy (SERS), and impedance (spectroscopy).

## 5.5    Structural and Computational Biology / Max Perutz Labs

Nucleic acids and proteins are the key building blocks of life, yet many essential aspects of their relationship remain enigmatic. Our research aims to decipher the fundamental rules behind the interactions between nucleic acids and proteins in crowded environments, understand the impact these interactions have had in shaping life's evolutionary history and study their role in present-day systems. In conjunction with experiments, we use and develop computational biology techniques, including molecular dynamics simulations, free energy and, entropy calculations, and structural bioinformatics methods. Moreover, we develop novel strategies of physicochemical bioinformatics, an approach to representing, analyzing, and comparing biological sequences as physicochemical objects, which they invariably are. By combining a rigorous, atomistic description of individual biomolecules with the richness of modern-day proteomic and genomic datasets, we strive to discover new fundamental principles behind the organization of biological matter and explain essential biological phenomena from a quantitative, physicochemical perspective.

Bojan Zagrovic

Until recently, proteins were considered as nature's robots performing both unique chemical transformations or specifically interacting with their cognate binding partners under environmental conditions suitable for living organisms. The common understanding is that these functionalities rely on the existence of stably folded protein scaffolds. However, this structure-function paradigm has been put in question: it is now acknowledged that an increasing number of proteins lack stably folded tertiary structures and that this intrinsic flexibility contributes to their biological functionality. The emerging picture is that proteins have evolved to increase the diversity of their conformational ensembles substantially. Even in seemingly random-coil-like disordered proteins, there is a hidden structural simplicity that needs to be addressed by appropriate experimental techniques and theoretical concepts to grasp the essential properties of the underlying structural components. A hallmark of our research is the integrative application of a novel computational biology concept (meta-structure concept) and information-rich NMR spectroscopy directed towards a better understanding of the underlying mechanisms of significant biological problems. Finally, as much of protein function is predicated on dynamics, we are developing novel methodological approaches that combine biochemistry, bioorganic chemistry, and NMR spectroscopy to unravel the microscopic details of functionally important protein plasticity with potential applications in drug development programs.

Robert Konrat

## 5.6   Theoretical Chemistry



Our work focuses on computational structural biology of RNA. In the last two decades RNA has emerged as a key regulator of cellular processes and by studying RNA structure, we obtain insights into the molecular mechanisms by which this regulation is achieved. My group develops algorithms and computational methods for RNA structure related problems, such as prediction of secondary and tertiary structures, interactions between RNAs, RNA folding dynamics, or the design of novel gene-regulatory elements such as artificial riboswitches.

Ivo Hofacker



Our research is driven by understanding chemical phenomena using contemporary computational and theoretical methods. We investigate chemical problems related to the structure, spectroscopy, dynamics, and function of molecular systems. Our area of research combines ab initio electronic structure theory and Density Functional Theory with reaction dynamics. The marriage of these fields allows us to understand chemical processes, not only from a stationary point of view but also dynamically. Our expertise focuses on the proper treatment of molecular systems after light irradiation, but we also study interesting chemical reactions that occur in the electronic ground state.

Leticia Gonzalez



His main expertise is the development of deterministic and stochastic models for the study of complex processes in biological systems. The processes are described on a coarse-grained level and operate on discrete (energy) landscapes. His current research focuses on computational models of the structure, dynamics, and evolution of chemical reaction networks, emphasizing metabolic networks. As PI in several research projects, he gained rich experience in the challenges of interdisciplinary research. In addition, he possesses, over many years, a successful teaching record in the fields of Cheminformatics and Systems Biology.

Christoph Flamm



We model the interaction of light and matter as well as chemical reactions in real-time. An important tool that we use in this context is machine learning. We mostly employ artificial neural networks for the prediction of electronic energies, forces, and other molecular properties with the aim of highly accurate dynamics simulations. Other research interests comprise conventional on-the-fly ab initio molecular dynamics with emphasis on nonadiabatic dynamics (see sharc-md.org) as well as simulations of multiphoton ionization and time-resolved photoelectron spectroscopy.

Philipp Marquetand