Content

1. General 4
1.1 Preface 3
1.2 Mission and Organisation 4
1.3 General Activities and Highlights of 2015 6

2. Research 11
2.1 Theme 1 – Synthesis, Characterisation, Reactivity and
Properties of Molecules 13
Biocatalysis 15
Heterogeneous Catalysis and Sustainable Chemistry 19
Homogeneous, Supramolecular Catalysis and Spectroelectrochemistry.. 23
Metals in Catalysis, Biomimetics & Inorganic Materials 27
Co-ordination and Organometallic Chemistry 31
Organic and Organometallic Chemistry 35
Synthetic & Bio-Organic Chemistry..... 39
Synthetic Organic Chemistry 43

2.2 Theme 2 - Physical Chemistry and Spectroscopy 47
Biomolecular Analysis and Spectroscopy 49
Biophysical Organic Chemistry 53
Raymond and Beverly Sackler
Laboratory for Astrophysics 57
Molecular Nano-Optics and Spins 59
Molecular Photonics 61
Surface Chemistry and Catalysis 67

2.3 Theme 3 - Theoretical Chemistry 69
Computational Chemistry..... 71
Theoretical Chemistry 75
Theoretical Chemistry 79

2.4 HRSMC Co-operations 81
2.5 Memberships and awards 85
2.6 The HRSMC Fellowships 95

3. Education and Research Training 97
3.1 HRSMC Education Programme..... 99
3.2 Symposium 101
3.3 PhD Graduations (in order of graduation date)
& first job 97
after PhD Graduation 102
3.4 HRSMC Excellence Master
'Sustainability: the Molecular Approach'..... 105

4. Annexes..... 107
4.1 Annex 1 - HRSMC Organisation 107
4.2 Annex 2 - Financial Account 2015 109
4.3 Annex 3 - - Staff and Temporary Personnel 2015 110
4.4 Annex 4 – Publications 121

1. General

1.1 Preface

This annual report presents an overview of the research and educational activities of the graduate research school 'Holland Research School of Molecular Chemistry' (HRSMC) during 2015. The HRSMC is a consortium of several departments of three universities: the University of Amsterdam (UvA), VU University Amsterdam (VU) and Leiden University (UL). The University of Amsterdam legally represents the HRSMC. The research school was founded in 1994 and has been re-accredited by the Royal Netherlands Academy of Arts and Sciences (KNAW) in 1999, 2005 and 2012. The HRSMC is now in its fourth period 2012-2018.

The research takes place in the heart of chemistry and focuses on the physical, chemical and biological properties of small to moderately sized molecules in relation to their electronic and spatial structures. The HRSMC creates the conditions for a fruitful collaboration between the research groups, exerts itself to improve their infrastructure, and offers an extensive training programme for the PhD students in inorganic, organic, physical and theoretical chemistry. This annual report presents a survey of the activities and achievements of the HRSMC, both educational and scientific, as well as the scientific achievements of the participating research groups, clusters in the three HRSMC research themes: (1) Synthesis, Characterisation, Reactivity and Properties of Molecules, (2) Physical Chemistry and Spectroscopy, and (3) Theoretical Chemistry.

The year 2015 has been an extraordinary year. Besides organizing several educational activities, the HRSMC established a new Fellowship Programme. It provides funding for foreign researchers of postdoc level and higher to visit and collaborate with HRSMC-affiliated research groups, aiming specifically to set up new and challenging research lines. In 2015, there have been two application rounds, in April and October.
Furthermore, in 2015 twelve students participated in the HRSMC-NWO Excellence Master Graduate programme *'Sustainability: the Molecular Approach'.* Within this programme, a special highlight was the appointment of two PhD students. In the summer of 2015, the HRSMC has granted two proposals for PhD research written by chemistry students Hans de Bruijn (appointed at the Leiden University) and Kaj van Vliet (appointed at the University of Amsterdam).

With its broad educational activities and graduate and fellowship programmes, the HRSMC offers an excellent platform for interuniversity and multidisciplinary cooperation, as well as an incentive for worldclass education and research in molecular chemistry and physics.

1.2 Mission and Organisation

Mission

The HRSMC is a graduate research school in which research groups from the two Universities in Amsterdam and Leiden University participate. In accordance with the resolutions of the Government concerning the Graduate Research Schools, the HRSMC aims to set up and maintain a high-level training programme for its PhD students. In addition to the research training, the HRSMC offers a selection of courses to the students, which are collected in chapter 3.1 and on the HRSMC website (www.hrsmc.nl). Some of these courses are given by staff members from all three universities, others by guest lecturers from abroad. Furthermore, summer schools are regularly organised on the main research themes of the HRSMC. A certificate is presented to those PhD students, who have fulfilled their education programme (see Annex 4.5).
In order to promote the co-operation and exchanges of expertise and ideas, the members are informed about the activities and facilities of the research groups via reports, symposia, the news page of the HRSMC website and the HRSMC newsletter.

Advances and real breakthroughs in chemistry require a thorough understanding at the molecular level. To obtain the latter a concerted effort is paramount, both in research and education, combining synthesis, spectroscopic characterization and theoretical and computational description of molecular systems. The HRSMC is the only research school in the Netherlands with a mission in a broad field that addresses challenges society currently faces in areas like sustainability, energy, and health from a molecular perspective. Both in research and education the HRSMC efforts are internationally recognized. The highly challenging and exciting research- and educational environment attracts young and ambitious molecular scientists from all over the world. The status of HRSMC as a top leading research school is further underpinned by its track record in acquiring grants and awards and by the very good to excellent scores in QANU and other research reviews.

Organisation

The University of Amsterdam legally represents the HRSMC and provides the core financial support to cover personnel costs and costs for key activities, that is required to be a sustainable organisation / that is required to sustain the overall organisation. The HRSMC comprises research groups of the following institutes and universities:
- The van 't Hoff Institute of Molecular Chemistry (HIMS) of the University of Amsterdam (UvA)
- The Institute for Electrons and Molecular Structure (EMS) and the Institute for Lasers, Life and Biophotonics Amsterdam (LaserLaB Amsterdam) of the VU University Amsterdam (VU)
- The Leiden Institute of Chemistry (LIC), Leiden Observatory (LO) and the Leiden Institute of Physics (LION) of the Leiden University (UL).

The management consists of a board of three members and a scientific director (Prof. dr. W.J. Buma). In 2015, the HRSMC board consisted of Prof. dr. F.M. Bickelhaupt (VU), chairman, Prof. dr. M.T.M. Koper (UL) and Prof. dr. C.J. Elsevier (UvA).

The scientific director is assisted by an executive secretary (Mrs. Drs. H.E. Zwaan – van der Plas) and administrative officers (Mrs. R. Weijer and Mrs. M.C.H. Smits-Weijers). In addition, an external advisory committee, the PhD platform and internal committees for education and research advise the board (see Annex 4.1).

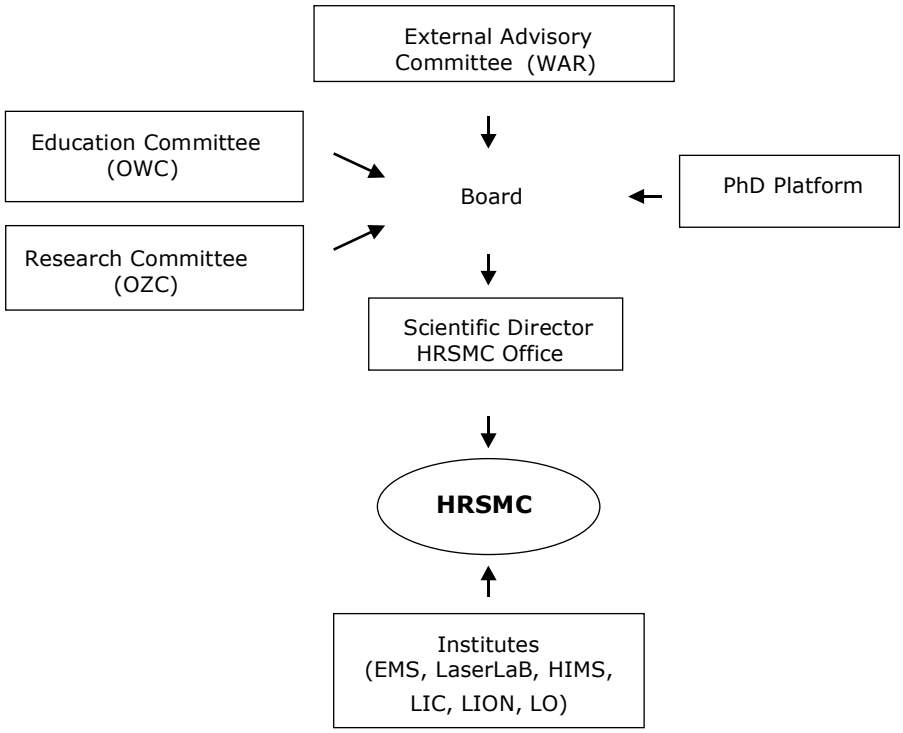


Figure 1.1 Schematic organisation of the HRSMC

The organisation of the HRSMC is schematically depicted in Fig. 1.1; Annex 4.1. gives the composition of the committees and the PhD platform. On December 31, 2015 about 350 persons were employed within the HRSMC (several are not full-time involved in research, for details see Annex 4.3).

1.3 General Activities and Highlights of 2015

In 2015, the HRSMC has put much effort in providing the PhD students with outstanding courses and maintaining the co-operations with other research groups and institutions.

Educational Activities

The annual HRMSC Symposium was held at the VU University Amsterdam on November 5, 2015. Besides the guest lecture of Prof. dr. ir. B.M. (Bert) Weckhuysen (UU), there were lectures of five PhD students and three lectures by senior scientists. In addition, the Dick Stufkens prize was awarded to Dr. Tatu Kumpulainen (former UvA PhD student; presently University of Geneva, Switzerland), who also gave a lecture. In 2008 this annual prize has been established by the board of the HRSMC for the most outstanding PhD thesis within the HRSMC. The prize, consisting of (i) a certificate and (ii) 1,000 Euro in cash, is named after the scientific director of the HRSMC from 1997 to 2001.
The symposium, which was attended by ca. 190 scientists, included poster sessions with 44 posters, mainly presented by PhD students. Further details regarding this symposium can be found in Chapter 3.2.
The HRSMC educational activities of 2015 consisted of:

- The two weeks HRSMC Course *'Molecular Simulation'*, organized under the auspices of CECAM (5-16 January 2015, UvA)
- HRSMC Course *'Physical Methods in Inorganic Chemistry'* (29 January - 6 February 2015, UL/UvA)
- HRSMC introduction meeting for new PhD members of the HRSMC (January 29 2015, UvA)
- HRSMC TULIP School *'Modern Developments in Spectroscopy*' (14 - 17 April 2015, De Witte Raaf Noordwijk)
- HRSMC 4-day '*Proposal Writing'* course in combination with 1-day '*Peer Review'* course (5-9 October 2015, UL)
- The KNCV/HRSMC '*Career Advice Activity'* for PhD students and postdocs (13 October 2015, UL Gorlaeus; the KNCV is the Royal Dutch Chemistry Association).

An overview of all HRSMC inter-university Courses and Summer Schools can be found in Chapter 3.1. In this chapter, more information can be found as well on the educational activities of 2015 described above.

HRSMC Excellence Master/Graduate Programme "Sustainability, the Molecular Approach"

Apart from providing and organizing an outstanding educational programme for PhD students which is also accessible to (advanced) MSc students, the HRSMC has been elected in 2012 as one of the thirteen Graduate Schools to receive substantial funding from NWO. With this funding the HRSMC can offer young PhD students the opportunity to develop their own research ideas within the framework of the programme *"Sustainability, the Molecular Approach"*. The funding is part of NWO's Graduate Programme and aims to develop Dutch PhD Educational Programmes. On December 31, 2015 nine MSc students participated in this Excellence Program and three students graduated in the period of August-October 2015.

In 2015, the HRSMC has granted two proposals for PhD research written by chemistry students Hans de Bruijn (appointed at the Leiden University) and Kaj van Vliet (appointed at the University of Amsterdam).
More information about this programme can be found in Chapter 3.4.

Fellowship Programme

As already mentioned in the preface, the HRSMC established in 2015 a new Fellowship Programme. It provides funds for foreign researchers of postdoc level and higher to visit HRSMC-affiliated research groups. In 2015, there have been two rounds, in April and October. More information about this programme can be found in Chapter 2.6.

Research highlights

In 2015, the staff members have been very successful in receiving funding and prestigious awards. A selection is given below:

- Prof. dr. Joost Reek (UvA) became a member of the KNAW and has been appointed as NIOK director.
- Prof. dr. Gadi Rothenberg (UvA), Prof. dr. Joost Reek (UvA) and Prof. dr. Ben Feringa (RUG) have been awarded a two million euro TOP-PUNT grant by the Netherlands Organisation for Scientific Research (NWO) for their collaboration on "Catalysis in Confined Spaces".
- Prof. dr. Bas de Bruin (UvA) has been elected as 'Lecturer of the Year 2015' by the students of the Faculty of Science.
- Dr. Tati Fernández-Ibáñez (UvA) and Dr. Moniek Tromp (UvA) have both received funding through the LIFT programme of the Netherlands Organisation for Scientific Research NWO. In two public-private partnership projects a PhD student and a postdoc researcher will be employed.
- Prof. dr. Paola Gori-Giorgi (VU) has received an ERC Consolidator Grant for her project `Improving the accuracy and reliability of electronic structure calculations: New exchange-correlation functionals from a rigorous expansion at infinite coupling strength'.
- Dr. Jörg Meyer (LU) has been awarded an NWO VIDI fellowship for his research project: 'Chemical reactions: hot or not?'.
- Dr. Annemieke Petrignani (UvA) has been awarded an NWO VIDI fellowship for her research project: 'Shapes and Sizes of Hydrocarbons in Space'.
- Dr. Moniek Tromp (UvA) has been awarded an NWO VIDI fellowship for her research project: 'The active site in the spotlight!'. Furthermore, she was nominated in the VIVA400 list 2015, i.e., one of the most inspirational Dutch women of 2015.
- Dr. Freek Ariese (VU) obtained a grant from the Netherlands Space Office for a PhD project 'Fast Raman imaging for biomarker detection on planetary surfaces'.
- The SOLARDAM consortium, which includes HRSMC members Prof. dr. Matthias Bickelhaupt, Prof. dr. Wybren Jan Buma, Prof. dr. Joost Reek and Prof. dr. Luuk Visscher, has received initial funding from the Amsterdam Academic Alliance (AAA). With this funding for SOLARDAM, VU and UvA have the unique opportunity to establish a coherent solar energy research programme based on the concentrated expertise in the Amsterdam area.

- The European consortium Laserlab-Europe, which includes LaserLaB Amsterdam and the groups of Ariese (VU), Buma/Woutersen/Zhang (UvA) and Brouwer/Williams (UvA), successfully applied for a 10 ME Horizon2020 grant and will continue their joint research activities, networking activities, and offer transnational access to external users to their highly specialized laser facilities.

Publications

Publications from all HRSMC research groups published in 2015 can be found in Annex 4.4. Many of these publications appeared in high-impact journals, a selection is given below:

- Korstanje, T. J.; Ivar van der Vlugt, J.; Elsevier, C. J.; de Bruin, B. Hydrogenation of Carboxylic Acids with a Homogeneous Cobalt Catalyst. *Science* **2015**, *350* (6258).
- Grundner, S.; Markovits, M. A. C.; Li, G.; Tromp, M.; Pidko, E. A.; Hensen, E. J. M.; Jentys, A.; Sanchez-Sanchez, M.; Lercher, J. A.; Olah, G. A.; et al. Single-Site Trinuclear Copper Oxygen Clusters in Mordenite for Selective Conversion of Methane to Methanol. *Nature Communications* **2015**, *6*, 7546.
- Hennig, R.; Heidrich, J.; Saur, M.; Schmueser, L.; Roeters, S. J.; Hellmann, N.; Woutersen, S.; Bonn, M.; Weidner, T.; Markl, J.; et al. IM30 Triggers Membrane Fusion in Cyanobacteria and Chloroplasts. *Nature Communications* **2015**, *6*, 7018.
- Tan, E. M. M.; Amirjalayer, S.; Smolarek, S.; Vdovin, A.; Buma, W. J.; Zerbetto, F. Fast Photodynamics of Azobenzene Probed by Scanning Excited-State Potential Energy Surfaces Using Slow Spectroscopy. *Nature communications* **2015**, *6*, 5860.
- Calle-Vallejo, F.; Loffreda, D.; Koper, M. T. M.; Sautet, P. Introducing Structural Sensitivity into Adsorption–energy Scaling Relations by Means of Coordination Numbers. *Nature Chemistry* **2015**, *7* (5), 403–410
- Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y. Y.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I.; Schouten, K. J. P.; Mul, G.; Koper, M. T. M. Electrocatalytic Reduction of Carbon Dioxide to Carbon Monoxide and Methane at an Immobilized Cobalt Protoporphyrin. *Nature Communications* **2015**, *6*, 8177
- Vreeken, V.; Siegler, M. A.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. C-H Activation of Benzene by a Photoactivated Ni(II)(azide): Formation of a Transient Nickel Nitrido Complex. *Angewandte Chemie (International ed. in English)* **2015**, *54* (24), 7055–7059.
- Broere, D. L. J.; Metz, L. L.; de Bruin, B.; Reek, J. N. H.; Siegler, M. A.; van der Vlugt, J. I. Redox-Active Ligand-Induced Homolytic Bond Activation. *Angewandte Chemie International Edition* **2015**, *54* (5), 1516–1520.
- Geer, A. M.; Serrano, A. L.; de Bruin, B.; Ciriano, M. A.; Tejel, C.; de, B. B.; Ciriano, M. A.; Tejel, C. Terminal Phosphanido Rhodium Complexes Mediating Catalytic P-P and P-C Bond Formation. *Angewandte Chemie (International ed. in English)* **2015**, *54* (2), 472–475.
- Lichtenberg, C.; Viciu, L.; Adelhardt, M.; Sutter, J. J.; Meyer, K.; de, B. B.; Grutzmacher, H.; de Bruin, B.; Gruetzmacher, H. Low-Valent Iron(i) Amido Olefin Complexes as Promotors for Dehydrogenation Reactions. *Angewandte Chemie (International ed. in English)* **2015**, *54* (19), 5766–5771.

- Rebreyend, C.; de Bruin, B.; de, B. B. Photolytic N2 Splitting: A Road to Sustainable NH3 Production?. *Angewandte Chemie (International ed. in English)* **2015**, *54* (1), 42–44.
- Schwab, M. M.; Himmel, D.; Kratzert, D.; Radtke, V.; Weis, P.; Krossing, I.; Kacprzak, S.; Weber, S.; Ray, K.; Scheidt, E.-W.; et al. Ni(cod)2][Al(OR(F))4], a Source for Naked Nickel(I) Chemistry. *Angewandte Chemie (International ed. in English)* **2015**, *54* (49), 14706–14709.
- Vreeken, V.; de, B. B.; Reek, J. N. H.; van, der V. J. I.; Siegler, M. A.; Lutz, M.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. C-H Activation of Benzene by a Photoactivated NiII(azide): Formation of a Transient Nickel Nitrido Complex. *Angewandte Chemie (International ed. in English)* **2015**, *54* (24), 7055–7059.
- Vreeken, V.; Siegler, M. A.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. C-H Activation of Benzene by a Photoactivated Ni(II)(azide): Formation of a Transient Nickel Nitrido Complex. *Angewandte Chemie (International ed. in English)* **2015**, *54* (24), 7055–7059.
- Kong, L.; Askes, S. H. C.; Bonnet, S.; Kros, A.; Campbell, F. Temporal Control of Membrane Fusion through Photolabile PEGylation of Liposome Membranes. *Angewandte Chemie, International Edition* **2016**, *55* (4), 1396–1400.
- Borger, J. E.; Ehlers, A. W.; Lutz, M.; Slootweg, J. C.; Lammertsma, K. Stabilization and Transfer of the Transient [Mes*P4](-) Butterfly Anion Using BPh3. *Angewandte Chemie (International ed. in English)* **2016**, *55* (2), 613–617.
- De Graaff, C.; Bensch, L.; Boersma, S. J.; Cioc, R. C.; van, L. M. J.; Janssen, E.; Orru, R. V. A.; Ruijter, E.; Turner, N. J.; de Graaff, C.; et al. Asymmetric Synthesis of Tetracyclic Pyrroloindolines and Constrained Tryptamines by a Switchable Cascade Reaction. *Angewandte Chemie (International ed. in English)* **2015**, *54* (47), 14133–14136.
- Orrit, M. Single-Molecule Chemistry Is More than Superresolved Fluorescence Microscopy. *Angewandte Chemie (International ed. in English)* **2015**, *54* (28), 8004–8005
- Meuzelaar, H.; Panman, M. R.; Woutersen, S. Guanidinium-Induced Denaturation by Breaking of Salt Bridges. *Angewandte Chemie, International Edition* **2015**, *54* (50), 15255–15259.
- Suhina, T.; Weber, B.; Carpentier, C. E.; Lorincz, K.; Schall, P.; Bonn, D.; Brouwer, A. M. Fluorescence Microscopy Visualization of Contacts between Objects. *Angewandte Chemie (International ed. in English)* **2015**, *54* (12), 3688–3691.
- Goesten, M. G.; Fonseca Guerra, C.; Kapteijn, F.; Gascon, J.; Bickelhaupt, F. M. Six-Coordinate Group 13 Complexes: The Role of D Orbitals and Electron-Rich Multi-Center Bonding. *Angewandte Chemie, International Edition* **2015**, *54* (41), 12034–12038.
- Sinha, I.; Fonseca Guerra, C.; Müller, J. A Highly Stabilizing silver(I)-Mediated Base Pair in Parallel-Stranded DNA. *Angewandte Chemie (International ed. in English)* **2015**, *54* (12), 3603–3606.
- García-Simón, C.; Gramage-Doria, R.; Raoufmoghaddam, S.; Parella, T.; Costas, M.; Ribas, X.; Reek, J. N. H. Enantioselective Hydroformylation by a Rh-Catalyst Entrapped in a Supramolecular Metallocage. *Journal of the American Chemical Society* **2015**, *137* (7), 2680–2687.

- Goswami, M.; Lyaskovskyy, V.; Domingos, S. R.; Buma, W. J.; Woutersen, S.; Troeppner, O.; Ivanović-Burmazović, I.; Lu, H.; Cui, X.; Zhang, X. P.; et al. Characterization of Porphyrin-Co(III)-"Nitrene Radical" Species Relevant in Catalytic Nitrene Transfer Reactions. *Journal of the American Chemical Society* **2015**, *137* (16), 5468–5479

Research collaborations

Besides its broad educational activities, graduate and fellowship programmes, the HRSMC aims to be an excellent platform for interuniversity and multidisciplinary cooperation between groups of the HRSMC. There are many collaborations on a formal basis (see chapter 2.4) and on an informal basis, i.e., to advice, brainstorm, and share expertise and equipment (see annex 4.6). These collaborations resulted in about 11 joint publications in 2015, while several joint applications at CW-NWO were awarded.

(Personnel) mutations

At the Institute for Electrons and Molecular Structure (EMS) of the Vrije Universiteit (VU):

- Prof. Koop Lammertsma has been appointed as Distinguished Visiting Professor at the University of Johannesburg for 5 years, 3 months each year.
- Dr. Paola Gori-Giorgi has been appointed as University Research Chair Professor as of November 1, 2015.

At the Leiden Institute of Chemistry (LIC), Leiden Observatory (LO) and the Leiden Institute of Physics (LION) of the Universiteit Leiden (UL):

- Dr. Jörg Meyer started in Leiden in a Tenure Track position in the Theoretical Chemistry Group of Prof. G.J. Kroes. Dr. J. Meyer joined the HRSMC within HRSMC research theme 3. With his membership, theme 3 is reinforced as till then only two groups from the VU University Amsterdam and University of Amsterdam participated in this theme.
- In July 2015, Dr. Irene Groot has been appointed on a tenure-track position within the Catalysis and Surface Chemistry Group of the Leiden Institute of Chemistry.

At the van 't Hoff Institute of Molecular Chemistry (HIMS) of the Universiteit van Amsterdam (UvA):

- Dr. Jan van Maarseveen has been appointed as professor of Bio-Inspired Organic Synthesis as of July 1, 2015.
- Dr. Francesco Mutti, has been appointed as assistant professor in Biocatalysis at the Van 't Hoff Institute for Molecular Sciences (HIMS), joined the HRSMC starting September 1, 2015. His research, focused on novel bio-inspired synthetic pathways, will complement the strategy of the UvA Research Priority Area Sustainable Chemistry.
- In January 2015, Dr. M. Ángeles (Tati) Fernández-Ibáñez has been appointed as assistant professor (tenure-track) in the Synthetic Organic Chemistry group.

2. Research

The research topics of the HRSMC are collected in the three research themes 'Synthesis, Characterisation, Reactivity and Properties of Molecules' (Theme 1), 'Physical Chemistry and Spectroscopy' (Theme 2), and 'Theoretical Chemistry' (Theme 3). Of course the co-operations are not restricted to research groups of a single theme. Table 2.1 gives an overview of the research groups involved in the HRSMC in 2015. The names of all staff members, graduate students, postdocs and technical staff are listed in Annex 4.3.

Table 2.1 HRSMC research themes, corresponding research groups and their staff members in 2015.

Theme	**Group (University, institute)** staff members
1	**Biocatalysis (UvA, HIMS)** Dr. F. Mutti
	Heterogeneous Catalysis and Sustainable Chemistry (UvA, HIMS) Prof. dr.G. Rothenberg[1], Dr. S. Grecea, Dr. N.R. Shiju, Dr. N. Yan
	Homogeneous, Supramolecular and Bio-Inspired Catalysis (UvA, HIMS) Prof. dr. B. de Bruin[1], Prof. dr. J.N.H. Reek[1], Dr. M. Tromp, Dr. Ir. J.I. van der Vlugt
	Metals in Catalysis, Biomimetics & Inorganic Materials (UL, LIC) Prof. dr. E. Bouwman[1], Dr. S. Bonnet, Dr. D. Hetterscheid
	Molecular Inorganic Chemistry (UvA, HIMS) Prof. dr. C.J. Elsevier[1]
	Organic and Organometallic Chemistry (VU, EMS) Prof. dr. K. Lammertsma, Dr. A.W. Ehlers, Dr. J.C. Slootweg
	Synthetic and Bio-organic Chemistry (VU, EMS) Prof. dr. ir. R.V.A. Orru, Dr. E. Ruijter
	Synthetic Organic Chemistry (UvA, HIMS) Prof. dr. H. Hiemstra[1], Prof. dr. J.H. van Maarseveen, Prof. dr. P. Timmerman, Dr. M.Á. Fernández-Ibáñez, Dr. S. Ingemann
2	**Biomolecular Spectroscopy (VU, EMS)** Dr. F. Ariese
	Biophysical Organic Chemistry (UL, LIC) Prof. dr. H.J.M. de Groot, Dr. Alia, Dr. F. Buda
	Raymond and Beverly Sackler Laboratory Astrophysics and Astrochemistry (UL, LION) Prof. dr. H. Linnartz
	Molecular Nano-Optics and Spins (UL, LION) Prof. dr. E.J.J. Groenen, Prof. dr. M. Orrit, Dr. P. Gast, Dr. M. I. Huber
	Molecular Photonics (UvA, HIMS) Prof. dr. A.M. Brouwer, Prof. dr. W.J. Buma, Prof. dr. S. Woutersen, Dr. R. M. Williams, Dr. H. Zhang, Prof. dr. J. Oomens (Radboud University)
	Surface Chemistry and Catalysis (UL, LIC) Prof. dr. M. Koper[1], Dr. W.T. Fu, Dr. I.M.N. Groot, Dr. D. Hetterscheid, Dr. L.B.F. Juurlink

3	**Computational Chemistry (UvA, HIMS)** Prof. dr. P.G. Bolhuis, Prof. dr. E.J. Meijer, Dr. B. Ensing, Dr. D. Dubbeldam, Dr. J. Vreede
	Theoretical Chemistry (VU, EMS) Prof. dr. F.M. Bickelhaupt[1], Prof. dr. L. Visscher, Dr. C. Fonseca Guerra, Prof. dr. P. Gori Giorgi, Dr. O. Gritsenko
	Theoretical Chemistry (UL, LIC) Dr. J. Meyer

[1]also NIOK

2.1 Theme 1 - Synthesis, Characterisation, Reactivity and Properties of Molecules

Aims, activities and achievements

The design and synthesis of compounds with novel structures are among the most essential activities in molecular chemistry research. The incentives to prepare such new molecules are, apart from curiosity, their anticipated physical, chemical or biological properties. Strategic aspects of the HRSMC synthetic research are the development of new (bio)catalytic reactions and the investigation of their mechanisms, the synthesis of magnetic and conducting materials, and the development of methodologies for the synthesis of bioactive compounds. A great variety of techniques is used for the synthesis of the compounds as well as for the elucidation of their molecular structure and physical-chemical and biological properties. From the three universities eight different groups are active in this area.

The **Biocatalysis** group is focused on cutting-edge research at the interphase between the chemical and the biological sciences It requires therefore a high level of multidisciplinary expertise, encompassing organic synthesis, bioorganic chemistry, biochemistry, enzyme engineering and molecular biology.

Collaborations with other groups at HIMS and at other Universities complement and support our research, in particular regarding X-ray crystallisation of new enzymes and computational studied.

The mission of the **Heterogeneous Catalysis and Sustainable Chemistry group** is to discover new catalysts and materials for sustainable chemistry applications. We start from fundamental concepts and develop practical applications. These include gas-to-liquids, biomass-to-liquids, biomass to chemicals and finding new catalytic routes to a variety of industrial materials. Our strengths are in catalyst design, catalyst synthesis and testing, and characterisation under real-life conditions. HCSC is a highly interdisciplinary group (inorganic and organic chemists, physicists, chemical engineers, electronics experts, materials scientists, chemometricians and computational chemists) and all our projects benefit from this.

The **Homogeneous, Supramolecular and Bio-Inspired Catalysis** group develops new tools for transition metal catalysis, based on rational ligand design, supramolecular concepts and bio-inspired approaches. With these new tools new and existing reactions are developed with a focus on high atom-efficiency, control of chemo-, regio-, and stereo-selectivity, and optimized activity and stability of the catalyst. In addition to development of novel reaction relevant for bio-renewable conversion, we also study reaction for green energy applications (water oxidation, proton reduction, formic acid decomposition). In addition, new solutions to homogeneous catalyst separation and recycling are investigated.

The **Metals in Catalysis, Biomimetics & Inorganic Materials (MCBIM)** group is involved in the synthesis and study of the properties of transition-metal coordination compounds and their applications as homogeneous catalysts, medicinal compounds, models for the active sites in metalloproteins, and molecular materials.

The research activities of the **Molecular Inorganic Chemistry** group are in the field of molecular inorganic and organometallic chemistry and concern the mechanisms of selective metal-catalysed reactions. The main aim is to synthesize new metal compounds

that show novel (catalytic) properties of bond formation and breaking. Furthermore, efforts are made to address immobilization and compartmentalization of molecular inorganic compounds that are used as (pre) catalysts, in order to promote recycling of the ligand and/or such a catalyst.

The **Organic and Organometallic Chemistry group** synthesizes novel organophosphorous compounds in the context of sustainability and catalysis by focusing on Al/P- and B/P-based frustrated Lewis pairs (FLPs), white phosphorus (P4), phosphinidenes akin to the Fischer and Schrock carbene complexes, P,N-ligands for homogeneous catalysis, and organosilicates as entry to enantioselective catalysis. They are also involved in the design of novel light-absorbing chromophores. All their molecular designs are supported by ab initio and DFT calculations.

The central theme in the **Synthetic and Bio-organic Chemistry** group is the development of new synthetic methodology for the efficient and selective generation of (libraries of) biologically relevant molecules. Key topics are improvement of atom and process efficiency in organic synthesis, the development of novel tandem and multicomponent reactions for diversity and/or biology oriented synthesis, and application of advanced (bio)catalysis in the synthesis of complex and diverse molecules.

The **Synthetic Organic Chemistry (SOC) group** develops new synthetic methodologies, in particular directed to the total synthesis of novel, and structurally challenging bioactive natural products. Key areas of the group ’s research are asymmetric organocatalysis with novel chiral Brønsted acids and Cinchona alkaloid-derived bases, and the development of novel peptide C-terminal activation methodologies, the synthesis of cyclic peptides and peptide rotaxanes via novel cyclisation strategies. A new research line is directed at the discovery and development of robust methods for the synthesis of high value chemicals and materials using the C-H functionalization strategy.

Biocatalysis

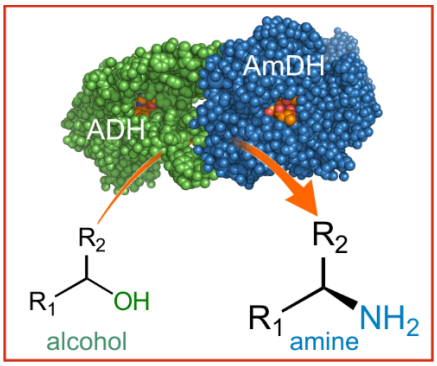
Dr. F. Mutti

Research topics

- The Biocatalysis group carries out cutting-edge research at the interphase between the chemical and the biological sciences. The research focuses on:
- The development of novel biocatalytic systems for the sustainable manufacture of chemical products.
- Identification and characterisation of novel enzymes.
- Engineering of enzymes to improve existing activities or introduce new activities.
- Kinetic and thermodynamic measurements of enzymatic reactions.
- Elucidation of enzymatic reaction mechanisms.
- Creation of artificial enzymes.
-

Summary of research activities and group highlights 2015

The major highlight from the Biocatalysis group has been a publication in Science (impact factor 33.61, DOI: 10.1126/science.aac9283). In this article, we have described the redox self-sufficient, catalytic enzymatic conversion of alcohols to amines whose schematic view is depicted below.



More in general, multi-step chemical reactions in one pot avoid the need for isolation of intermediates and purification steps. In this context, hydrogen-borrowing processes possess the most elevated atom economy as the electrons liberated in the oxidative step are quantitatively utilized in the interconnected reductive step. As a consequence, stoichiometric amounts of sacrificial cosubstrates for the regeneration of the nicotinamide coenzymes are not required. We have successfully developed this concept for two different biocatalytic processes. In the previously mentioned study, we investigated the biocatalytic hydrogen-borrowing amination of primary and secondary alcohols because amines constitute the major targets or intermediates for the production of active pharmaceutical ingredients, fine chemicals, agrochemicals, but also polymers, dyes, plasticizing agents, etc. Our method relies on the tandem combination of alcohol dehydrogenases (ADHs) with amine dehydrogenases (AmDHs) to carry out the amination of structurally diverse aromatic and aliphatic alcohols, yielding up to 96% conversion and 99% enantiomeric excess (R). Furthermore, primary alcohols were also aminated with up to 99% conversion. This redox self-sufficient cascade requires ammonium as a simple

and inexpensive source of nitrogen and generates water as the sole by-product. In the second concomitant study, the biocatalytic hydrogen-borrowing concept was applied to the synthesis of α-chiral substituted carboxylic acids from α,β-unsaturated aldehydes via the combination of ene-reductases (ERs) with aldehyde dehydrogenases (AldDHs). Initially, we focused on the biocatalytic synthesis of chiral α-substituted hydrocinnamic acids and acetylated unnatural amino acids since these compounds are important targets for pharmaceuticals. Later on, the applicability of the process was also validated for the synthesis of α-chiral aliphatic acids and heterocycles. The conversion of the α,β-unsaturated aldehydes to the related α-chiral substituted carboxylic acids proceeded generally with elevated yield as well as chemo- and stereo-selectivity. This strategy has several advantages: i) the starting material is an α-substituted α,β-unsaturated aldehyde, a class of compounds extremely reactive for the biocatalytic C=C double bond reduction, whereas α,β-unsaturated carboxylic acids are completely unreactive; ii) no external hydride source from a sacrificial substrate (e.g. glucose, formate) is required; iii) no additional reagent is required; iv) the only by-product is water.

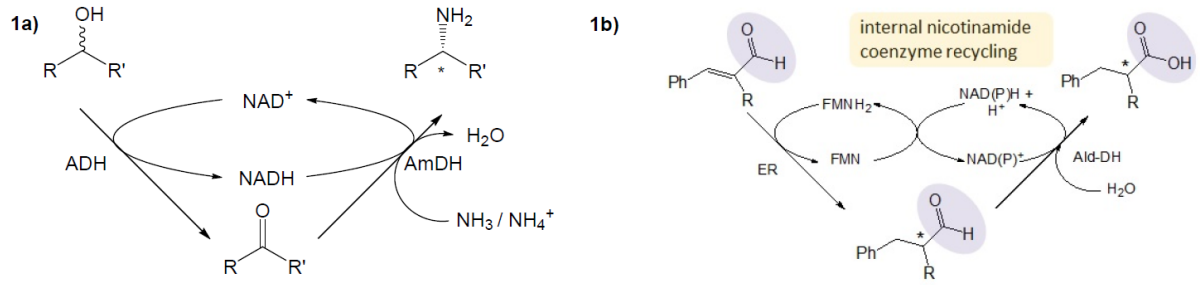
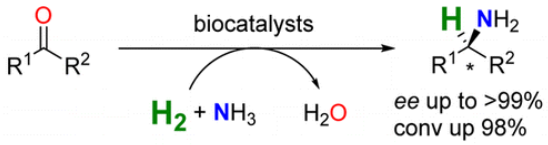


Figure 1. Our biocatalytic hydrogen-borrowing processes: 1a) asymmetric amination of alcohols; 1b) conversion of α-substituted α,β-unsaturated aldehydes to α-chiral carboxylic acids.

Finally, in a collaboration with the University of Graz, the Biocatalysis group has presented a new approach for the asymmetric reductive amination of ketones employing ω-transaminases. The method relies on a sophisticated network constituted by three enzymes: a ω-transaminase, an alanine dehydrogenase and a Fe/S dioxygen tolerant hydrogenase. The system requires 5 equivalents of alanine and a catalytic amount of NAD (nicotine adenine dinucleotide) as cofactor, the latter recycled at the expense of molecular hydrogen:



Key publications 2012-2015

- Mutti, F. G.; Knaus, T.; Scrutton, N. S.; Breuer, M.; Turner, N. J. Conversion of Alcohols to Enantiopure Amines through Dual-Enzyme Hydrogen-Borrowing Cascades. *Science* **2015**, *349* (6255), 1525–1529.
- Holzer, A. K.; Hiebler, K.; Mutti, F. G.; Simon, R. C.; Kroutil, W.; Lauterbach, L.; Lenz, O.; Kroutil, W. Asymmetric Biocatalytic Amination of Ketones at the Expense of NH3 and Molecular Hydrogen. *Org. Lett.* **2015**, *17* (10), 2431–2433.

- Knaus, T.; Mutti, F. G.; Humphreys, L. D.; Turner, N. J.; Scrutton, N. S. Systematic Methodology for the Development of Biocatalytic Hydrogen-Borrowing Cascades: Application to the Synthesis of Chiral α-Substituted Carboxylic Acids from α-Substituted A,β-Unsaturated Aldehydes. *Org. Biomol. Chem.* **2015**, *13* (1), 223–233.
- Sattler, J. H.; Fuchs, M.; Mutti, F. G.; Grischek, B.; Engel, P.; Pfeffer, J.; Woodley, J. M.; Kroutil, W. Introducing an In Situ Capping Strategy in Systems Biocatalysis To Access 6-Aminohexanoic Acid. *Angew. Chemie Int. Ed.* **2014**, *53* (51), 14153–14157.
- Mutti, F. G.; Kroutil, W. Asymmetric Bio-Amination of Ketones in Organic Solvents. *Adv. Synth. Catal.* **2012**, *354* (18), 3409–3413.
- Sattler, J. H.; Fuchs, M.; Tauber, K.; Mutti, F. G.; Faber, K.; Pfeffer, J.; Haas, T.; Kroutil, W. Redox Self-Sufficient Biocatalyst Network for the Amination of Primary Alcohols. *Angew. Chemie Int. Ed.* **2012**, *51* (36), 9156–9159.

Future developments

The research of the Biocatalysis group will continue to focus on the biocatalytic synthesis of optically active amines using amine dehydrogenases. The substrate scope (and the current limitations) of the known amine dehydrogenases has been elucidated recently. The current set of available amine dehydrogenases can aminate ketones to afford only (R)-configured amines. Furthermore, the source of nitrogen is limited to ammonia and ammonium cations. Therefore, we are aiming at the protein engineering of a new toolbox of amine dehydrogenases that will be capable of: i) aminating prochiral ketones to afford also (S)-configured amines; ii) aminating a wide range of more complex ketones, in particular sterically demanding ketones; iii) performing the amination of ketones and aldehydes using more complex amines than ammonia to give chiral secondary and tertiary amines.

Another aspect of our research plan is the creation of one-pot multi-step enzymatic processes for the conversion of simple molecules as starting material (ideally originated from renewable resources) into high valuable chemical products. This goal is pursued through the combination of isolated enzymes in vitro, whose biocatalytic properties are optimised by protein as well as medium engineering. Additionally, new biocatalytic pathways are created and also introduced into bacterial whole cells. Other ongoing projects are related to the application of enzymes in non-aqueous systems. Biocatalysis in non-aqueous media often shows various advantages and different properties compared to aqueous biocatalysis such as: 1) enhanced enzyme thermostability; 2) ease of product recovery and enzyme recycling; 3) increased substrate solubility; 4) suppression of unwanted water dependent side reactions; 5) influence on thermodynamic equilibrium; and on kinetics; 6) influence on chemo-, stereo-, regio- and enantioselectivity; 7) decrease or elimination of substrate/product inhibition. In this context, we are investigating the properties of different family of enzymes, principally oxidoreductases and transferases, in non-aqueous media. These enzymes will be applied as free and immobilised enzymes. Batch reactions and flow systems will be investigated.

Finally, we are also investigating the possibility to create novel artificial enzymes that may be able to catalyse chemical reactions that are unknown in nature. This artificial (bio)catalysts can be integrated in principle into artificial pathways to solve challenging synthetic problems, shorten synthetic routes and improve efficiency. As an example, we will set up a collaboration with the SOC group (Dr. Fernandez-Ibanez, UvA) for the

development artificial metalloenzymes for the metal-catalyzed C-H functionalization. In particular, we will explore initially the C-H alkenylation of simple arenes. We expect that the confined environment tailored by the metalloenzyme will foster elevated catalytic activities and selectivities. Our design for the synthesis of artificial metalloenzymes is to incorporate a pyridine residue capable of coordinating to the transition metal and catalyzed the C-H alkenylation of simple arenes. After proving the concept with simple arenes, this methodology will be applied to the synthesis of bioactive products of industrial relevance.

Heterogeneous Catalysis and Sustainable Chemistry

Prof. dr.G. Rothenberg, Dr. S. Grecea, Dr. N.R. Shiju, Dr. N. Yan (UvA)

Summary of research activities

Our activities are focused on catalyst and materials discovery and development. We try and answer important fundamental questions in catalysis and sustainable chemistry. In our view, "important" means something that affects the lives of many people, so our focus lies more on bulk chemicals and sustainable energy applications. Details of all the group's projects are available on our website, http://hims.uva.nl/hcsc

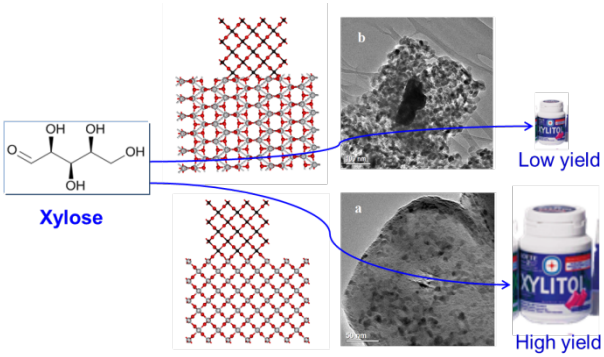
Group highlights 2015

Lignin solubilisation and fractionation in liquid ammonia

As part of the SmartMix CatchBio project, we have developed a new method for solubilising lignin using liquid ammonia. Lignin is nature's richest source of aromatics, yet it is usually burned as a leftover product in biorefining. Using liquid ammonia at 80 C, we managed to solubilise different wood and grass lignins within minutes, enabling their fractionation to useful aromatic derivatives. This project, a collaboration between the Suschem RPA and Wageningen University, opens opportunities for lignin valorisation in future biorefineries using the unique properties of liquid ammonia, a highly coordinating yet non-protic solvent. The results were published in Green Chemistry, the leading scientific journal in the area of sustainable chemistry.

Conversion of biomass into industrially important chemicals

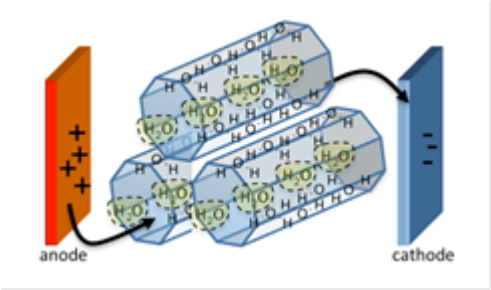
As part of our programme for converting lignocellulosic biomass into various industrially important chemicals, we studied the hydrogenation of xylose (a sugar obtained by the hydrolysis of beechwood hemicellulose) to xylitol, an extensively used compound in the food, cosmetics, and pharmaceutical sectors. With an estimated market of $340m, xylitol is one of the most popular sweeteners. Currently, xylitol is made via catalytic hydrogenation over RANEY® nickel. Although this catalyst is cheap, it deactivates quickly due to leaching and/or poisoning. Any leached Ni must be removed, leading to additional costs. In this work, we found that Ru supported on TiO2 is a highly efficient catalyst. However, we also found that the same TiO2 support with different crystal structures (anatase or rutile) gives very different catalytic efficiency. Characterization of catalysts showed that (mis)matching between the active species and the support is the secret. Similar crystal structures of RuO2 and rutile titania ensure a better interaction during the heating steps of catalyst synthesis. This helps maintain the initial good dispersion of the active species on the support, leading to better activity and selectivity.



Better matching between rutile RuO_2 and rutile titania support leads to smaller Ru particles and higher catalytic activity.

High proton conductivity in cyanide bridged metal-organic frameworks

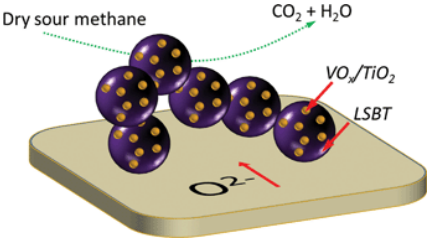
We have shown that metal organic frameworks (MOFs) with cyanide-bridges and highly hydrophilic open channels are excellent proton conductive materials. They enable high proton conductivity, as much as 10−3 Scm−1. The MOF's channels contain two types of water molecules: coordinated ('in-the-framework') water and lattice (absorbed) water. Our studies show that it is the lattice water which is critical for the proton conductivity. The lattice water molecules form a hydrogen-bonding network, through which protons hop along via the Grotthuss mechanism. The fact that (unlike most MOFs) this material is also stable both in water and at relatively high temperatures (up to 150 °C) makes it a promising candidate for real-life applications. As we showed earlier, this class of materials has also special luminescence and magnetic properties. Combining these with ionic conductivity opens opportunities for designing proton-conducting switches controlled by temperature, light and/or external magnetic fields.



Fuel cells

The fuel cells research was launched at HIMS in the year of 2015 during which we completed the constructions of two electrochemical setups. Regarding the research, we started with developing the sulfur/coke-resisting anode catalyst of solid oxide fuel cells. In particular, we discovered that the doped SrTiO3 catalyst exhibited excellent stability and moderate activity towards methane electro-oxidation in the presence of sulfur poisons. Through an in-situ measurement, we understood that the sulfur adsorbates on the electrocatalyst actually promoted the activation of methane. To further enhance the activity of the titanate anode, we then developed a "vanadia grafting" technique. In addition, we succeeded in understanding the degradation mechanism of protonic ceramic electrolyte at ambient conditions, performing the first "metal-free" electrocatalyst trial for

the cathode of proton-exchange membrane fuel cells, and developing a novel electrochemical route for "CO2 to fuels" while generating electricity.



Other activities

HCSC has strong ongoing collaborations with Fudan University (Shanghai, China) and with the Center of Interface Dynamics for Sustainability (Chengdu, China) with joint research projects funded by NWO and by the NSFC and the local Shanghai government. The group also has a long-term ongoing collaboration funded by Solvay on catalysis for sustainable processes.

Grants and prizes

• NWO TOP-PUNT Grant awarded to Prof. Gadi Rothenberg, Prof. Joost Reek and RuG as partner
• STW take off awarded to Prof. Gadi Rothenberg
• NSFC-NWO Advanced Materials grant awarded to Dr. N.R. Shiju and Prof. Gadi Rothenberg
• New materials for sustainable water-alcohol separations, CSC fellowship awarded to Mr. Yiwen Tang.
• New routes from lactic acid to acrylic acid, CSC fellowship awarded to Mr. Wei Zhang

Future Developments

The group is building expertise in electrochemistry and fuel cells, and developing further its knowledge in catalysis for industrial applications, MOFs for molecular separation and catalytic reactions, sustainable processes and predictive modelling.

Key publications 2015

- High proton conductivity in cyanide-bridged metal-organic frameworks: understanding the role of water. Y. Gao, R. Broersen, W. Hageman, N. Yan, M.C. Mittelmeijer-Hazeleger, G. Rothenberg and S. Tanase, *J. Mater. Chem. A.* **2015**, *3*, 22347-22352.

- Discovery and understanding of the ambient-condition degradation of doped barium cerate proton-conducting perovskite oxide in solid oxide fuel cells. N. Yan, Y. Zeng, B. Shalchi, W. Wang, T. Gao, G. Rothenberg and J.L. Luo., *J. Electrochem. Soc.* **2015**, *162*, F1408-F1414 .

- A novel one-dimension chain built of vanadyl ions and pyrazine-2,5-dicarboxylate. M. Lankelma, J. de Boer, M. Ferbinteanu, A.L. Dantas Ramos, R. Tanasa, G. Rothenberg and S. Tanase, *Dalton Trans.* **2015**, *44*, 11380-11387.

- Catalytic acetoxylation of lactic acid to 2-acetoxypropionic acid, en route to acrylic acid. R. Beerthuis, M. Granollers, D.R. Brown, H.J. Salavagione, G. Rothenberg and N.R. Shiju, *RSC Adv.* **2015**, *5*, 4103-4108.

- Catalytic routes towards acrylic acid, adipic acid and ε-caprolactam starting from biorenewables. R. Beerthuis, G. Rothenberg and N.R. Shiju, *Green Chem.* **2015**, *17*, 1341-1361.

- Lignin solubilisation and gentle fractionation in liquid ammonia. Z. Strassberger, F. van der Klis, D. S. van Es, S. Tanase, P. Prinsen and G. Rothenberg, *Green Chem,* **2015,** *17*, 325-334.

Homogeneous, Supramolecular Catalysis and Spectro-electrochemistry

Prof. dr. J.N.H. Reek, Prof. dr. B. de Bruin, Dr. Ir. J.I. van der Vlugt, Dr. M. Tromp (UvA)

Research topics

- Development of new approaches in transition metal catalysis and catalyst recovery, including supramolecular approach, ligand design, bioinspired approaches, noninnocent ligands and metal complexes in unusual oxidation states.
- Combinatorial catalysis and kinetic analysis using robotics and HTE.
- Development of new reactions using rational approaches based on spectroscopic analysis, kinetics and dft calculations.
- Application of a diverse set of analytical techniques and their application in homogeneous and heterogeneous catalysis, photocatalysis, redox catalysis and biocatalysis.
- Energy and electron transfer in (supra)molecular dyad and triad systems driven and controlled by light absorption and/or a redox reaction, relevant for photodriven reactions.
- Kinetics, in situ spectroscopy and DFT calculations on reaction mechanisms
- Bio-inspired approached, including catalyst encapsulation, bifunctional catalysis, catalyst selection
- Hydroformylation, hydrogenation, C-H activation, small molecule activation
- Metalloradicals and catalysis
- Application of reactive ligands (redox-active, chemoresponsive) for bond functionalization and catalysis
- C1-carbene chemistry
- Development of advanced spectroscopic techniques as tools in catalysis.

Summary of research activities

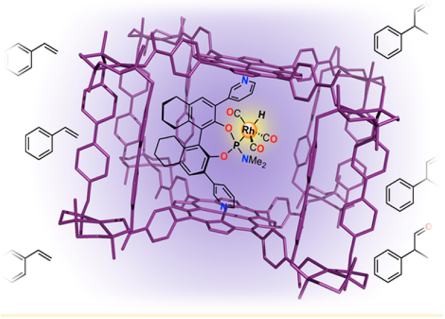
The mission of the research group is the development of supramolecular and bio-inspired tools to enhance the field of transition metal catalysis. Eventually these new tools should lead to the discovery of new catalyst systems that display unrivaled selectivities and activities for reactions that are relevant to the fine chemical or bulk industry, or contribute to societal challenges such as the transition to alternative energy sources or bio-based economy.

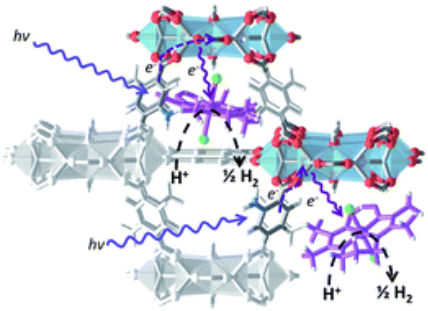
Research highlights per staff member

Prof. dr. Joost Reek

We continued our efforts to develop bio-inspired supramolecular catalysts for various transformations. In one example, we have generated a system in which a chiral rhodium complex is encapsulated in a self-assembled metallocage (figure left below). Once placed in confined space the catalyst converted styrene into chiral aldehyde with high selectivity. Also in the area of catalysis for green energy applications we have been exploring various bio-inspired supramolecular approaches. We have used METAMORphos as a proto-

reactive ligand in formic acid dehydrogenation, which is important in the context of hydrogen storage. In collaboration with a Gascon from Delft, we have generated cobalt catalyst in the confined spaces of a MOF. This systems has been demonstrated to be active in the light-driven hydrogen formation reaction (right figure below), which is important in the context of our solar to fuel program.

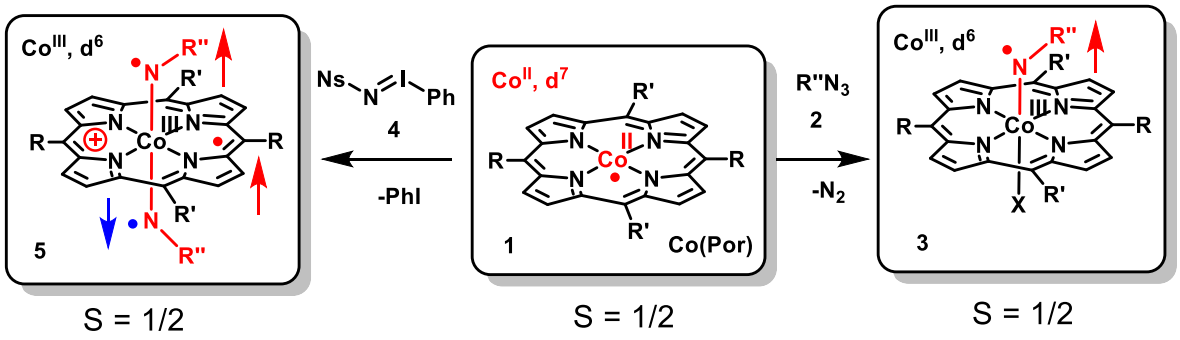




- Enantioselective hydroformylation by a Rh-catalyst entrapped in a supramolecular metallocage García-Simón, C.; Gramage-Doria, R.; Raoufmoghaddam, S.; Parella, T.; Costas*, M.; Ribas*, X.; and Reek*, J. N.H. *J.Am. Chem. Soc.* **2015**, *137*, 2680-2687.
- Co@ NH 2-MIL-125 (Ti): cobaloxime-derived metal--organic framework-based composite for light-driven H 2 production. Nasalevich, M. A.; Becker, R.; Ramos-Fernandez, E. V.; Castellanos, S.; Veber, S. L.; Fedin, M. V.; Kapteijn, F.; Reek*, J. N. H.; van der Vlugt,* J. I.; and Gascon*, J. *Energy Environ. Sci.* **2015**, *8*, 364-375.
- Dehydrogenation of formic acid by Ir--bisMETAMORPhos complexes: experimental and computational insight into the role of a cooperative ligand. Oldenhof, S.; Lutz, M.; de Bruin, B.; van der Vlugt, J. I.; and Reek*, J. N. H. *Chem. Sci.* **2015**, *6*, 1027-1034.

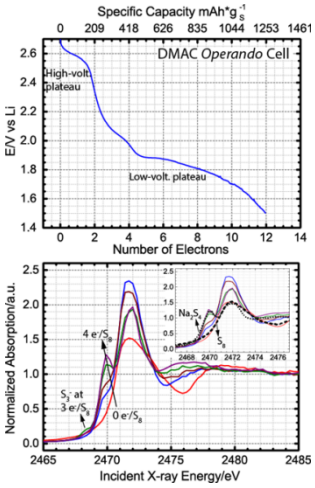
Prof. dr. Bas de Bruin

Besides the work on acid hydrogenation (as described above in the group highlight), the sub-group of de Bruin further contributed the field of metallo-radical catalysis. One of the highlights in this field is a study reported in JACS describing detailed spectroscopic characterization of the nitrene-radical intermediates of key relevance in (por)Co-catalyzed nitrene-transfer reactions. These key-intermediates were characterized with several techniques (EPR, XAS, UV-Vis, ESI-MS, IR, VCD). Several unexpected insights evolved from this study, such as the fact that mono- and bis-nitrene intermediates can be formed of which the latter are quite unstable, and the fact that mono-nitrene species are 6-coordinate. This insight is of importance for further development of efficient nitrene-transfer catalysis, in particular for selective C-H bond amination.



- Hydrogenation of Carboxylic Acids with a Homogeneous Cobalt Catalyst, Korstanje, T.J.; van der Vlugt, J.I.; Elsevier, C.J.*; de Bruin, B.*, *Science*, **2015**, *350* (6258), 298-302. DOI: 10.1126/science.aaa8938. [link]
- Dynamic Ligand Reactivity in a Rhodium Pincer Complex, Tang, Z.; Otten, E.; Reek, J.N.H.; van der Vlugt, J.I.*; de Bruin, B.*, *Chem. Eur. J.,* **2015**, *21*, 12683–12693. [link] 'Hot Paper'. Front Cover. Cover Profile.
- Characterization of Porphyrin-Co(III)-'Nitrene radical' species relevant in catalytic nitrene transfer reactions. Goswami, M.; Lyaskovskyy, V.; Domingos, S.R.; Buma, W.J.; Woutersen, S.; Troeppner, O.; Ivanović-Burmazović, I.; Lu, H.; Cui, X.; Zhang, X.P.*; Reijerse, E.J.; DeBeer, S.; van Schooneveld, M.M.; Pfaff, F. F.; Ray, K.; de Bruin, B.*, *J. Am. Chem. Soc.,* **2015**, *137*, 5468−5479. [link]
-

Dr. Moniek Tromp



The development, application and interpretation of X-ray absorption and X-ray emission spectroscopy has been continued and expanded (JPhysChemC2015), showing great potential in obtaining detailed electronic properties from the data directly (without complicated simulation/analysis procedures).

At the same time our efforts in the electrochemical field were awarded by the successful development of a spectro-electrochemical cell for the operando X-ray absorption spectroscopy study of batteries (JES2015). The cell allows spatial- and time-resolved characterization of species in the individual electrodes as well as the electrolyte, during charging and discharging, thereby providing novel insights in mechanisms and deactivation processes, important for the development of novel high capacity and stable battery systems for, for example, the automotive industry.

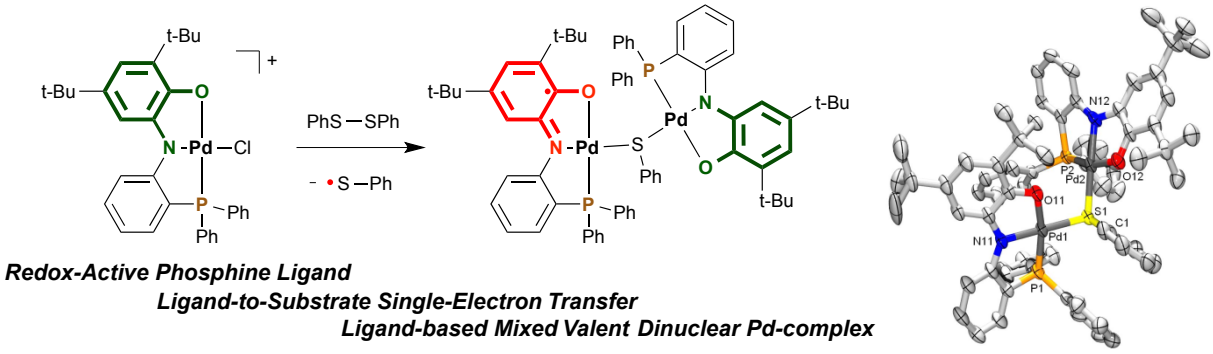
An important application of our advanced spectroscopy methods led, in the heterogeneous catalysis field, towards a breakthrough in understanding the structure and electronics of the catalytically active Cu site for the important methane to methanol (gas-to-liquid) reaction (NatureComm215).

- R. J. Thomas, J. Kas, P. Glatzel, M. Al Samarai, F. M. F. de Groot, R. A. Mori, M. Kavcic, M. Zitnik, K. Bucar, J. J. Rehr, M. Tromp, 'Resonant Inelastic X-ray Scattering of molybdenum oxides and sulfides', *J. Phys. Chem. C* **2015**, *119*(5), 2419–2426.

- Y. Gorlin, A. Siebel, M. Piana, T. Huthwelker, H. Jha, G. Monsch, F. Kraus, H. A. Gasteiger, M. Tromp, 'Operando Characterization of Intermediates Produced in a Lithium-Sulfur Battery', *J. Electrochem. Soc.* **2015**, *162*(7), A1146-A1155.
- S. Grundner, M. Markovits, G. Li, M. Tromp, E. A. Pidko, E.J.M. Hensen, A. Jentys, M. Sanchez-Sanchez, J.A. Lercher, 'Single site trinuclear copper oxygen clusters in mordenite for the selective methane to methanol conversion', *Nature Commun*. **2015**, *6*, 7546.

Dr.ir. Jarl Ivar van der Vlugt

The sub-group of van der Vlugt continued research in the field of reactive ligand-induced substrate activation. One of the highlights is a study reported in ACIE detailing the homolytic activation of homodiatomic bonds (e.g. disulfides) on closed-shell Pd(II) platforms, via redox-active ligand-to-substrate single electron transfer. This work enables the formation of unique ligand-based mixed-valent dinuclear architectures, which have interesting switchable photochemical and magnetochemical properties. Furthermore, the conceptual design of a new flexidentate ligand led to the first example of reversible facile cyclometalation on Rh(I), with isolation of a rare Rh-(C-H) agostic complex. Finally, the use of a reactive pincer ligand has allowed the activation of a well-defined nickel-azido species, with intermediacy of a transient nickel-nitrido complex. These developments and mechanistic insights are of relevance for a number of catalytic applications, which are currently under investigation.



Redox-Active Phosphine Ligand
Ligand-to-Substrate Single-Electron Transfer
Ligand-based Mixed Valent Dinuclear Pd-complex

- Efficient C-H activation of arenes by a photoactivated Ni^{II}(azide) – Formation of a transient nickel nitrido complex, V. Vreeken, M. Lutz, B. de Bruin, J. N. H. Reek, M.A. Siegler, J.I. van der Vlugt* *Angew. Chem. Int. Ed.* **2015**, *54*, 7055-7059.
- Facile synthesis and versatile reactivity of an unusual cyclometalated Rh^{I} pincer complex, L.S. Jongbloed, B. de Bruin, J.N.H. Reek, M. Lutz, J.I. van der Vlugt* *Chem. Eur. J.* **2015**, *21*, 7297-7305.
- Redox-active ligand-induced homolytic bond activation, D.L.J. Broere, L.L. Metz, B. de Bruin, J.N.H. Reek, M.A. Siegler, J.I. van der Vlugt* *Angew. Chem. Int. Ed.* **2015**, *54*, 1516-1520.

Metals in Catalysis, Biomimetics & Inorganic Materials

Prof. dr. E. Bouwman, Dr. S. Bonnet, Dr. D.G.H. Hetterscheid (UL)

Research topics

- Inorganic chemistry
- Homogeneous- and photo-catalysis (reported within NIOK)
- Biomimetic and bioinorganic chemistry
- Molecular materials

Summary of research activities

Copper(I) hydridotrispyrazolylborate complexes have been developed to be employed as sensitizers for ethene sensors. A series of hydridotrispyrazolylborate ligands was prepared, with a number of different substituents based on the common template $[Tp^{CF3,4\text{-}RPh}]^-$ (R = NMe_2, OMe, H, F, Cl, CF_3 or NO_2). The X-ray crystal structures of many of the resulting ethene and carbonyl complexes have been determined; the complexes all have nearly identical coordination cavities. The substituents R were selected based on their Hammett σp parameters and their compatibility with the forcing conditions required for the synthesis of the ligands. The resulting ethene and carbonyl complexes were studied using NMR and IR spectroscopy; the properties such as the chemical shifts of the ethene protons and CO-stretching frequencies were found to match nicely to the expectations based on the σp parameters of the substituents. The compounds were used in gas-detection experiments with ethene and ethanol (for comparison) and were found to be extremely effective gas sensors with detection limits well below 100 ppb for ethene and 1 ppm for ethanol. The kinetics of the interactions between the gases and the copper(I) complexes were studied and found to comply with expectations with considerably higher equilibrium dissociation constants for ethanol than for ethene. A mechanism has been proposed that explains the observed type and intensity of the response of the sensors upon exposure to ethene gas and their correspondence with the Hammett σp parameters of the substituents. (van Dijkman, T.F.; Siegler, M.A.; Bouwman, E., *Dalton Trans.* **2015**, *44*, 21109)

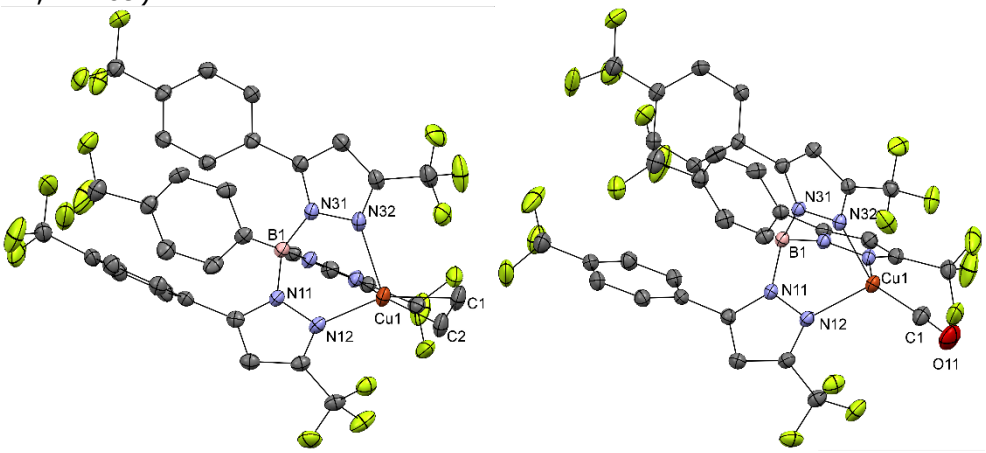
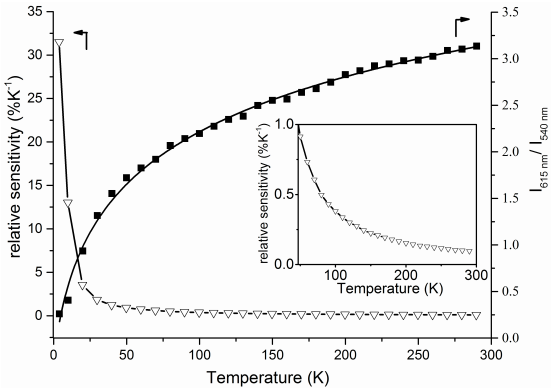


Figure:Structure of the compounds [Cu(I)($Tp^{CF3,4\text{-}CF3Ph}$)(ethene)] (left) and [Cu(I)($Tp^{CF3,4\text{-}CF3Ph}$)(CO)] (right).

Luminescent lanthanoid coordination polymers are developed that may have potential applications in sensing of e.g. small molecules or temperature. A ratiometric thermometer based on a mixed-metal Ln^{III} metal-organic framework has been obtained that has good sensitivity in a wide temperature range from 4 to 290 K with a quantum yield of 22% at room temperature. The sensing mechanism in the europium-doped compound $Tb_{0.95}Eu_{0.05}H\mathbf{L}$ ($H_4\mathbf{L}$ = 5-hydroxy-1,2,4-benzenetricarboxylic acid) is based not only on phonon-assisted energy transfer from Tb^{III} to Eu^{III} centers, but also on phonon-assisted energy migration between neighbouring Tb^{III} ions. It shows good performance in a wide temperature range, especially in the range of 4–50 K, reaching a sensitivity up to 31% K^{-1} at 4 K (see Figure). (Liu, X.; Akerboom, S.; de Jong, M.; Mutikainen, I.; Tanase, S.; Meijerink, A.; Bouwman, E., *Inorg. Chem.* **2015**, *54*, 11323).



Transition metal complexes, and among them those based on ruthenium, are part of a wide family of "photopharmacological" compounds that can switch between a biologically inactive and a biologically active state upon light irradiation. To be activated, many photopharmaceutical compounds require UV or blue light, which does not penetrate very far in living tissues. To solve this problem, we integrated a light-activatable ruthenium compounds into the formulation of red-to-blue upconverting liposomes. Using these liposomes, the red light from a commercial phototherapeutic laser was transformed locally into blue excitation that was transferred non-radiatively to the nearby complex, thus activating it (Askes, S. H. C.; Kloz, M.; Kennis, J. T. M.; Bruylants, G.; Bonnet, S.; *Phys. Chem. Chem. Phys.* **2015**, *17*, 27380). Unfortunately, TTA upconversion is an oxygen-sensitive process, and it had up to now to be performed under inert atmosphere. However, we demonstrated recently that biocompatible antioxidants such as sulfites could lower the oxygen concentration to a level where efficient red-to-blue upconversion can be directly observed under air (Askes, S. H. C.; López Mora, N.; Harkes, R.; Koning, R. I.; Koster, B.; Schmidt, T.; Kros, A.; Bonnet, S.; *Chem. Commun.* **2015**, *51*, 9137).

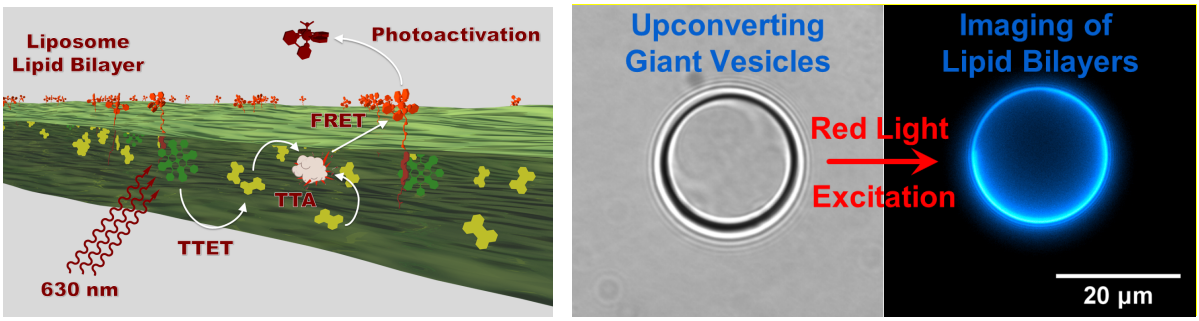


Figure: Left: red-to-blue triplet-triplet annihilation (TTA) upconversion followed by non-radiative energy transfer (FRET) in the bilayer of liposomes functionalized with blue-light sensitive ruthenium compounds. Right: visualization of red-to-blue upconverting giant unilamellar vesicles in air in presence of sulphites.

Another topic studied at MCBIM is photocatalysis in presence of lipid bilayers. Recently, unidirectional photocatalytic electron transfer from a hydrophilic electron donor encapsulated in the interior of a liposome, to a hydrophilic electron acceptor on the other side of the membrane, has been demonstrated using a simple membrane-soluble electron relay, 1-methoxy-N-methylphenazinium (MMP^+). The total amount of photoproduct exceeds the number of moles of MMP^+ present, thus showing that the transport of electrons is catalytic (Limburg, B.; Bouwman, E.; Bonnet, S.; *Chem. Commun.* **2015**, *51*, 17128). Such strategies, coupled to water oxidation and water reduction, may help developing efficient systems for artificial water splitting.

In order to store solar energy as a chemical fuel, water oxidation catalysts are required that operate on a very flat potential energy landscape. Such catalyst are illusive as scaling relationships dictate a significant deviation of such a path since one cannot stabilize unstable intermediates without over-stabilization of stable catalytic intermediates by modifications of the catalyst structure alone. In this approach the mechanism of water oxidation is studied in detail by a plethora of in situ spectroscopy and characterization techniques coupled to electrochemistry to firmly establish which species are present at the electrode interface during the catalytic reaction. This allows one to convincingly connect the observed kinetics to the actual structure of the true active species, which is indispensable for drawing reliable conclusions concerning the catalytic mechanism. We have recently published a preliminary study concerning iron based water oxidation catalysts demonstrating the huge potential of these techniques (Kottrup, K. G.; Hetterscheid, D. G. H., *Chem. Commun.* **2016**, *52*, 2643). Currently, we are employing these techniques to investigate the influence of the second coordination sphere, in order to break scaling relationships in case of molecular iron and copper based water oxidation catalysts.

Key publications 2012-2015

- Limburg, B.; Bouwman, E.; Bonnet, S.; Catalytic photoinduced electron transport across a lipid bilayer mediated by a membrane-soluble electron relay. *Chem. Commun.*, **2015**, *51*, 17128.
- V. H. S. van Rixel, A. Busemann, A. J. Göttle, S. Bonnet; Preparation, stability, and photoreactivity of thiolato ruthenium polypyridyl complexes: can cysteine derivatives protect ruthenium-based anticancer complexes? *J. Inorg. Biochem*. **2015**, *150,* 174.
- Ording-Wenker, E.C.M.; Van der Plas, M.; Siegler, M.A.; Bonnet, S.; Bickelhaupt, F.M.; Fonseca Guerra, C.F.; Bouwman, E.; Thermodynamics of the Cu^{II} μ-Thiolate and Cu^{I} Disulfide Equilibrium: A Combined Experimental and Theoretical Study. *Inorg. Chem.* **2014**, *53*, 8494.
- Ording-Wenker, E.C.M.; Van der Plas, M.; Siegler, M.A.; Fonseca Guerra, C.F.; Bouwman, E.; Protonation of a Biologically Relevant Cu^{II} μ-Thiolate Complex: Ligand Dissociation or Formation of a Protonated Cu^{I} Disulfide Species? *Chem.-Eur. J.* **2014**, *20*, 16913.
- Kottrup, K. G.; Hetterscheid. D. G. H., "Evaluation of iron-based electrocatalysts for water oxidation – an on-line mass spectrometry approach." *Chem. Commun*, **2016**, *53*, 2643.

Future developments

In the topic of biomimetics we plan to continue the research towards the electrocatalytic reduction of protons to form dihydrogen. Future studies will be directed to the synthesis of novel ligand systems including both heterocyclic carbene groups, thiolate functions and proton-acceptor sites. In collaboration with Célia Fonseca Guerra and Matthias Bickelhaupt the study of the reactivity of pyridine-disulfide ligands with copper ions will be expanded to other metals, notably cobalt, iron and manganese, but also to other nitrogen-containing ligands, notably imidazoles. The research concerning the copper-ethene interactions will be further developed with the aim to generate small, low-cost sensors for ethene detection.

The research of Dr. Bonnet will develop in three directions: the first one aims at developing light-activatable ruthenium-based anticancer prodrugs with low toxicity in the dark and high toxicity under light irradiation. Part of this research aims at developing biocompatible upconversion systems that allow for triggering high-energy photochemistry with low-energy light. Six PhD students and two postdocs have started working on this topic in 2012-2014. The second topic aimed at developing biological application of spin-crossover inorganic complexes, for example for sensing analytes. Collaboration with graphene experts (Gregory Schneider, LIC) and with surface physicists (LION, Van Ruitenbeek, Van der Molen) are currently undergoing (1 PhD). Finally, Bonnet's expertise in photochemistry will combine perfectly with the focus on homogeneous catalysis of the Bouwman group, to perform photocatalysis.

Co-ordination and Organometallic Chemistry

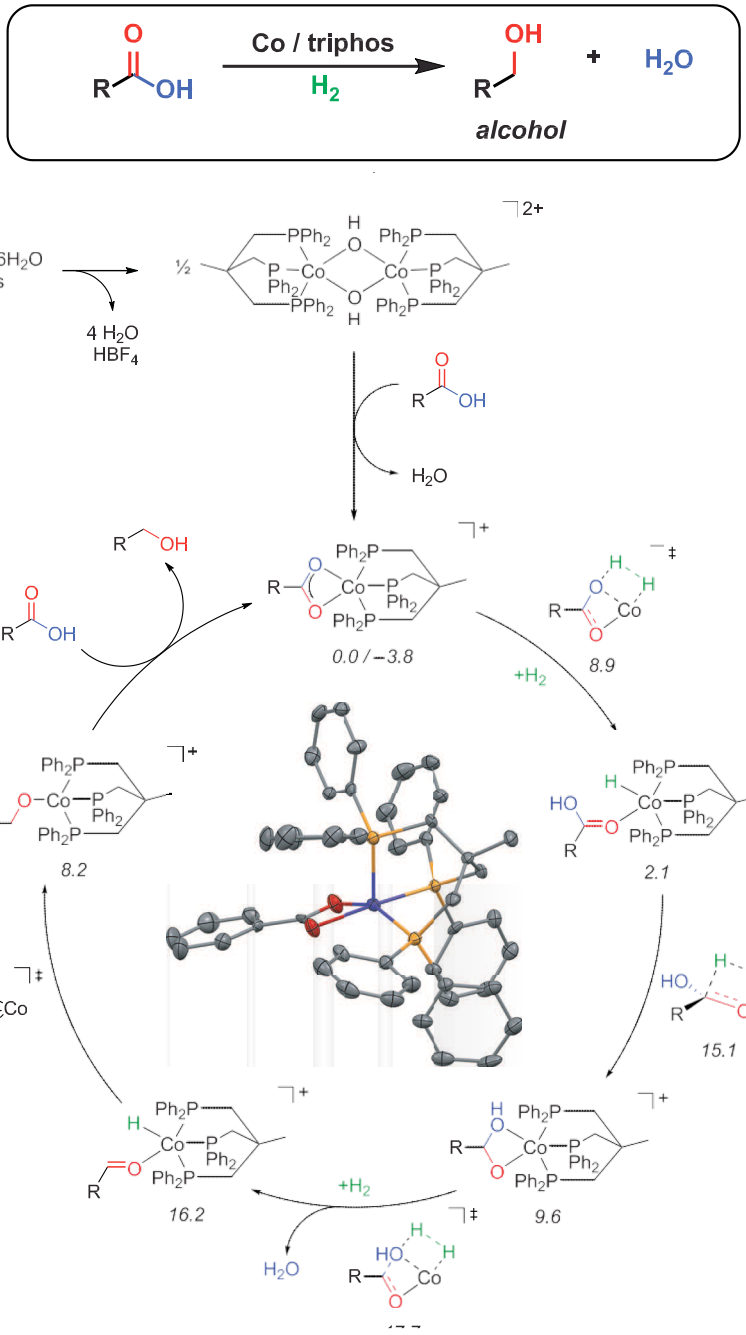
Prof. dr. C.J. Elsevier

Research topics
Organometallic and coordination chemistry
Catalytic bond-formation and -breaking
High-pressure NMR and transition metal NMR spectroscopy
Heterogenization of homogeneous catalysts

Summary of research activities
The group Molecular Inorganic Chemistry at the University of Amsterdam is involved in fundamental research in Coordination and Organometallic Chemistry, notably the synthesis, characterization and application of organometallic compounds and homogeneous catalysts. We try to approach catalysis in a rational way by studying single steps and constitute new catalytic cycles from these building blocks. We also engage in finding alternatives to existing reactions, for instance hydrogenations, by knowledge-driven choice and engineering of the metal-ligand combinations. The counterpart lies in careful analysis of the mechanism of homogeneous catalytic, metal-mediated reactions and to discover new solutions and improvement of processes, based on understanding of its details. Organometallic chemistry, which resides at the basis of all catalytic processes, is the main topic of the activities in the group. The reactions concerned are mainly bond-forming and bond-breaking reactions between carbon and the other elements, with emphasis on carbon, hydrogen, and late transition metals. Processes studied are, e.g., hydrogenation, hydrosilylation, C-C coupling reactions. Several of these have been studied under pressure and in neoteric solvents, e.g. supercritical fluids. Spectroscopic studies of reactions under pressure are carried out to evaluate the reaction and intermediates under conditions similar to those in the catalytic reactions studied. The research of the group has partly aimed at the design and implementation of self-organizing amphiphilic metal-organic molecules, especially a novel class of metallo-amphiphiles that are characterized by the intrinsic presence of a metallic group as part of the amphiphile, that acts as the polar headgroup. These systems are particularly amenable to the formation of micelles and inverted micelles, or vesicles, with the aim to enhance catalysis and bond activation taking place at the interface of polar and apolar media (such as water/alkane). Other methodologies for heterogenization, immobilization and recycling of homogeneous catalysts receive attention.
N-heterocyclic carbene (NHC) ligands as well as rigid bidentate N-ligands in late transition metal compounds aimed at catalytic carbon-element bond forming reactions continues to be an important research topic in the group. Currently, a focal point of our research concerns the design and application of transition metal complexes with heteroditopic bis-carbene and carbene-N-ligands for organometallic chemistry and applications in homogeneous catalysis.

In 2015 Ties Korstanje conceived the homogeneously catalyzed hydrogenation of carboxylic acids to alcohols using earth-abundant cobalt. The catalyst pairs $Co(BF_4)_2{\cdot}6H_2O$ with a tridentate phosphine ligand; it is able to reduce a wide range of

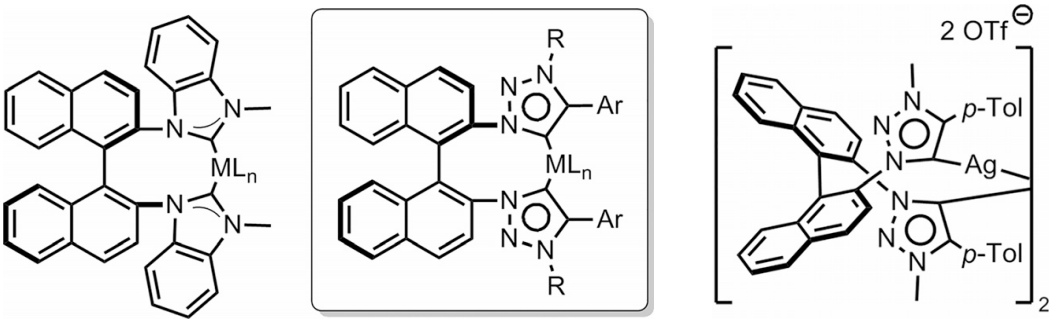
esters and carboxylic acids under relatively mild conditions (100°C, 80 bar H_2) and reaches turnover numbers of up to 8000. The reduction of esters and carboxylic acids to alcohols is a highly relevant conversion for biomass conversion as well as for the pharmaceutical and fine-chemical industries. It is commonly performed using stoichiometric reagents and the catalytic hydrogenation of the acids previously required the use of precious metals. This work was executed in collaboration with prof. Bas de Bruin.



Homogeneous catalysts for the hydrogenation of esters and acids under mild reaction conditions are internationally pursued with vigor, especially varieties involving first-row transition metals. Such reactions are still hardly known, especially involving metals such as cobalt or iron. We have now reached *carboxylic acid* a major break-through by employing $Co(BF_4)_2 \cdot 6H_2O$ together with a tridentate phosphine, obviating the use of

ruthenium-based catalysts. A special feature of this catalyst is that it even hydrogenates a host of carboxylic acids, which are even harder to reduce than esters. The mechanism of the reaction (see figure) was studied by kinetics and spectroscopy with detection of crucial d^7 Co(II) intermediates. Our studies have resulted in a paper in Science.

The project by Ruben Drost has been finalized. The conceptually interesting 'partial poisoning protocol' that has been reported last year, has been published. This protocol allows to conclusively distinguish between molecular and nano-particle catalysts and consists of three steps: Poison validation, partial poisoning and confirmation of the viability of the method through orthogonal control experiments. Together they form a comprehensive method that provides reliable results for studies in catalysis.



Soraya Sluijter has finalized her studies involving transition metal compounds featuring chelating di(NHC) and related compounds for catalytic transfer hydrogenation. Several of these appear to be very active in ketone and ester hydrogenation. Late transition metal complexes involving mesoionic carbene moieties have been synthesized and their catalytic abilities toward hydrogenation and hydrogenolysis as well as enantiselective hydrosilylation were studied. Soraya Sluijter has written her thesis and several papers that have all but one been published.

Key publications 2013-2015

- Drost, R.M.; Bouwens, T.; Van Leest, N.P.; De Bruin, B.; Elsevier, C.J.; Convenient Transfer Semihydrogenation Methodology for Alkynes Using a PdII-NHC Precatalyst, *ACS Catalysis* **2014***, 4*, 1349-1357.
- Sluijter, S.N.; Elsevier, C.J.; Synthesis and Reactivity of Heteroditopic Dicarbene Rhodium(I) and Iridium(1) Complexes Bearing Chelating 1,2,3-Triazolylidene-Imidazolylidene Ligands, *Organometallics* **2014**, *33*, 6389-6397.
- Sluijter, S.N.; Jongkind, L.J.; Elsevier, C.J.; Synthesis of BINAM-based chiral di-1,2,3-triazolylidene complexes and application of the di-NHC Rh(I) catalyst in enantioselective hydrosilylation. *Eur.J.Inorg.Chem*., **2015**, *18*, 2948-2955.
- Drost, R.M.; Rosar, V.; Marta, S.D.; Lutz, M.; Dimitri, N.; Milani, B.; de Bruin, B.; Elsevier, C.J.; Pd-catalyzed *Z*-selective semihydrogenation of alkynes: determining the type of active species. *Chem.Cat.Chem*., **2015**, *7*, 2095-2107.
- Korstanje, T.J.; van der Vlugt, J.I.; Elsevier, C.J.; de Bruin, B.; Hydrogenation of carboxylic acids with a homogeneous cobalt catalyst. *Science*, **2015**, 350, 298-302.

Future developments

Research efforts will generally continue to be aimed at design and synthesis of organometallic compounds for stoichiometric and homogeneous catalytic reactions, particularly the addition of small molecules to unsaturated compounds, carbon-element bond forming and reduction reactions. In this respect, the important recent discovery that late-transition metal N-heterocyclic carbene compounds are stable and exceptionally selective catalysts for selective hydrogenation reactions, either using molecular hydrogen or hydrogen transfer agents, will receive continued attention. Applications of NMR spectroscopy, especially concerning heavier elements and transition metals in particular, will also continue to receive attention.

Organic and Organometallic Chemistry

Prof. dr. K. Lammertsma, Dr. A.W. Ehlers, Dr. J.C. Slootweg (VU)

Research topics

- The design of and catalysis with frustrated Lewis pairs.
- Syntheses and applications of organophosphorus reagents and compounds.
- Catalytic reactions that eliminate organophosphorus waste.
- Transition metal complexes with phosphorus ligands.
- Sustainable building blocks, polydentate ligands, and catalysts.
- Synthesis of chiral silicates.

Summary of research activities

Our organophosphorus research explores new vistas with focus on the sustainability of phosphorus, an essential element in the life cycle, that is becoming scarce at the current rate of consumption of the world's reserves. By combining synthetic methodologies with high-level theoretical modeling, new reagents, tailor-made building blocks, novel compounds classes, catalysts, ligands, and (opto-electronic and polymeric) materials are designed in atom- and step-efficient manners for synthetic and catalytic applications. By exploring the relationship between phosphorus and carbon, the electronic influence on transition metals, and the valency of phosphorus, new venues are probed for the sustainable and versatile use of organophosphorus compounds.

Group highlights 2016

Phosphorus

White phosphorus (P_4) is the starting material of most organophosphorus products produced by the chemical industry, but there are still no practical methods to accomplish this conversion directly and selectively. Such methods are needed if the current synthetic route via PCl_3 is to be circumvented. Alternatives that use alkali metals or transition metals are nonselective, low-yielding, expensive, and/or impractical. Insight is needed on how to selectively activate P_4. We are developing approaches akin to frustrated Lewis pair (FLP) chemistry. This methodology provides ample opportunities for selective functionalization.

Phosphorus is an enabling element in many FLPs. The design of rigid Al/P-based FLPs stands out favorably against comparable B/P-based ones that, so far, attract most attention. Electronic and steric tuning enables the Al- and B-sites to act similarly with subtle differences, while the rigidity of the FLPs can be controlled by manipulating the carbon spacer between the Lewis acid and base sites. We have developed distinguishing features for the activation of small molecules like dihydrogen (H_2), carbon dioxide (CO_2) and other small molecules.

Phosphorus containing ligands are crucial to give numerous coordination complexes their specific function in a broad diversity of catalytic reactions. Chiral ligands are a must in enantioselective catalysis, i.e., catalytic asymmetric synthesis, to obtain, e.g., bioactive

compounds with desirable pharmaceutical properties. This activity of the catalysts is achieved by tuning ligands. Hence the convenient access to chiral ligands is most relevant. Despite an immense number of P-ligands, few 1,3-N/P-ligands are known due to the limited synthetic routes. Particularly such ligands are extremely tunable. To remedy this deficiency we have developed a simple protocol to access 1,3-N/P-ligands and are exploring the potential of their organometallic complexes in homogeneous catalysis.

One of the biggest scientific challenges that our society faces is the depletion of phosphorus resources that are essential for all life on earth. Over two thirds of the world's reserve of phosphorus is located in Morocco/Western Sahara, setting the stage for political unpredictability. To reduce this resource dependency, it is imperative to develop new technologies for the preservation of phosphorus. We are amongst the first to address the sustainability in phosphorus. Setting the process in motion constitutes a paradigm shift, trailing by decades the universal focus on energy and CO_2. We are developing methods to reduce phosphine oxides for recycling of phosphorus compounds. We are also pursuing catalytic reactions, like the Wittig reaction, to circumvent the waste of stoichiometric amounts of phosphorus products. These approaches will also give an impetus to CO_2 reduction technology.

Silicon

Silicates with five carbon substituents are remarkably stable in spite of the absence electronegative groups. Yet, in solution they show dynamic behavior with the stereoisomers undergoing rapid stereomutations. We have characterized several stereoisomers by NMR spectroscopy. The origin of the interchange of the ligands on pentacoordinate elements has long been discussed in terms of the Berry pseudorotation and Ugi’s turnstile rotation, which are derived from the mechanisms earlier presented by Muetterties. Our rigorous computational analysis has shown that also the turnstile rotation is, in fact, a Berry pseudorotation. By introducing ample steric hindrance some of the pseudorotations can be blocked, thereby simplifying the dynamics of the silicates. We have now shown what the consequences are for the Desargues-Levi Graph and how configurationally stable, chiral silicates can be developed. The insights obtained from this research are crucial for developing chiral ligands for organometallic complexes to enable directed catalytic asymmetric synthesis with predictable enantiomeric outcomes.

Energy

Supramolecular antenna systems harvest a much broader spectrum of light and thereby enable capturing more energy. We have developed such systems based on extended and fused NDI based on extensive computational surveys. These antenna’s absorb light in the 600-750 nm range and we have prototypes that should absorb above 800 nm. Our first paper in this area was featured on the cover of Chemistry – A European Journal.

Key publications 2012-2015 (Max 5)

- Devillard, M.; Declercq, R.; Nicolas, E.; Ehlers, A.W.;Backs, J.; Saffon-Merceron, N.; Bouhadir, G.; Slootweg, J.C.; Uhl, W.; Bourissou, D.; A significant but constrained

geometry Pt -> Al interaction: fixation of CO_2 and CS_2, activation of H_2 and $PhCONH_2$ *J. Am. Chem. Soc.* **2016**, *138*, 4917-4926.

- Borger, J.E.; Ehlers, A.W.; Lutz, M.; Slootweg, J.C.; Lammertsma, K.; Transferring $[RP_4]^-$ using a BPh_3 stabilized butterfly anion, *Angew. Chem. Int. Ed.* **2016**, *55*, 613–617.
- Borger, J.E.; Ehlers, A.W.; Lutz, M.; Slootweg, J.C.; Lammertsma, K.; Functionalization of P_4 by means of a Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutane anion, *Angew. Chem. Int. Ed.* **2014**, *53*, 12836-12839.
- Van Dijk, T.; Burck, S.; Rong, M.K.; Rosenthal, A.J.; Nieger, M.; Slootweg, J.C.; Lammertsma, K.; Facile Synthesis of Phospha-amidines and Phospha-amidinates using Nitrilium Ions as Imine Synthon, *Angew. Chem. Int. Ed.* **2014**, *53*, 9068=9071.
- Rombouts, J.A.; Ravensbergen, J.; Frese, R.N.; Kennis, J.T.M.; Ehlers, A.W.; Slootweg, J.C.; Ruijter, E.; Lammertsma, K.; Orru, R.V.A.; Synthesis and photophysics of a red-light absorbing supramolecular chromophore system, *Chem. Eur. J.* **2014**, *20*, 10285-10291.

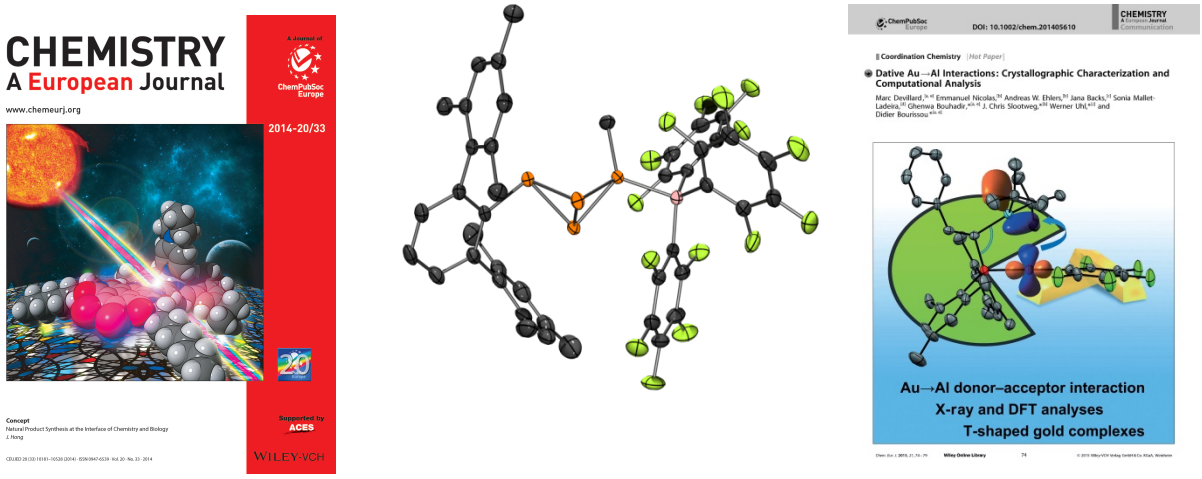


Figure: front cover (left) and frontispiece (right) of publications in 2014. Middle: X-ray structure of functionalized white phosphorus.

Future developments

Our research is directed to use our expertise in organophosphorus chemistry blended with a physical-organic approach to advance sustainability in phosphorus. The issue is of eminent importance as phosphate ore, the source of all phosphorus products, is rapidly being depleted. As phosphorus is an essential element in the life cycle, it is important that the chemical sector implements sustainability in phosphorus. This is still not the case. Our research will focus on all aspects of closing the cycles for use and re-use of phosphorus products, eliminating waste, while advancing the beneficial feature of novel compounds, ligands, catalysts, and materials.

Synthetic & Bio-Organic Chemistry

Prof. dr. ir. R.V.A. Orru, Dr. E. Ruijter (VU)

Research topics

- Natural product synthesis
- Diversity-oriented synthesis
- Multicomponent reactions
- Biocatalysis
- Palladium catalysis

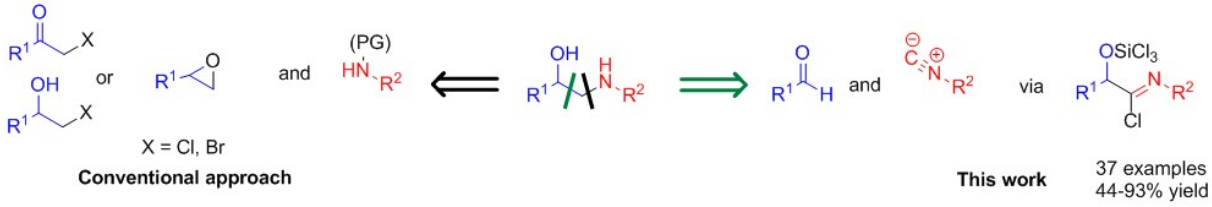
Summary of research activities

Our main research interest focuses on sustainable synthetic method development employing cascade, domino (or tandem) processes. This approach, using simple starting materials to generate highly diverse libraries of functionalized small molecules in a single step, is not only very efficient, versatile, and environmentally friendly, but importantly provides rapid access to key compounds for small molecular probes for chemical biology research, building blocks for medicines or ligands for catalysis.

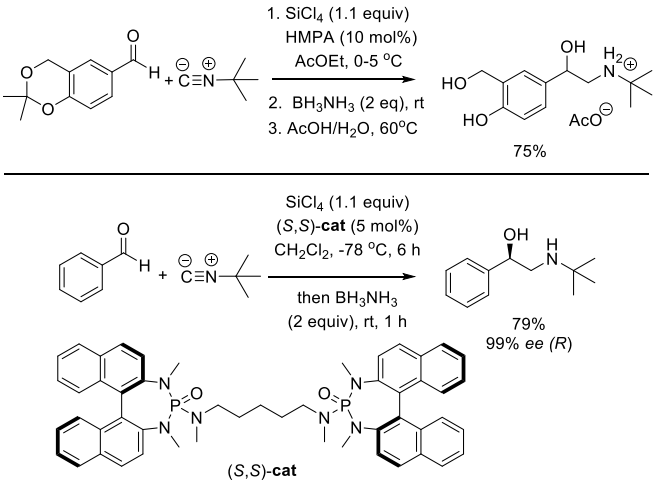
Mechanistic aspects, stereochemistry using biocatalysis, optimization towards robust procedures, and synthetic utility are all studied in-depth and our chemistry proved successful for the synthesis of specific biologically active target molecules (antitumor, antibiotics, hepatitis C) as well as novel chemotypes with potential applications in diverse fields ranging from material sciences and ligands for catalysis to chemical biology and drug discovery.As a result, SBOC is one of the leading players in the field of multicomponent and cascade reactions and their application in the synthesis of biologically relevant molecules.

Group highlights 2015

One-pot Synthesis of N-substituted β-Amino Alcohols from Aldehydes and Isocyanides (Cioc *et al.*, *Chem. Eur. J.* **2015**, *21*, 7808)

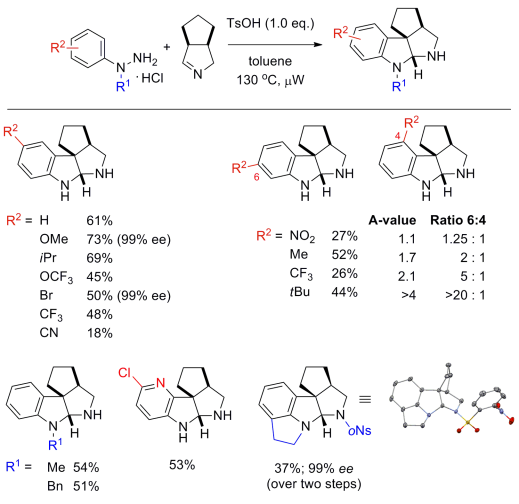


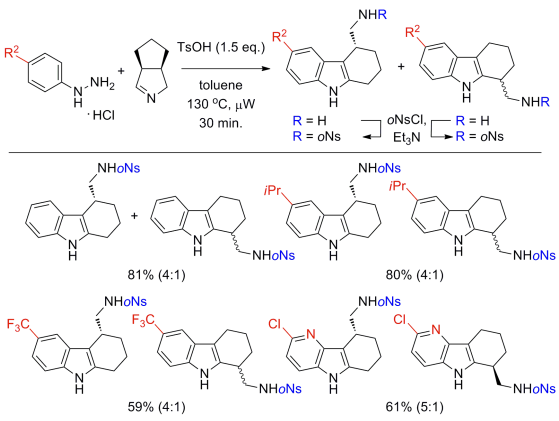
β-Amino alcohols constitute a diverse class of bioactive molecules including import drugs against a variety of conditions, such as salbutamol (asthma) and propanolol (heart disease). These compounds are typically synthesized by ring opening of the corresponding epoxides or substitution of α-halo ketones followed by reduction. However, these classical approaches suffer from limitations such as lack of regioselectivity, limited commercial availability of the required electrophiles, and double alkylation of primary amine nucleophiles. Moreover, these approaches proceed with poor yield for amines with bulky substituents (R^2 = *e.g.* *t*Bu or *i*Pr), which are however required for the most bioactive representatives of this class. We employed an alternative retrosynthetic disconnection of the central C-C bond by means of a reductive Passerini-type reaction. We found the reactions works well over a broad range of aldehyde and isocyanide inputs, espcially with bulky R^2 substituents, making the method complementary (and in many saces superior) to the classical approaches. The method was readily upgraded to a catalytic asymmetric version by the use of a chiral Lewis base organocatalyst. Finally, the mathod was used in an efficient synthesis of the widely used asthma drug, salbutamol.



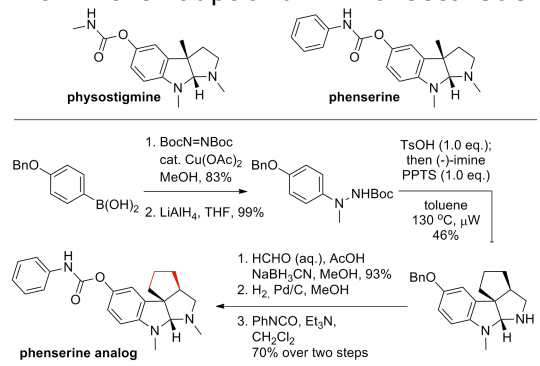
Asymmetric Synthesis of Tetracyclic Pyrroloindolines and Constrained Tryptamines by a Switchable Cascade Reaction (de Graaff *et al.*, *Angew. Chem. Int. Ed.* **2015**, 54, 14133)

Following our recent success with the used of biocatalytically generated bicyclic imines in Ugi-type multicomponent reaction (as in our highly efficient synthesis of the important hepatitis C drug, telaprevir; *Chem. Commun.* **2010**, *46*, 7918), we envisioned the use of these versatile reagents in other complexity-generating cascade processes. Specifically, we investigated their utility in the interrupted Fischer indole synthesis to give tetracyclic pyrroloindolines by trapping of the intermediate iminium species by the pendant amino group. Under specific conditions, we were able to construct a diverse range of these complex, natural product-like molecules with excellent stereocontrol. Interestingly, we found that a minor modification of the reaction conditions (a slight increase in the stoichiometry of the Brønsted acid mediator) led to a complete switch in the course of the reaction, instead affording tricyclic tryptamine derivatives. As both classes of products are of significant medicinal interest, we demonstrated the utililty of our method in the stereoselective synthesis of a phenserine analog of potential interest for the treatment of





Alzheimer's disease. We also synthesized two tricyclic tryptamine derivatives of significant pharmaceutical interest, a 5-HT_6 serotonin receptor antagonist and a TRPV1 inhibitor with >99% ee in a short and efficient reaction sequence. Based on our observations and various control experiments, we have proposed a mechanism for the reaction accounting for the observed switch in the ractions outcome. DFT Calculations to support this mechanism are currently ongoing in collaboration with Prof. Bickelhaupt and Dr. Fonseca Guerra.



Key publications 2012-2015

- de Graaff, C.; Ruijter, E.; Orru, R.V.A.; Recent Advances in Asymmetric Multicomponent Reactions, *Chem. Soc. Rev.* **2012**, *41*, 3969-4009.
- Vlaar, T.; Cioc, R.C.; Mampuys, P.; Maes, B.U.W.; Orru, R.V.A.; Ruijter, E.; Sustainable Synthesis of Diverse Privileged Heterocycles by Palladium-Catalyzed Aerobic Oxidative Isocyanide Insertion, *Angew. Chem. Int. Ed.* **2012**, *51*, 13058-13061.
- Vlaar, T.; Ruijter, E.; Maes, B.U.W.; Orru, R.V.A.; Palladium-Catalyzed Migratory Insertion of Isocyanides: An Emerging Platform in Cross-Coupling Chemistry, *Angew. Chem. Int. Ed.* **2013,** *52*, 7084-7097.
- Cioc, R.C.; van der Niet, D.J.H.; Janssen, E.; Ruijter, E.; Orru, R.V.A.; One-pot Synthesis of *N*-substituted β-Amino Alcohols from Aldehydes and Isocyanides, *Chem. Eur. J.* **2015**, *21*, 7808-7813.
- de Graaff, C.; Bensch, L.; Boersma, S.J.; Cioc, R.C.; van Lint, M.J.; Janssen, E.; Turner, N.J.; Orru, R.V.A.; Ruijter, E.; Asymmetric Synthesis of Tetracyclic Pyrroloindolines and Constrained Tryptamines by a Switchable Cascade Reaction, *Angew. Chem. Int. Ed.* **2015**, 54, 14133-14136.

Future developments

The research of the Synthetic & Bio-organic Chemistry group will continue to focus on cascade processes in context of the topics mentioned above. Based upon a growing understanding of mechanistic aspects of *e.g.* (non-classical) isocyanide chemistry, we rationally design new processes affording complex, valuable scaffold structures.

Homogeneous catalysis, in particular palladium catalysis, also plays a key role in the development of novel domino reactions. The utilization of our novel cascade methodology for the chemo- and stereoselective synthesis of complex molecular targets such as natural products will play an increasingly important role in our research. To this end we will develop exceedingly robust protocols to contruct multiple chemical bonds in a single operation, thereby establishing atom and step efficient approaches for the efficient and inherently sustainable synthesis of complex molecular targets.

Synthetic Organic Chemistry

Prof. dr. H. Hiemstra, Prof. dr. P. Timmerman, Prof. dr. J.H. van Maarseveen, Dr. S. Ingemann (UvA), Dr. M.A. Fernández Ibáñez

Research topics

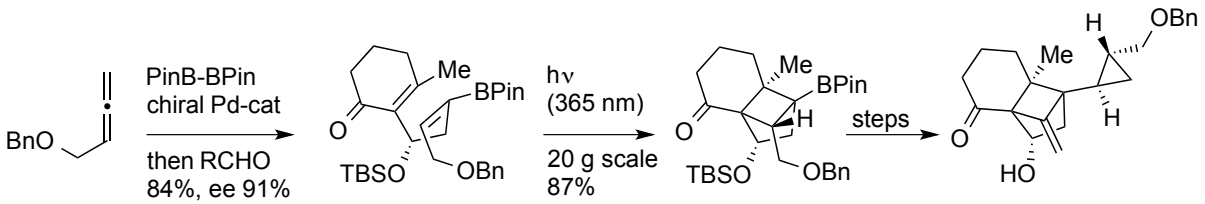
- Synthetic methodology development
- Target-oriented synthesis
- Organocatalysis
- Chemical biology

Summary of research activities

The research in the Synthetic Organic Chemistry group is directed at the development of efficient and selective, diversity-oriented synthetic methodology, in particular catalytic procedures, and target-oriented preparation of molecules of relevance in chemistry, biology and medicine. The main target molecules are novel enantiopure organocatalysts, indole and tetrahydroisoquinoline alkaloids, small cyclic peptides and model systems for lasso peptides and 4-membered ring-containing terpenes, like aquatolide and solanoeclepin A, the hatching agent of potato cyst nematodes. A new research line is directed at the discovery and development of robust methods for the synthesis of high value chemicals and materials using the C-H functionalization strategy.

Group highlights 2015

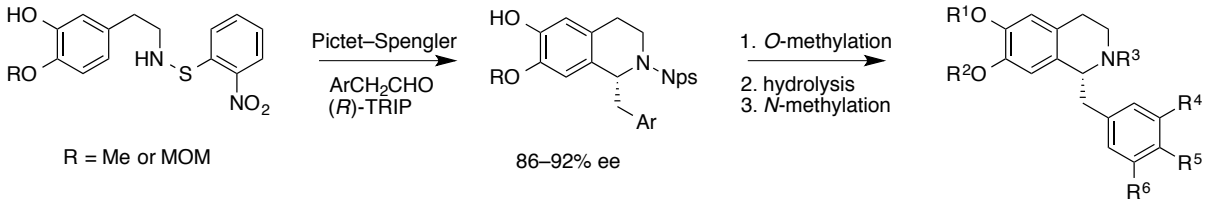
Formal Total Synthesis of Solanoeclepin A: In our synthetic approach to solanoeclepin A (hatching agent of potato cyst nematodes) an enantioselective synthesis of an intermediate in the Tanino total synthesis of solanoeclepin A has been developed. The key step was an intramolecular [2+2] photocycloaddition, which led to the tricyclo[5.2.1.$0^{1,6}$]decane core in six steps. The photosubstrate was prepared through a catalytic asymmetric allene diborylation in high enantiomeric excess. The [2+2] photocycloaddition proceeded in high yield on irradiation at 365 nm on 20 g scale in a flow system. Other important steps were the replacement of a boronate group at the quaternary carbon by a vinyl group and diastereoselective cyclopropanation of an allylic alcohol (see Scheme below).



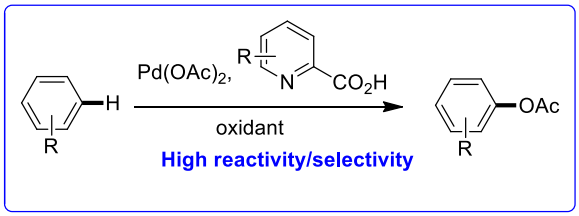
Other Research Highlights:

A general procedure for the synthesis of 1-benzyl-1,2,3,4-tetrahydroisoquinolines was developed, based on organocatalytic, regio- and enantioselective Pictet-Spengler

reactions (86–92% ee) of *N*-(*o*-nitrophenylsulfenyl)-2-arylethylamines with arylacetaldehydes. The presence of the *o*-nitrophenylsulfenyl group, together with the MOM-protection in the catechol part of the tetrahydroisoquinoline ring system appeared to be a productive combination. To demonstrate the versatility of this approach, ten biologically and pharmaceutically relevant alkaloids were prepared using (*R*)-TRIP as the chiral catalyst: (*R*)-norcoclaurine, (*R*)-coclaurine, (*R*)-norreticuline, (*R*)-reticuline, (*R*)-trimemetoquinol, (*R*)-armepavine, (*R*)-norprotosinomenine, (*R*)-protosinomenine, (*R*)-laudanosine and (*R*)-5-methoxylaudanosine.

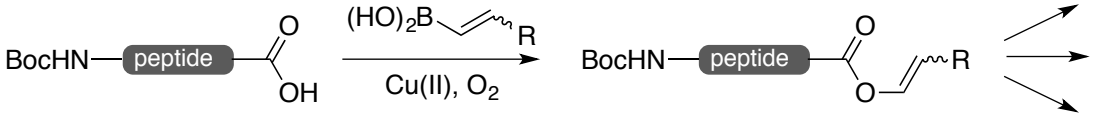


A new catalytic system for the direct C-H acetoxylation of simple arenes based on $Pd(OAc)_2$ and picolinic acid ligand was developed, that shows high reactivity and site selectivity. This system proved to be active at low catalyst loading leading to the highest TON reported to date for palladium-catalyzed C-H acetoxylation of benzene.



In the project towards the development of the templated synthesis of peptide rotaxanes considerable progress has been made. All key-reactions have been optimized, are robust and run well on a preparative scale. Unfortunately, so far, all used templates did not give any rotaxane formation. Presumably due to too much felixibility in the system both CuAAC reactions had occurred at the same side of the ring fragment. The current end-game focusses on more rigid templates and a ketal instead of oxime linkage between the thread and ring fragments.

In the project using Chan-Lam-Evans (CLE) Cu(II)-mediated esterification of peptides from aryl boroxines it was found that also alkenyl boronic acids are suitable substrates. Currently, the scope of this new reaction is determined.



Key publications 2012-2015 (max 5)

- Popovic, S.; Bieräugel, H.; Detz, R. J.; Kluwer, A. M.; Koole, J. A. A.; Streefkerk, D. E.; Hiemstra, H.; van Maarseveen, J. H.; Epimerization-free C-terminal peptide activation, *Chem. Eur. J.* **2013**, *19*, 16934-16937.

- Ingemann, S.; Hiemstra, H.; Cinchonas and Cupreidines, Comprehensive Enantioselective Organocatalysis, Volume 1: Privileged Catalysts, Chapter 6, p. 119-160; Ed. P. I. Dalko, Wiley-VCH: Weinheim, **2013**.
- Mons, E.; Wanner, M.J.; Ingemann, S.; van Maarseveen, J.H.; Hiemstra, H. Organocatalytic enantioselective Pictet-Spengler reactions for the synthesis of 1-substituted 1,2,3,4-tetrahydroisoquinolines, *J. Org. Chem.* **2014**, 79, 7380-7390.
- Smeenk, L. E. J.; Timmers-Parohi, D.; Benschop, J. J.; Puijk, W. C.; Hiemstra, H.; Van Maarseveen, J. H.; Timmerman, P. Reconstructing the Discontinuous and Conformational β1/β3-Loop Binding Site on hFSH/hCG by Using Highly Constrained Multicyclic Peptides, *ChemBioChem*, **2015**, *16*, 91-99.

Future developments

Our novel Cu(II)-catalyzed CLE-esterification method to make activated peptide aryl esters will be expanded to enol esters. Hydroformylation of peptide enol esters introduces an aldehyde that serves as a versatile handle for further functionalization. CLE-activated peptides will be elaborated further to disclose the natural C2-symmetric cyclic peptide series that show promising antibiotic properties.

Next to strained lactams, a general synthetic approach towards the natural and novel lasso peptide series is being developed. Because of their high molecular density peptide rotaxanes show a small organic molecule-like behaviour making them attractive privileged structures for pharmaceutical research. Bacteria are able to synthesize peptide rotaxanes in which the thread fragment is completely mechanically locked in the ring fragment. Elucidation of the biosynthetic pathway revealed that the ring was made via clipping around the thread. Currently, methods are developed based on the use of templating molecules that enable clipping of a peptide around another peptide arriving at peptide-rotaxanes.

In the joint HIMS-Pepscan project on protein mimetics (supported by STW) we will expand the CLIPS chemistry to scaffolds onto which more than one peptide may be bound. Each peptide will be connected onto such a scaffold at three positions using robust orthogonal reactions. As a result, a single peptide-decorated scaffold will be able to mimic multiple protein epitopes. We will aim at the incorporation of non-canonical amino acids in phage-display libraries arriving at large libraries for screening on antibiotic properties.

Bacterium lipid membrane molecules may be used as biomarkers (proxies) to study ancient climate. Together with NIOZ (Texel) bacterial membrane molecules will be prepared of which only very minute amounts could be isolated from natural sources. Total synthesis of these molecules will be used to confirm the structures of these lipids. These specific ladderane-derived lipids will be made based on our know-how on photochemical [2+2]-photocycloadditions to give cyclobutanes.

Our research directed at the total synthesis of solanoeclepin A, the hatching agent of potato cyst nematodes, will now be concentrated on the coupling of the eastern substructure with the western part.

Chiral Brønsted acid organocatalysis will remain an important tool to effect iminium ion cyclizations (mainly of the Pictet-Spengler type) with high enantioselectivity. The

attention will be directed toward the application of this approach in the total synthesis of bioactive natural isoquinoline alkaloids.

Our research towards the efficient functionalization of C–H bonds, will now concentrate in the discovery of new bidentate ligands capable of increasing the reactivity and selectivity of these processes as well as the development of novel traceless directing groups. The new methodologies will be used in more complex molecules to prove the versatility of these methodologies.

2.2 Theme 2 - Physical Chemistry and Spectroscopy

The interaction between light and molecular matter is central in a large number of fundamental and applied research areas in molecular chemistry and physics. In HRSMC it is employed to probe and utilize fundamental processes such as reaction mechanisms and dynamics, catalytic events, energy and electron transfer, conformational dynamics, and dynamic life processes. Concurrently, advanced spectroscopic techniques are used to elucidate inter- and circumstellar chemistry, and for analytical applications. Many of the groups working in this area are renowned for their development and application of new spectroscopic techniques. Various groups in the Netherlands conduct scientific research in spectroscopy, but photo-chemical and photo-physical research of inorganic and organic compounds in gas and condensed phases is increasingly confined to groups within HRSMC.

In the **Biomolecular Spectroscopy group** of VU-LaserLaB Amsterdam, laser spectroscopic methods, in particular Raman Spectroscopy in a variety of modes are developed for biophotonics, biomedical and other purposes. Emphasis is currently on the development of special Raman modes for future Mars missions, surface enhancement and resonance enhancement of Raman signals. non-linear Raman spectroscopy (SRS) for fast imaging and for the in-flow detection of micro/nanoparticles, spectroscopy at the nanoscale based on scanning near-field optical microscopy (SNOM), and depth analysis through nontransparent samples using time-resolved Raman spectroscopy.

The **Biophysical Organic Chemistry group** is highly recognized for its studies in high-resolution Magic Angle Spinning Solid State NMR studies. The research takes place in the European centre for ultra-high field solid state NMR in Leiden and is carried out also in combination with quantum chemical modeling (Buda) and mesoscale simulations (Sevink). The main focus is on the relation between electronic/spatial structure and function of membrane proteins involved in visual signal transduction and photosynthetic energy conversion. In addition, ultrahigh field micro-MRI (Alia) allows imaging and visualizing the metabolic processes in vivo. The aim is to translate the understanding of general principles used in natural systems into concepts for novel artificial devices.

In the **Raymond and Beverly Sackler Laboratory for Astrophysics** experimental studies are performed that focus on simulating the chemical processes in the interstellar medium. Part of the experiments is performed with the aim to provide spectroscopic data, both of molecular gas phase transients and ices, to interpret and guide astronomical observations. Other experiments study the cryogenic formation of new molecules on interstellar dust grains upon vacuum UV irradiation or bombardment with atoms for fully controlled conditions. Besides bottom-up research – generating more complex species from smaller precursors – recently also top-down astrochemical processes are studied experimentally, by investigating the photo-induced dissociation of astronomically relevant PAHs.

In the **Molecular Nano-Optics and Spins**, the subgroup of Orrit is interested in the optical detection and study of single fluorescent molecules and of single gold nanoparticles. The projects have contacts with biophysics, physical chemistry, soft matter physics and solid state physics. Important new developments are the uses of gold nanorods for single-protein sensing and for fluorescence enhancement of single emitters.

The subgroup of Groenen concentrates on the development and application of electron-paramagnetic-resonance (EPR) spectroscopy. Resolution, sensitivity and stability of EPR at high microwave frequencies are being enhanced continuously, which brings new applications within reach. Presently the focus is on the study of the (electronic) structure and dynamics of biomolecules and transient intermediates of enzymatic reactions using spin labels and transition metal ions.

The **Molecular Photonics** group aims to extend the fundamental knowledge of excited states. The spectroscopic tools and the scientific competences that are required to do this enable the team to enter into numerous projects in which light-matter interaction is essential. This leads to the application of a photonic approach to the broader scientific and technological fields of molecular biology, polymer science, nanoscience, catalysis, solar energy conversion and medical imaging and phototherapies.

The **Surface Chemistry and Catalysis group** studies chemical reactions of interest for sustianable energy conversion on well-defined, mostly single crystalline, surfaces at the molecular level, and on surfaces modified with well-defined molecular catalysts. The group combines state-of-the-art experimental setups to study surface catalytic reactions using a variety of spectroscopic techniques, both at the metal-uhv and metal-liquid interface, with computational techniques. Their aim is to unravel mechanistic and kinetic aspects of important catalytic reactions that feature in industrial processes, fuel reforming, fuel cells, the hydrogen economy, and environmental catalysis. The group is also part of NRSC-Catalysis and NIOK.

Biomolecular Analysis and Spectroscopy

Dr. F. Ariese (VU)

Research topics

- Pico-second time-gated Raman spectroscopy for analyzing nontransparant samples
- Optimization of Raman methods for (fossilized) bacteria for future Mars missions.
- Surface-enhanced, resonance and UV-resonance Raman spectroscopy
- Stimulated Raman scattering, for microscopy and for identifying microparticles
- Spectroscopy at the nanoscale

Summary of research activities

Time-resolved Raman spectroscopy (TRRS) with a picosecond Ti:sapphire system and fast gated ICCD detection can be used to record Raman spectra from deeper layers through diffusely scattering media. A paper was published on the applicability of TRRS for bonelike inclusions of varied shapes and depth inside artificial tissue samples.

In order to contribute to the development of new instrumentation for future planetary studies (e.g., Mars), we work on optimizing Raman characterization methods for (fossilized) bacteria on mineral backgrounds. Focus is on the detection of biomarkers such as UV protective compounds in earth extremophiles, also hidden within a mineral matrix. For excitation wavelength flexibility an OPO-based laser system is used, which can be tuned across the strong absorption bands of certain compounds (e.g., carotenoids). The above mentioned TRRS system can be applied for depth analysis and fluorescence suppression, and thus enabled us to detect carotenoid-containing bacteria through several mm of a mineral top layer. A new PhD project will focus on new modes for faster imaging of subsurface layers.

In collaboration with Prof. J.F. de Boer (LaserLaB Amsterdam) there is an ongoing PhD project on the development of nonlinear Raman spectroscopy (SRS) for ultrafast biomedical imaging. A picosecond microscope system was constructed and characterized in terms of noise distributions and optimal power ratios for pump and probe lasers. With some modifications the system is now also suitable for long-wavelength SRS. SRS microscopic images were obtained for zebrafish embryos and C. elegans worms, showing the lipid distribution on the basis of the local abundance of C-H stretch vibrational modes. In collaboration with the Bonnet group (Leiden), SRS imaging was also performed on cells undergoing membrane disruption in the presence of amphiphilic ruthenium-cholesterol complexes.

In a new collaborative project within the TA-COAST program, SRS and conventional Raman is employed for the detection and identification of man-made micro/ nanoparticles from environmental matrices. Following density separation these microplastic particles can be detected either on a flat filter using Raman and/or SRS microscopy. We are also studying ways to use SRS for fast detection in flow systems.

In collaboration with other groups at LaserLaB VU (Prof. D. Iannuzzi) and with Philips, a PhD project is carried out on nanospectroscopy: a combination of AFM technology and molecular spectroscopic techniques such as Raman and fluorescence. The project is part of the nanonextNL initiative, cluster 9A. The first project was aimed at nanoscale

absorption and reflection measurements using a ferrule-top AFM with scanning near-field optical spectroscopy (SNOM), which resulted in spectroscopic images with a spatial resolution below the diffraction limit. The setup was also used to characterise of so-called VCSEL laser emission profiles at the nanometer scale and changes therein as a result of accellerated stress tests (temperature, humidity).
A Raman study was carried out on the bending vibration in the presence of salts, in particular halide ions. At increasing salt concentrations, changes in peak positions and band widths are observed as a result of water-halide interactions and the breaking of hydrogen bonds.
Since January 2014, Freek Ariese is also part-time (50%) visiting professor at the Department of Inorganic and Physicsl Chemistry of the Indian Institute of Science in Bangalore. On average 6 months per year he is embedded in the Raman spectroscopy group of prof. S. Umapathy, initiating new Raman research projects and supervising PhD students. The projects at IISc include Ultrafast Raman spectroscopy of excited-state molecules, subsurface Raman spectroscopy and 3D tomography, low-frequency Raman spectroscopy and Raman microscope imaging for pathological studies.

Key publications 2012-2015 (max 5)

- Van Hoorn C.H.; Mank AJG; Ariese F; Iannuzzi D: Using ferrule-top opto-mechanical probes as a new tool in VCSEL reliability experiments. *Optics Express* **2015**, *23*, 30318-30328.
- Verkaaik, M.F.C.; Hooijschuur JH; Davies, G.R.; Ariese, F. Raman spectroscopic techniques for planetary exploration: detecting microorganisms through minerals. Astrobiology; **2015**, *15*, 697-707.
- Moester, M.J.B.; Ariese, F; de Boer, J.F. Optimized signal-to-noise ratio with shot noise limited detection in Stimulated Raman Scattering microscopy. *J. Eur.Opt. Soc.* **2015**, *10*, art nr 15022.
- Iping Petterson, I.E.; Esmonde-White F.W.L; de Wilde. W.; Morris, M.D.; and Ariese F: Tissue phantoms to compare spatial and temporal offset modes of deep Raman spectroscopy. *Analyst*; **2015**, *140*, 2504-2512.
- Lammers, I; Lhiaubet-Vallet, V.; Ariese, F.; Miranda, M.A.; Gooijer, C. Binding of naproxen enantiomers to human serum albumin studied by fluorescence and room-temperature phosphorescence. *Anal. Chim. Acta A* **2013**, *105,* 67-73.

Future developments

Following a successful NWO-Middelgroot application, a flexible-wavelength OPO system was constructed, with SHG and THG options for the signal as well as the idler output. The next phase will consider the wavelength-dependence of resonance-enhancement of carotenoids, in bacteria and perhaps also in the retina.
Time-resolved Raman using fast gated detection is being explored to reject fluorescence interference and for time-gated detection for depth profiling, contrast studies and applications to biomedical imaging.
We will continue to work on the development of new Raman instrumentation for future Mars missions. Focus is on optimizing Raman characterization methods for (fossilized) bacteria on mineral backgrounds, and the detection of biomarkers such as UV protective compounds in earth extremophiles. Both resonance as well as time-resolved approaches

will be explored further, in particular for subsurface analysis. New surface imaging modes will be developed based on line scanning or 2D imaging with tunable filters/lasers rather than using a spectrograph.
Nonlinear Raman spectroscopy (SRS) will be tested further, specifically for following the uptake and distribution of chemicals by microorganisms, and for ultrafast biomedical imaging of neurotransmitter dynamics. A system will be built for SRS in flow for microplastic identification.
In the field of nanospectroscopy, the combination of AFM with near-field optical spectroscopy will be further developed, including nanoscale absorption and fluorescence imaging, nanoscale photophysical processes and nanoscale spectroscopy under challenging conditions.
A consorium has been established to study degradation processes in paint and polymer coatings. Understanding these processes is crucial for both art conservation as well as the coatings/polymer industry (TA-COAST proposal submitted).
The parttime visiting professorship of F. Ariese at the Raman Spectroscopy group of Prof. S. Umapathy, Indian institute of Science, Bangalore, will be continued. This collaboration is highly inspiring and fruitful, and provides excellent opportunities for exploring new Raman modes and new applications, including femtosecond stimulated Raman of excited state dynamics, resonance Raman studies of triplet excited states, Raman optical activity (ROA), and terahertz Raman.

Biophysical Organic Chemistry

Prof. dr. H.J.M. de Groot, Dr. F. Buda (UL), Dr. A. Sevink

Research topics

- Membrane Proteins and Solid State NMR, Natural and Artificial Photosynthesis

Summary of research activities

The long term goal of our group is to reach understanding of structure, dynamics and functional mechanisms of membrane proteins and self-organized biological assemblies and to translate this knowledge into new concepts for nano-devices, medicine, and new materials of technical importance. Central fundamental research theme is the electronic and spatial structure of membrane proteins involved in photosynthetic energy conversion and visual signal transduction. Quantum chemical calculations based on density functional theory (DFT), *ab-initio* Molecular Dynamics (AIMD) simulations, and mesoscale simulations on large supramolecular aggregates are also performed in our group to translate spectroscopic information into models and to investigate functional mechanisms. The fundamental research in the field of rhodopsin and the photosynthetic energy transformation has a spin off towards applications and research in the field of g-protein coupled receptors and artificial photosynthesis.

Group highlights 2015

Modulation of spectral properties of membrane proteins

Proteorhodopsins are heptahelical membrane proteins which function as light-driven proton pumps. They use *all-trans*-retinal A1 as a ligand and chromophore and absorb visible light (520–540 nm). In this work, we describe modulation of the absorbance band of the proteorhodopsin from Monterey Bay SAR 86 gammaproteobacteria (PR), its red-shifted double mutant PR-D212N/F234S (PR-DNFS) and Gloeobacter rhodopsin (GR). This was approached using three analogues of *all-trans*-retinal A1, which differ in their electronic and conformational properties: *all-trans*-6,7-*s-trans*-locked retinal A1, all-transphenyl-retinal A1 and all-*trans*-retinal A2. We further probed the effect of these retinal analogues on the proton pump activity of the proteorhodopsins. Our results indicate that, whereas the constraints of the retinal-binding pocket differ for the proteorhodopsins, at least two of the retinal analogues are capable of shifting the absorbance bands of the pigments either bathochromically or hypsochromically, while maintaining their proton pump activity. Furthermore, the shifts implemented by the analogues add up to the shift induced by the double mutation in PR-DNFS. This type of chromophore substitution may present attractive applications in the field of optogenetics, towards increasing the flexibility of optogenetic tools or for membrane potential probes.

Water oxidation catalysts

We have demonstrated for the first time the photoelectrochemical properties of a $BiVO_4$ photoanode in conjunction with a molecular catalyst. When the Ru-based molecular catalyst (RuCat) is coupled to a $BiVO_4$ light-absorber the performance of this photoanode improves particularly in the low-bias region (<1.0 V vs RHE). The RuCat-$BiVO_4$

photoanode shows a higher photocurrent than CoPi-$BiVO_4$ under front illumination, and a 0.1 V more cathodic onset potential. The former can be partly explained by the low light absorption of the RuCat (<5% light absorption in the UV−vis−NIR range). For the latter, we propose that the linkers in the RuCat reduce the surface recombination in $BiVO_4$ to a greater extent than CoPi. Finally, we observe that the fill factor of the RuCat-$BiVO_4$ JV characteristic improves after the stability test. The results not only show the feasibility and potential of the solid state/molecular heterojunctions but also represent a proof of principle to improve conventional all-solidstate systems such as CoPi-$BiVO_4$.

Quantum chemical modeling

Environmentally friendly and cost-effective dye-sensitized solar cells (DSSCs) are a potential alternative to silicon based photovoltaics for solar energy conversion. Moreover, DSSCs can be equipped with molecular catalysts for direct conversion and storage of solar energy into fuel. A major obstacle hampering the performance of DSSC devices is the internal losses from recombination between the electron injected into the semiconductor and the hole on the oxidized dye. To address this issue we have investigated the electron injection from a terrylene-based chromophore to the TiO_2 semiconductor bridged by a phenyl-amide-phenyl molecular rectifier. The mechanism of electron transfer is studied by means of quantum dynamics simulations using an extended Hückel Hamiltonian. It is found that the inclusion of the nuclear motion is necessary to observe the photoinduced electron transfer. In particular, the fluctuations of the dihedral angle between the terrylene and the phenyl ring modulate the localization and thus the electronic coupling between the donor and acceptor states involved in the injection process. The electron propagation shows characteristic oscillatory features that correlate with interatomic distance fluctuations in the bridge, which are associated to the vibrational modes driving the process. The understanding of such effects is important for the design of functional dyes with optimal injection and rectification properties.

Key publications 2012-2015 (max 5)

- Saleem Joya, K.; Subbaiyan, N.K.; Souza, F.D.; De Groot, H.J.M.; Surface-Immobilized Single-Site Iridium Complexes for Electrocatalytic Water Splitting, *Angew. Chem. Int. Ed.* **2012***, 51,* 9601-9605.
- Alia, A.; Buda, F.; De Groot, H.J.M.; Matysik, J.; Solid-State NMR of Nanomachines Involved in Photosynthetic Energy Conversion, *Annual Review of Biophysics* **2013**, *42*, 675-699.
- Eisenmayer, T.J.; Buda, F.; Real-time Simulations of Photoinduced Coherent Charge Transfer and Proton-Coupled Electron Transfer, *ChemPhysChem* **2014**, *15*, 3258-3263.
- de Respinis, M.; Joya, K.S.; de Groot, H.J.M.; D'Souza, F.; Smith, W.A.; van de Krol, R.; Dam, B.; Solar Water Splitting Combining a $BiVO_4$ Light Absorber with a Ru-Based Molecular Cocatalyst, *J. Phys. Chem. C* **2015**, *119*, 7275−7281.
- Monti, A.; Negre, C.F.A.; Batista, V.S.; Rego, L.G.C.; de Groot, H.J.M; Buda, F.; Crucial Role of Nuclear Dynamics for Electron Injection in a Dye–Semiconductor Complex, *J. Phys. Chem. Lett.* **2015**, *6*, 2393–2398.

Future developments

Development of advanced ultra-high field solid-state MAS NMR technology for structure and structure-function determination: NMR structure determination is both an important and a highly significant enabling technology for our energy conversion studies. We will continue our efforts to develop and apply methodology for structure determination with solid state NMR in high and ultra-high magnetic fields.

Quantum-classical and mesoscale simulations: Theoretical modeling is an integral part of our research (i) to translate spectroscopic information directly into models for the spatial and electronic structure and (ii) to formulate detailed hypotheses regarding operational mechanisms. We will focus on the mechanisms of charge separation and water splitting in natural and artificial photosynthesis.

From natural photosynthesis to artificial photosynthesis: Self-organised antenna and reaction center complexes are currently becoming widely considered as a paradigm for solar cell research. We plan to use a combination of solid state NMR and state-of-the-art modeling tools to resolve the structural dynamics and chemistry of crucial catalytic reactions in photosynthesis. A minimal model for the multi-electron water splitting catalytic cycle in photosystem II (PSII) can serve as a starting point for the design of photoanodes comprising multivalent metal clusters embedded in man-made smart matrices. We expect to give proof of principle that including hierarchical organizational principles from biology can lead to improved photovoltaics technology.

Raymond and Beverly Sackler Laboratory for Astrophysics

Prof. dr. H. Linnartz (UL)

Research topics

- High resolution IR (2500-4000 cm^{-1}) and UV/VIS (200-1000 nm) spectroscopy
- Molecular transients of astrophysical interest
- Interstellar ice: spectroscopy and astrochemistry
- CW, pulsed and broad band cavity enhanced technology
- Supersonic plasma expansions
- Ion trap TOF (PAH) photodynamics

Summary of research activities

Eight experimental setups simulate different processes taking place in the interstellar medium, varying from dark and dense interstellar clouds to protoplanetary disks. Spectroscopy is used to identify new molecules in space, both in the gas phase and in the solid state, and surface techniques are applied to characterize solid state formation schemes leading to molecular complexity in space. See also: www.laboratory-astrophysics.eu.

Group highlights 2015

The highlight of 2015 have been a number of non-energetic ice processing studies that show that complex organic molecules (COMs) can be formed in the solid state under dark interstellar cloud conditions. By studying H-atom addition and abstraction reactions of CO-ice, not only the solid state formation of formaldehyde and methanol were confirmed, but backbone reactions also resulted in the formation of glycol aldehyde and ethylene glycol. Suc species have been observed in space in dark clouds using large radio telescopes. In such clouds UV light plays a minor role, as the clouds are largely shielded from the interstellar radiation field. This means, chemical triggers have to be delivered in a different way and atom addition reactions, resulting in molecular radicals that can diffuse, provide an efficient mechanism to form such species. The results have been published in Experimental evidence for glycolaldehyde and ethylene glycol formation by surface hydrogenation of CO molecules under dense molecular cloud conditions; G. Fedoseev, T. Lamberts, S. Ioppolo, H.M. Cuppen, H. Linnartz, MNRAS 448 (2015) 1288

Key publications 2012-2015

- Linnartz, H.; Fedoseev, G.; Ioppolo,S; Atom addition reactions in interstellar ices; *Int. Rev. Phys. Chem.* **2015**, *34*, 205.
- Bossa, J.B.; B. Mate, B.; Fransen, C.; Cazaux, S.; Pilling, S.; Monteiro Rocha, W.R.; Ortigoso, J.; Linnartz, H. Porosity and band-strength measurements of multi-phase composite ices; *Astrophys. J.*, **2015**, *814*, A47
- Zhen, J.; Castellanos, P.; Paardekooper, D.M.; Linnartz, H.; Tielens, A.G.G.M.; Laboratory formation of fullerenes from PAHs: Top-down interstellar chemistry, *Astrophys. J.* **2014**, *797*, L30.
- Zhao, D.; Doney, K.D.; Linnartz, H.; Laboratory gas-phase detection of the cyclopropenyl cation (c-C3H3+), *Astrophys. J.* **2014**, *791*, L28.

- Bertin, M.; Fayolle, E.C.; Romanzin, C.; Poderoso, H.A.M.; Michaut, X.; Philippe, L.; Jeseck; P.; Oberg, K.I.; Linnartz, H.; Filion, J.-H.; Indirect UV photodesorption from CO:N2 binary ices - an efficient grain-gas process, *Astrophys. J.* **2013**, *779*, 120.

Future developments

Funding within EUROPAH, a new 4 MEUro FP8 network will help in further developing the photodissociation studies of PAHs as well as research on PAHs embedded in interstellar water ices.

Molecular Nano-Optics and Spins

Prof. dr. E.J.J. Groenen, Prof. dr. M. Orrit, Dr. P. Gast, Dr. M. I. Huber (UL)

Research topics

- Electronic and geometric structure determination and dynamics by multifrequency, cw and pulsed Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR).
- Single-molecule fluorescence and absorption spectroscopy, microscopy of single metal nanoparticles, optical trapping and diffusion of single nanoparticles.
- Photophysics, conformational dynamics and relaxation processes of (bio)molecular systems probed by high-resolution, site-selective laser spectroscopy and optical hole-burning.

Summary of research activities

In the past few years, the Orrit subgroup has focused on the interplay of light and heat for the detection and study of single objects. The energy absorbed by a nanoparticle and released as heat in the environment can be used to detect and study the absorbing object. Recently, the sensitivity of these absorption experiments reached the single-molecule limit. The heat released upon absorption can also be used to activate various motions of single molecules, for example conformational changes of FRET-labeled peptides. We are currently studying vapor nanobubbles forming upon heating of a gold nanosphere in liquids. One of group's foci is the optical manipulation and study of gold nanoparticles. We have recently trapped single gold nanorods as small as 60 nm in length and 25 nm in diameter and studied their rotation and translation dynamics in the optical trap.

Following the enhancement of the sensitivity and stability of continuous-wave EPR spectroscopy at the unusually high microwave frequency of 275 GHz, the Groenen subgroup has started several projects in which use is made of a multi-frequency EPR-approach to study the electronic structure of transition-metal sites in proteins and bio-inorganic model complexes. Alternative approaches to freeze-quench techniques are pioneered to study reaction intermediates and kinetics. We have demonstrated that spin-label EPR is an excellent tool to study the conformation of disordered proteins in the free and membrane-bound state. We have even detected aggregates of such proteins, which shows the scope of the approach.

Key publications 2012-2015 (max 5)

- Zijlstra, P.; Paulo, P.M.R.; Orrit, M.; Optical detection of single non-absorbing molecules using the surface plasmon resonance of a gold nanorod, *Nature Nanotechnology* **2012**, *7*, 379.
- Yuan, H.; Khatua, S.; Zijlstra, P.; Yorulmaz, M.; Orrit, M.; Thousand-fold enhancement of single-molecule fluorescence near a single gold nanorod, *Angew. Chem. Int. Ed.* **2013***, 52*, 1217-1221.

• Hou, L.; Yorulmaz, M.; Verhart, N. R., Orrit, M.; Explosive formation and dynamics of vapor nanobubbles around a continuously heated gold nanosphere, *New J. Phys.* **2015**, *17*, 013050.

Future developments

In the next few years, the Orrit subgroup expects to manipulate single gold nanoparticles in complex environments, to explore such local properties as mechanical responses (stiffness, viscosity) or refractive index, and to correlate them with local structures and processes. An exciting field of application will be the exploration of live cells with this technique. Another fascinating subject is the study of single-molecule dynamics by the temperature jump method. Within the next four years, we expect to apply this technique to complex protein dynamics on a single-molecule basis. Finally, low-temperature spectroscopy experiments will be exploited in quantum optical projects and for the study of charge carrier hopping in the vicinity of metal electrodes.

The Groenen subgroup will exploit the potential of multifrequency EPR in combination with high-field electron-nuclear double resonance in the study of enzymatic processes. A new approach will be pioneered at 275 GHz to try and increase the time resolution of kinetic EPR experiments. New methods will be explored to simulate strain in g-tensors and in zero-field-splitting tensors. In addition, methods will be developed further to study the dynamics and interactions of molecules and proteins, both in solutions and membrane related systems.

Molecular Photonics

Prof. dr. W.J. Buma, Prof. dr. A.M. Brouwer, Prof. dr. S. Woutersen, Dr. R. M. Williams, Dr. H. Zhang (UvA), Prof. dr. H.J. Bakker (AMOLF), Prof. dr. J. Oomens (Radboud University)

Research topics

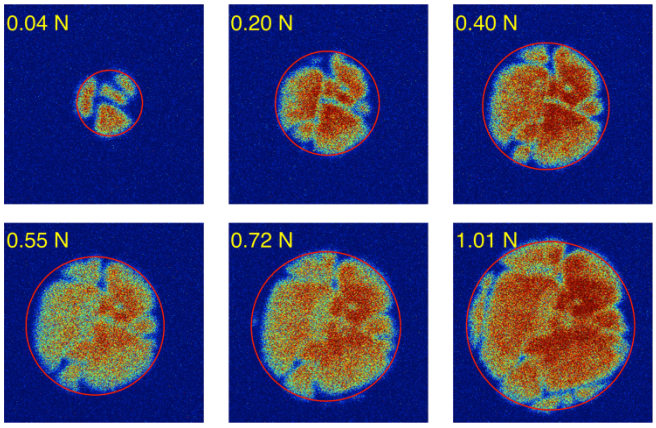
- Dynamics of supramolecular and biomolecular systems
- Photoprocesses in nanostructures
- Photochemical processes

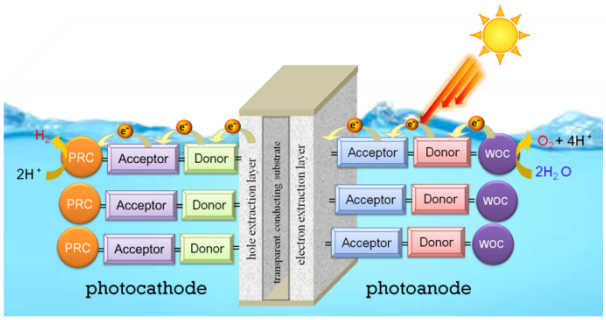
Summary of research activities

The Molecular Photonics group aims to advance the fundamental knowledge of the dynamics of excited states in molecules and nano-sized objects, and to contribute with its expertise to applications of the photosciences. Light-induced chemical conversions play a key role in many technological and biological processes - the most important of all being photosynthesis. Understanding the interaction of light and molecular matter is therefore highly significant. In particular we focus on the interaction of matter and light to design new molecules with pre-programmed properties. It is our ambition to understand how and why very specific light-active molecules perform specific functions. Highlights of our research activities in 2014 include the following.

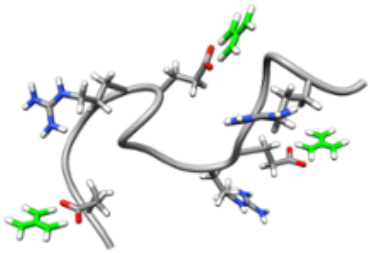
Group highlights 2015

We describe the first **direct visualization of mechanical contacts at the microscale by means of fluorescence microscopy**, using specifically developed probe molecules that fluoresce when confined in a contact. The figure shows how a roughly circular contact area is formed (with a radius increasing up to ~70 micrometers) when a plastic bead is pressed onto a glass slide to which the fluorescent molecules are covalently attached. The molecules light up where the bead touches the glass. The size of the contact is in perfect agreement with Hertz' classical theory of elastic deformation. We can also see details within the overall contact, related to the surface structure of the bead. The paper was published in *Angew. Chem. Int. Edit.* **2015**, *54*, 3688–3691. It opens up possibilities to directly observe mechanical contacts with high spatial and temporal resolution for the study of important physical phenomena such as friction.

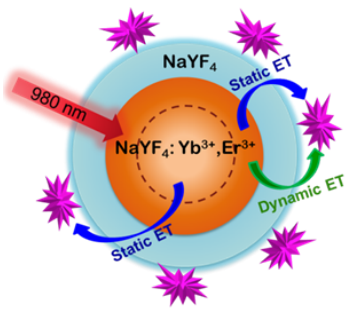




Holding on to the electrons in artificial photosynthesis We designed new clever molecules that can play a key role in the conversion of Solar-to-Fuel. The molecules hold on to an extra electron in such a way that these are not quickly trapped by oxygen and water, but can still be transported easily inside the material. Natural photosynthesis provides a blueprint for the construction of efficient artificial solar-to-fuel conversion systems: an "artificial leaf". The essence of molecule-based artificial photosynthetic devices is photo-induced electron transfer between donor and acceptor molecules in the photoelectrodes (see Figure). This generates charged intermediate species that can activate the catalyst for the water oxidation (WOC) and catalyst for proton reduction (PRC) for oxygen and hydrogen production. PhD student Hung-Cheng Chen developed a series of novel molecules (called benzo[ghi]perylenetriimides (BPTI's)) that strongly absorb light in the blue-green area of the sunlight spectrum. BPTI's are excellent electron acceptors for use as the photoanode. Studies show the potential of BPTI compounds as electron acceptors in devices for artificial photosynthesis aiming for water splitting and also are interesting electron-transport materials for organic solar cells. (see also references 1 and 2). http://atlasofscience.org/holding-on-to-the-electrons-in-artificial-photosynthesis/

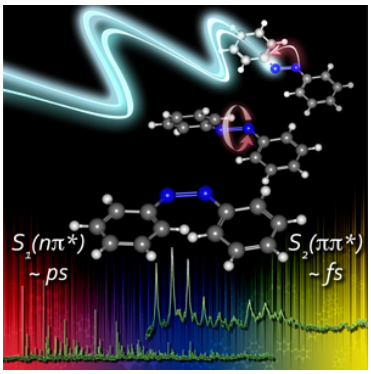


How guanidinium unfolds proteins Guanidinium is a commonly used denaturant, but the mechanism by which it unfolds proteins is still largely unknown. By studying specifically tailored peptides we have been able to solve this mystery. We find that guanidinium disrupts the folded protein conformation by breaking salt bridges. Two-dimensional infrared spectroscopy shows that guanidinium binds in a competitive manner to the carboxylate side groups involved in these salt bridges. The low guaninidium:carboxylate association constant explains the high guandininum concentrations that are typically required to denature proteins. We could even design peptides that fold (rather than unfold) upon adding guanidinium, simply by inserting salt bridges in the sequence that stabilize the unfolded state. This result was published in *Angewandte Chemie*, and contributes to our understanding of protein unfolding, which is believed to be involved in the pathogenesis of many diseases.



Biophotonic nanomaterials Understanding the excitation energy migration and interaction mechanisms in photonic nanomaterials as well as developing novel functional nanomaterials are an important research topic for application of these materials. In 2015 we have focused on (1) exploration of new luminescence upconversion mechanisms in space-confined systems, typically in NaFY4 based

upconversion nanocomplexes. Experimental discoveries have led to new nano-constructions with potentially high upconversion efficiencies (*Chem. Soc. Rev.* **2015**, *44*, 1331); (2) understanding at a subcellular level the translocation of the upconversion nanoparticles and their interaction with a biological environment. Relevant dynamical processes have been monitored. The subcellular picture of cytotoxicity provides a firm and sound basis for the biomedical application of this sort of nanomaterials; (3) how to improve the excitation energy utilization in FRET-related biomedical applications of upconversion nanoplatforms. For typical core-shell nanostructures dynamic- and static energy transfer were separated for the first time and excitation energy utilization efficiency was improved by more than an order of magnitude (*J. Phem. Chem. Letters* **2015**, *6*, 2518).



Azobenzene: fast dynamics probed by slow spectroscopies Azobenzene is the prima donna amongst photoswitches finding extensive applications in areas ranging from molecular probes to molecular nanotechnology and photopharmacology. Despite its huge popularity, the operational mechanism behind the structural changes was not at all clear. Using jet-cooled molecular beam and multiphoton ionization techniques we have been able to obtain the first high-resolution excitation spectra of the electronically excited states that control and steer photoisomerisation (*Nat. Commun.* **2015**, *6*, 5860). These spectra reveal directly the forces the molecule is subjected to upon photon absorption and allow to study dynamics occurring on a femtosecond timescale with nanosecond lasers. From the results it becomes clear that (i) dynamics occur on a completely different time scale than assumed up till now, (ii) changes in spatial structure are considerably different from what has been previously proposed, and (iii) out of the many proposed photoisomerisation pathways an inversion-assisted torsional pathway with a barrier of ~2 kcal/mol is the correct one. The studies on azobenzene are also important because there is a vast amount of photoresponsive systems for which high-resolution spectroscopy was thought to be out of reach because of prohibitively short lifetimes. The present studies show the potential of our methodologies for the study of their photodynamics.

Key publications 2012-2015

- Meuzelaar, H.; Panman, M.R.; Woutersen, S.; Guanidinium-induced denaturation by breaking of salt bridges, *Angew. Chem. Int. Ed.* **2015**, *54*, 15255-15259.
- Suhina, T.; Weber, B.; Carpentier, C. E.; Lorincz, K.; Schall, P.; Bonn, D.; Brouwer, A. M.; Fluorescence microscopy visualization of contacts between objects, *Angew. Chem. Int. Edit.* **2015**, *54*, 3688-3691.
- Tan, E.M.M.; Amirjalayer, S.; Smolarek, S.; Vdovin, A.; Zerbetto, F.; Buma, W.J.; Fast photodynamics of azobenzene probed by scanning excited state potential energy surfaces using slow spectroscopy, *Nat. Commun.* **2015**, *6*, 5860.
- Tu, L.; Liu, X.; Wu, F.; Zhang, H.; Excitation energy migration dynamics in upconversion nanomaterials, *Chem. Soc. Rev.* **2015**, *44*, 1331-1345.

• Panman, M.R.; Bakker B.H.; Den Uyl, D.; Kay, E.R.; Leigh, D.A.; Buma, W.J.; Brouwer, A.M.; Geenevasen, J.A.J.; Woutersen, S.; Water lubricates hydrogen-bonded molecular machines, *Nature Chem.* **2013**, *5*, 929-934.

Future developments

High-resolution laser spectroscopy will continue to be one of the main lines of research. Topical areas of application are molecular nanotechnology and (photo-induced) biomolecular conformational dynamics. The emphasis of this research will shift towards the time-resolved study of dynamical phenomena including photoreactivity. Another area we are developing concerns studies of inorganic nano-clusters of importance for (photo)catalytic applications and for understanding astrochemical phenomena. The strong collaborations with the Free Electron Laser facilities FELIX, FELICE, and FLARE will be continued and expanded. A final area of interest is the high-resolution spectroscopy of polycyclic aromatic hydrocarbons, which play an important role in the interstellar medium in particular in the process of star and planet formation. We work on this subject as part of the Dutch Astrochemistry Network (DAN). This subject will receive in the coming years further impetus by embedding of the VIDI laureate Annemieke Petrignani in the Molecular Photonics group who has her main activities in Laboratory Astrochemistry.

Fluorescence techniques will be used to monitor the mechanics of materials in collaboration with Daniel Bonn (Institute of Physics). We will address the mapping of mechanical contacts with super-resolution microscopy (ECHO project), the application of our successfully developed mechanofluorescent probes to problems in friction, and the detection of local free volume changes in polymers under strain. Another fluorescence based project is aimed at the monitoring of chemical reactions at the level of single molecules.

Focus will be directed at photo-induced processes in and properties of new materials for solar cells as well as the development and study of new systems for photodynamic therapy and antibacterial agents .

Photoinduced electron transfer is the key to harvesting solar light in the form of solar fuel generation. Our project together with the Homogeneous Catalysis group has led to much improved molecular photosensitizers for oxidative and reductive processes. The construction for the device for photochemical water splitting is in progress.

Molecular processes controlled by means of light switches continue to be a subject of interest in biology and in materials science. In the past years we have studied the dynamics of photoswitches, in collaborations with researchers in France, Germany and Japan. Our fundamental knowledge of photochemistry and availability of time-resolved spectroscopic methodologies form the basis for successful continuation of these collaborations.

We intend to continue our ongoing investigations of amyloid formation by proteins and peptides [cooperations with Gijsje Koenderink (AMOLF) and Peter Bolhuis (UvA)] and of catalytic reaction mechanisms [cooperations with Joost Reek (UvA), Stefania Grecea

(UvA), Saeed Amirjalayer (University of Muenster), and Mary Pryce (Dublin City University)] using advanced infrared spectroscopy (2DIR, time-resolved IR, and VCD). In addition, we plan to apply IR spectroscopic methods to study soft-matter research problems such as liquid-liquid phase transitions [cooperation with Daniel Bonn (UvA) and Austen Angell (Arizona State University)].

In recent years we have further developed the concept of amplifying Vibrational Circular Dichroism using low-lying electronically excited states. Supported by a grant from NWO are now extending these efforts by using optical amplification of Vibrational Circular Dichroism and are constructing an experimental setup for measuring time-resolved vibrational circular dichroism (VCD) to investigate optically induced amplification of VCD, as well as structural dynamics of proteins and peptides. We furthermore have initiated together with the group of Visscher (VU), SCM, and BioTools a project in which we will develop and apply a versatile and efficient computational toolbox for the analysis of solution-state structure, conformation, and absolute configuration of chiral molecular systems using VCD.

The functional upconversion nanoplatform will be optimized for the diagnosis and therapy of cancer cells, as well as for bacteria in close collaboration with State Key Laboratory of Luminescence and Applications of China. We are developing new approaches to improve the upconversion efficiency from the structural optimization as well as doping concentration improvement. The new concept of fiber detection is developed and will be validated for biomedical applications.

Novel cancer therapeutic approaches are under development to combine specific chemistry reaction in vivo and photonic nanotechnology, in collaboration with L. Cruz (Leiden University Medical Center) and Percuros B.V. Specifically designed biorthogonal reaction will enable to improve the postoperative therapeutic efficacy and avoid the side effect induced by systemic cycling of relevant drugs during immunotherapy, radiotherapy and chemotherapy.

The fundamental physical picture of photoinduced energy migration in upconversion nanocomposites is going to be studied in order to unravel the role of active and inert shell. The aim of the study is to optimize the photoexcitation efficiency and realizing excitation and emission spectral modulation of relevant nanoplatforms. Single nanoparticle study and theoretical modeling will be performed in collaboration with Y. Mely (University of Strasbourg, France), and E.J. Meijer (computational chemistry, UvA), respectively.

Our work in the Advanced Research Center for Nanolithography will focus on the reactions that occur in hybrid materials under the influence of Deep Ultraviolet and Extreme Ultraviolet radiation. Both materials design and synthesis and mechanistic research based on product analysis and time-resolved spectroscopy are part of the research strategy of the Nanophotochemistry group.

Surface Chemistry and Catalysis

Prof. dr. M.T.M. Koper, Dr. D.G.H. Hetterscheid, Dr. L.B.F. Juurlink, Dr. I.M.N. Groot (UL)

Research topics

- Electrocatalysis for sustainable energy conversion, water splitting, carbon dioxide reduction
- Surfaces, both in UHV and electrochemical environments
- Theoretical electrochemistry
- Model catalysts
- In situ spectroscopy and in situ scanning probe imaging under realistic conditions

Summary of research activities

The research aim of the Surface Chemistry and Catalysis group is to probe and understand chemical reactions on well-defined, mostly single crystalline, surfaces at the molecular level. The group combines state-of-the-art experimental setups to study surface catalytic reactions using a variety of spectroscopic techniques, both at the metal-uhv and metal-liquid interface, with computational techniques based on density functional theory and dynamic Monte Carlo simulations.

Our aim is to unravel mechanistic and kinetic aspects of important catalytic reactions that feature in industrial processes, fuel reforming, fuel cells, the hydrogen economy, and environmental catalysis. Equipped with this fundamental insight, we aim to contribute to the rational design of catalysts. An important area of inspiration is biocatalysis and enzymes, and the comparison of reactions at different catalysts (metal surfaces, enzymes) at different interfaces (metal-gas, metal-liquid, enzyme-liquid).

The group currently has three main research themes: electrocatalysis at single-crystal and nanoparticulate electrodes (Koper), electrocatalysis at molecular catalysts (Hetterscheid), ultra-high vacuum surface science (Juurlink), and operando research in heterogeneous catalysis (Groot). Funding for our research comes from Leiden University, the Netherlands Organization for Scientific Research NWO (VICI, VIDI, TOP, ECHO, ASPECT, TA), various NWO-industry consortia and the European Union (various projects).

Group highlights 2015

See: http://casc.lic.leidenuniv.nl/news

Key publications 2012-2015

- Calle-Vallejo, F.; Loffreda, D.; Koper, M.T.M.; Sautet, P. Introducing structural sensitivity into adsorption-energy scaling relations by means of coordination numbers, *Nature Chemistry* **2015**, *7*, 403-410
- Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y.Y.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I, Schouten, K.J.P.; Mul, G.; Koper, M.T.M. , Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin, *Nature Communications*, **2015**, *6*, 8177, pp. 1-8.
- Chen, H.C.; Hetterscheid, D.G.H.; Williams, R.M.; van der Vlugt, J. I, Reek, J.N.H.; Brouwer, A.M. Platinum(II)-porphyrin as a sensitizer for visible-light driven water

oxidation in neutral phosphate buffer, *Energy & Environmental Science* **2015**, *8*, 975-982
- den Dunnen, A.; van der Niet, M.J.T.C.; Badan, C.; Koper, M.T.M.; Juurlink, L.B.F. Long-range influence of steps on water adsorption on clean and D-covered Pt surfaces, *Physical Chemistry Chemical Physics*, **2015**, *17*, 13, 8530-8537
- Schouten, K.J.P, Calle-Vallejo, F.; Koper, M.T.M. A step closer to the electrochemical production of liquid fuels, *Angew. Chem. Int. Ed.* **2014**, *53*, 10858-10860.

Future developments

The group will continue to strengthen its position on electrochemical and ultra-high-vacuum surface science and in particular in the combination of both. Future developments will include a more visible role of theoretical and computational chemistry, the bridging between heterogeneous and homogeneous electrocatalysis (with Dr. D. Hetterscheid), and the further deployment of in situ scanning probe methods, such as scanning tunneling microscopy (STM).

2.3 Theme 3 - Theoretical Chemistry

Understanding the structure of molecules and their chemistry from first principles represents the holy grail of theoretical chemistry. Many molecular properties can be understood directly from the electronic structure. When considering reactivity, it is usually necessary to consider the dynamics of the nuclei taking part in the reaction as well. The three theoretical chemistry groups of HRSMC work in both areas of research.
The research in the **Computational Physics and Chemistry** groups of Bolhuis and Meijer focuses on the study of materials, biological systems, and solution chemistry. Development and application of novel computational techniques and connection with experimental techniques are essential components of the research program. International collaboration with experimental and computational groups plays an important role.

The **Theoretical Chemistry** group from VuA concentrate their efforts on developing chemical theories and methods for rationally designing and spectroscopically characterizing molecules, nano-structures and materials as well as chemical processes toward these compounds, based on quantum mechanics and computer simulations. This ties in very well with the development of both density (matrix) functional (emeritus **Baerends**) and wave function based methods. Applications are being made to excitation energies and to many other response properties. The group is also active in structure and reactivity, molecular recognition and nanostructures, (bio)catalysis, accurate calculation of properties (NMR, electric field gradients) where relativistic effects are important, and biochemistry. The group also participates in the NRSC-Catalysis and NIOK.
This year the **Theoretical Group of Dr. J. Meyer** joined the HRSMC. His research aims at a better fundamental understanding of energy concersion at interfaces by combining existing as well as developing new computational techniques.

Computational Chemistry

Prof. dr. P.G. Bolhuis, Prof. dr. E.J. Meijer, Dr. B. Ensing, Dr. D. Dubbeldam, Dr. J. Vreede, Dr. R. Ni

Research topics

- Development of computational techniques to model properties of many-particle systems
- Nanoporous materials
- Micellar structures
- Reactivity in complex environment
- Polymers in flow
- Stability and structure of carbon materials
- Biological membranes
- Protein folding
- Photoactive proteins
- Signalling proteins
- Protein fiber formation
- Crystal stability and polymorphism
- Carbon materials

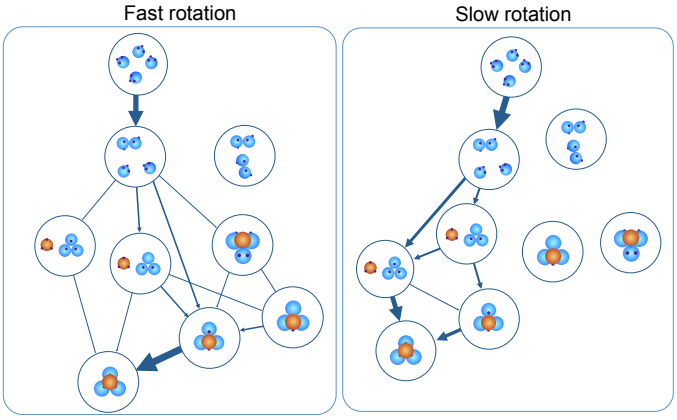
Summary of research activities

The group has kept a strong record in modeling complex phenomena in chemical, physical, and biological systems. Below highlights of the progress made in 2014 are listed.

Group highlights 2015

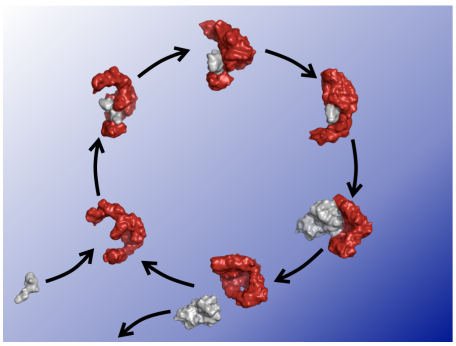
Soft (Bio)Matter (Researchers: Peter Bolhuis, Ran Ni)

Arthur Newton et al. describe how the rotation of nanoparticles such as proteins and colloids affects the self-assembly into complexes and clusters. In nature, molecular self-assembly plays animportant role: proteins stick to each other to form viruses, or protein complexes transmit signals in cellular networks. These self- assembly results depends on the dynamics and kinetics. Usually translation and rotation of particles are linked +via the so-called Stokes-Einstein relation. However, in recent years, experiments revealed that this coupling does not hold in tightly packed, crowded environments like the cytoplasm of the living cell. We investigated the effect of releasing the Stokes-Einstein coupling. While even for two particles already a strong effect on the association emerge, this gets more relevant for systems with multiple particles, where metastable intermediate states are possible. In a simulation of cluster



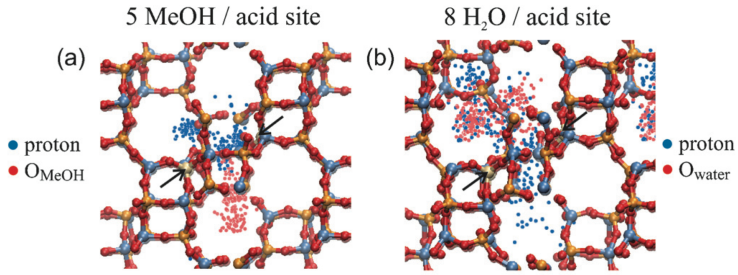
formation of four particles, varying the rotational diffusion significantly shifts the preference for the self-assembly routes (see figure). This was generalized to clusters of any size.
The figure shows change of assembly mechanism when reducing rotational diffusion. A circle depicts a metastable state. The black dots indicate where the particles can 'stick' to each other. One particle is colored orange in order to clarify the contrast. The thickness of the arrows reflects the probability of the assembly route. For slow rotation one route is clearly preferable compared to the other. Here 'frustrated' states (at the right) are avoided, resulting in significantly less kinetic hindrance and better yield.
The researchers argue that their results provide new opportunities for a better control of the bottom-up synthesis of functional materials. For example, it should be possible to design particles of which the rotation can be controlled with magnetic or electric fields.

Protein conformational changes (Researchers: Bolhuis, Vreede)
Trigger Factor (TF) is an ATP-independent chaperone protein that assists in folding and prevents misfolding. Up to now, it is a general unsolved question how chaperones assist in the folding of protein chains. Experimental methods that can probe at the length and timescales of inter-residue interactions are scarce, while the systems are too large—and the folding process too long to be studied by computer simulations. To overcome these obstacles, we performed molecular dynamics simulations at key moments along the folding pathway, and address the changes in the folding and unfolding dynamics of protein chains while in contact with TF. Our results provide the first detailed view on a chaperone-protein complex in different stages of folding and offers an explanation for the ability of TF to guide chains to their native state. Moreover, the results demonstrate the role of TF's flexibility in interacting with a wide range of client states. Overall, it explains how TF can interact with many types of substrates in various stages of folding, without the need for an ATP cycle to switch between encapsulation and liberation of client proteins.The figure illustrates the mechanism of TF assisted protein folding, with TF in red and the client protein in white. The cycle starts with TF interacting with an unfolded protein, which binds first to TF's outer appendages, followed by encapsulation. This way, TF stabilizes secondary structure elements, such as beta-sheets. TF releases the client protein upon folding, thus becoming available for binding another unfolded protein.



Chemical processes in complex environment (Researchers: Ensing and Meijer).
Chemical conversions in zeolites play an essential role in today's industrial catalysis. Within the field of heterogeneous catalysis, the conversion of methanol to hydrocarbons (MTH) or olefins (MTO) over acidic zeolites has received a lot of attention over the last decades because of its relevance in the search for alternative processes to produce hydrocarbon products. It can be considered a showcase example of complex zeolite-catalyzed chemistry as many factors affect the reactivity. These include framework flexibility, adsorption of various guest molecules, and competitive reaction pathways. We have demonstrated [De Wispelaere et *a*l, Chem. Eur. J, **21**, 9385] that by using first

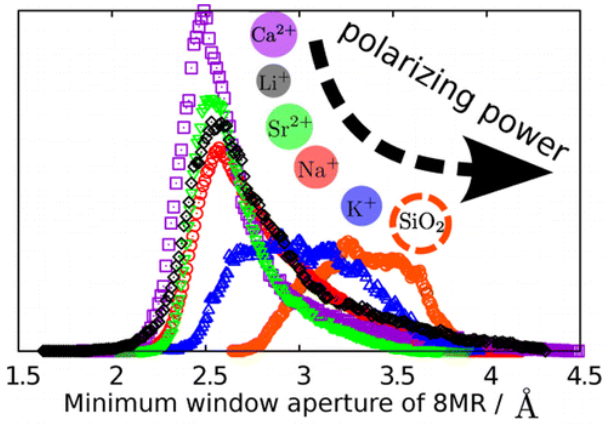
principle molecular dynamics techniques to capture this complexity can be elucidated, shown by means of two case studies. Firstly, the adsorption behavior of methanol and water in H-SAPO-34 at 350 ^{0}C is investigated. Hereby an important degree of framework flexibility and proton mobility was observed. Secondly, the methylation of benzene by methanol through a competitive direct and stepwise path- way in the AFI topology was studied. Both case studies clearly show that a first-principle molecular dynamics approach enables unprecedented insights into zeolite-catalyzed reactions at the nanometer scale to be obtained. The Figure shows representations of the displacement of a proton (blue) and a methanol or water oxygen atom (red) as observed in a 50 ps MD simulation of H-SAPO-34 zeolite filled with five methanol molecules (left) or eight water molecules (right) per acid site.



Nanomaterials (Researchers: Dubbeldam, Meijer, Ensing)

Molecular valves are becoming popular for potential biomedical applications. However, little is known concerning their performance in energy and environmental areas. Zeolite RHO shows unique pore deformations upon changes in hydration, cation siting, cation type, or temperature–pressure conditions. By varying the level of distortion of double eight-rings, it is possible to control the adsorption properties, which confer a molecular valve behavior to this material [Balestra et al, Chem. Mater **27**, 5657].

We reviewed [Torres-Knoop and Dubbeldam, ChemPhysChem **16**, 2046] the molecular mechanisms behind adsorption and the separations of mixtures in metal–organic frameworks and zeolites. Separation mechanisms can be based on differences in the affinity of the adsorbate with the framework and on entropic effects. To develop next-generation adsorbents, the separation efficiency of the materials needs to be improved. The performance under industrially relevant conditions largely depends on two factors: 1) the separation selectivity and 2) the pore volume capacity of the material. Enthalpic mechanisms can lead to increased selectivities, but these are mostly restricted to the low loading regime, and hence these mechanisms are unable to make use of all of the large-pore volume that a metal–organic framework can provide. Industrial processes routinely operate in the pore saturation regime. In this Review, we focused on entropic molecular separation mechanisms that are effective under these conditions and, in particular, on a recent methodology to obtain high selectivities at high pore loading.



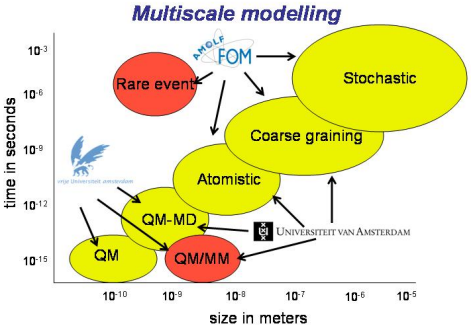
Separating acetylene from ethylene/acetylene mixtures containing is a technologically very important, but highly challenging task. We [R. Krishna] have contributed to a study

of a microporous metal–organic framework that in which the suitable pore/cage spaces preferentially take up much more acetylene than ethylene while the functional amine groups on the pore/cage surfaces further enforce their interactions with acetylene molecules, leading to its superior performance for this separation. The combination of simulations and and experimental characterizations collaboratively support this claim, underlying the potential of this material for the industrial usage of the removal of acetylene from ethylene/acetylene mixtures.

Key publications 2012-2015 (max 5)

- Díaz Leines, G.; Ensing, B.; Path Finding on High-Dimensional Free Energy Landscapes, *Phys. Rev. Lett.* **2012**, 020601, 109.
- Torres-Knoop, A.; Krishna, R.; Dubbeldam, D.; Separating Xylene Isomers by Commensurate Stacking of p-Xylene within Channels of MAF-X8, *Angew. Chem. Int. Ed.* **2014**, *53*, 7774.
- Zhu, L.; Bolhuis, P.G.; Vreede, J. The HAMP signal relay domain adopts multiple conformational states through collective piston and tilt motions, *PLoS Comput. Biol.* **2013**, *9*, e1002913,
- Pavlova, A.; Trinh T.T, van Santen R.A; Meijer E.J, *Clarifying the role of sodium in the silica oligomerization reaction*, Phys. Chem. Chem. Phys. **2013**, *1123*, 15.
- Newton, A.C.; Groenewold, J.; Kegel, W.K.; Bolhuis, P.G. Rotational diffusion affects the dynamical self-assembly pathways of patchy particles, *Proc. Nat. Acad. Sci.* **2015**, 15308, 112.

Future developments



Over the past years the research environment has been strengthened by establishing the Amsterdam Center for Multiscale Modeling (ACMM). The ACMM combines the groups of Baerends/Bickelhaupt/ Visscher (VU) and Bolhuis/Krishna/Meijer at (UvA) together with other groups active in computational science in the Amsterdam area. The ACMM has become the basis for the development and application of computational methods for research in the fields under 2). It also serves as a partner in external collaborations both nationally and internationally and will be a national and international training center. We have extended our staff by attracting David Dubbeldam.

Specific research topics will be in the field of complex (bio)molecular systems where we focus on the role of macromolecules in the cell (e.g. photoactive protein complexes, protein aggregation and protein folding, and cytoskeleton filaments), and on catalysis in solution and (semi-)structured environment, in particular confinement effects, enzymes, and catalytic surfaces. In the field of materials and engineering we will focus on novel nanoporous materials and novel carbon materials. We aim to broaden our teaching and training activities by converting the present ATOSIM MSc program into an international graduate school that combines a MSc and PhD training program in computational science.

Theoretical Chemistry

Prof. dr. F.M. Bickelhaupt, Prof. dr. L. Visscher, Prof. dr. E.J. Baerends (em.), Dr. C. Fonseca Guerra, Prof. dr. P. Gori Giorgi, Dr. I.A.C. Infante (VU)

Research topics

- Theoretical Organic Chemistry and Biocatalysis (Bickelhaupt)
- Quantum Chemistry and Multiscale Modeling (Visscher)
- Theoretical Chemistry / Density (Matrix) Functional Theory (Baerends)

Summary of research activities

The TC group develops molecular electronic structure theory and devises quantum chemical methods for the calculation of the electronic structure and the properties following from it. Research focuses on physical models, numerical methods and computer implementations. Density functional theory and density matrix theory and computational methods derived from these theories are central themes, as well as WFT and DFT methods for the simultaneous treatment of relativistic effects and electron correlation. A third point of focus is the conceptual development of chemistry in particular the development of models that enable a qualitative understanding, based on accurate calculations, of chemical reactivity and, thus, a more rational tuning of elementary chemical processes.

Actual electronic structure investigations ('applications') are carried out to understand and predict phenomena in a variety of chemical subdisciplines. Issues in chemical bonding, structure, and reactivity are addressed: rational, fragment-oriented design of catalysts; structure and bonding in various DNA motifs, molecular recognition in general and nanoswitches; metal-ligand and metal-metal bonding in organometallic chemistry including studies in photochemistry; complexation and solvation of (actinide) metal complexes; elementary chemical reactions; *ab initio* molecular dynamics (Car-Parrinello) for solvent effects on reactions. Methods are developed and applied for relativistic effects, which are needed in the study of heavy element chemistry and spectroscopy. Reactivity at and scattering from crystal surfaces is studied with a combination of electronic structure calculations (for the potential energy surfaces) and (quantum) dynamics for the nuclear motions (heterogeneous catalysis). Time-dependent DFT calculations of response properties afford detailed study of electronic absorption spectra and nonlinear optical properties of large molecules such as substituted and dimeric porphyrines and phthalocyanines. A new research line deals with astrochemistry.

Key publications 2012-2015

- Dommerholt, J.; Van Rooijen, O.; Borrmann, A.; Fonseca Guerra, C.; Bickelhaupt, F.M.; Van Delft, F.L.; Highly Accelerated Inverse Electron-Demand Cycloaddition of Electron-Deficient Azides with Aliphatic Cyclooctynes, *Nature Commun.* **2014**, *5*, 5378.

- Fernandez, I.; Bickelhaupt, F.M.; The Activation Strain Model and Molecular Orbital Theory: Understanding and Designing Chemical Reactions, *Chem. Soc. Rev.* **2014**, *43*, 4953-4967.
- Hoefener, S.; Gomes, A.S.P.; Visscher, L. Molecular properties via a subsystem density functional theory formulation: A common framework for electronic embedding, *J. Chem. Phys.* **2012**, *136*, 044104.
- Gomes, A.S.P.; Jacob, C.R.; Real, F.; Visscher, L.; Vallet, V. Towards systematically improvable models for actinides in condensed phase: the electronic spectrum of uranyl in $Cs_2UO_2Cl_4$ as a test case*,* Phys. Chem. Chem. Phys. **2013**, *15*, 15153.
- Malet, F.; Gori Giorgi, P.; Strong correlation in Kohn-Sham density functional theory, *Phys. Rev. Lett.* **2012**, *109*, 246402.
- Bernasconi, L.; Baerends E.J. A frontier orbital study with *ab initio* molecular dynamics of the effects of solvation on chemical reactivity: solvent-induced orbital control in FeO-activated hydroxylation reactions, *J. Am. Chem. Soc.* **2013**, *13,* 88567-8867.
- Giesbertz, K.J.H.; Gritsenko, O.V.; Baerends E.J. Response calculations based on an independent particle system with the exact one-particle density matrix: Excitation energies, *J. Chem. Phys.* **2012**, *136*, 0941104 / 1-12.

Future developments

In the project dealing with the conceptual development of chemistry we envisage:

1) Further extension of the activation strain model of chemical reactivity and its application to (bio)catalysis and archetypal organic reactions. The classes of organic reactions are extended from S_N2, E2 and proton transfer to pericyclic reactions. Also, we will more and more go from analyzing and understanding catalytic reactions toward rationally designing tailor-made catalysts.

2) In the fields of computational biochemistry and nanostructures, we will develop three lines of research: a) DNA structure and stability will be further developed towards DNA replication; and b) towards telomere structure, stability and function; c) molecular recognition will be extended towards supramolecular catalysts.

3) In the subproject on structure and bonding, the development is towards new structural motifs (e.g., stable 5-coordinate carbon).

In the project concerning development and application of multiscale and multilevel methods for the modeling of complex molecular systems we envisage:

1) Further development and application of subsystem methods in which subsystems are optimized individually and treated as frozen in the embedding of the other subsystems. We plan to include charge-transfer between subunits and to allow for partitioning in terms of subunits separated by strong (electron pair) bonds. Central in this development is the ability to treat selected subsystems with both (approximate) density functional techniques as well as with accurate wave function methods. One class of applications is the design of better components for light-harvesting devices, on which we will work in collaboration with biophysics groups in the Solardam initative.

2) Development of multiscale approaches that can efficiently utilize merging massively parallel computers. In computing one sees a change of paradigm with high-performance GPU cards and supercomputers emerging that consist of many thousands of compute

cores. In collaboration with the SCM company and the eScience Center we develop new algorithms to benefit from this revolution in computer hardware. We are thereby e.g. working on extending our PyADF scripting framework to enable automatic parallelization.
3) Work on methods suited for heavy element chemistry focuses on the relativistic multireference coupled cluster method and is carried out in the framework of the European DIRAC program. Applications concern primarily the chemistry and spectroscopy of actinide molecular complexes.

In the project dealing with the development of theory, methods and applications of density (matrix) functional theory we envisage:
1) Further development of density *matrix* functional theory (DMFT). We will investigate the extension of DMFT to time-dependent fields, and in particular develop the formalism for response properties (excitation energies). Orbital dependent functionals will be further developed and their potential to describe in particular weak bonding situations (dissociation) will be investigated.
2) In the field of homogeneous catalysis the special status of the ferryl ion (oxidoiron(IV)) will continue to be the main focus, but also a range of other metal-oxo compounds will investigated. Use of O_2 as stoichiometric oxidation reactant will be explored.
3) The calculation of chiral properties of molecules has become an important research field. The development of techniques for vibrational circular dichroism (VCD) will be continued, and work on vibrational Raman optical activity (ROA) has been started. The concept of "robustness" of VCD peaks, which we have introduced, greatly aids in the use of VCD for the determination of the absolute configuration of a molecule. It will be investigated for ROA as well. The next important problem for VCD is the sensitivity of the spectra to the conformation of a molecule. A long term goal is the theoretical understanding of the conformational effects, and to find on that basis a way to deal with this problem in absolute configuration determination.

In the project dealing with the conceptual development of chemistry we envisage:
1) Further extension of the activation strain model of chemical reactivity and its application to (bio)catalysis and archetypal organic reactions. The classes of organic reactions are extended from S_N2, E2 and proton transfer to pericyclic reactions. Also, we will more and more go from analyzing and understanding catalytic reactions toward rationally designing tailor-made catalysts.
2) In the fields of computational biochemistry and nanostructures, we will develop three lines of research: a) DNA structure and stability will be further developed towards DNA replication; and b) towards telomere structure, stability and function; c) molecular recognition will be extended towards supramolecular catalysts.
3) In the subproject on structure and bonding, the development is towards new structural motifs (e.g., stable 5-coordinate carbon).

Theoretical Chemistry

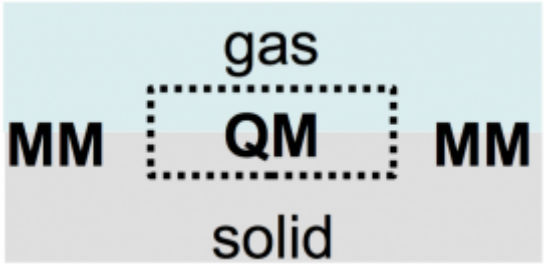
Dr. J. Meyer

Research Topics

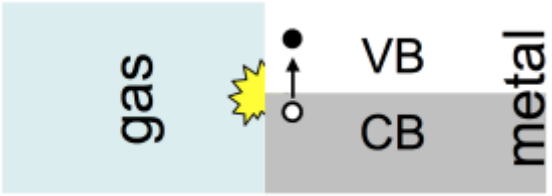
- Modelling of Energy Exchange at Interfaces (Meyer)

Summary of research activities

Chemical reactions go hand-in-hand with an energy exchange with the environment in which they take place. Surfaces offer a variety of energy dissipation channels, constituted by the nuclear and electronic degrees of freedom of the atoms at the interface. Aiming at an improved future harvesting of energy, we are developing and applying computational methods to obtain a better fundamental understanding of interfacial energy conversion dynamics.



Quantum mechanical (QM) modeling is required in order to accurately account for bond breaking and making during chemical reactions. Density-functional theory (DFT) in particular has proven to be a very successful tool in that respect, in particular when it comes to the description of metallic surfaces. Still, its computational effort limits the time and length scale that can be modeled in dynamical simulations. Already a simple back-on-the-envelope calculation using the speed of sound allows to estimate that these limitations can affect the description of heat transport in the solid via vibrations of the lattice (phonons). With our recently developed new "QM/Me" embedding scheme [2], which links QM- modeling to molecular mechanics (MM) for metallic systems, we can overcome such limitations.



Since there is no energetic gap between the valence band (VB) and the conduction band (CB) in metallic systems, chemical dynamics at the interface can easily excite electrons. This leads to the violation of one of the most fundamental approximations in theoretical modeling, the Born-Oppenheimer approximation, and provides another elementary channel for energy dissipation. Characterizing and quantifying these electron- hole-pair excitations[4] and including their effect on dynamics at an interface [1] poses a formidable theoretical challenge, which we are facing by the development and application of new computational methods.

[1] Rittmeyer, S. P.; Meyer, J.; Inaki, J. J.; Reuter, K. Electronic Friction-Based Vibrational Lifetimes of Molecular Adsorbates: Beyond the Independent-Atom Approximation. *Physical Review Letters* **2015**, *115* (4), 046102/1-046102/5.
[2] Meyer, J.; Reuter, K. Modellierung von Wärmedissipation Auf Der Nanoskala: Ein Einbettungsansatz Für Chemische Reaktionen Auf Metalloberflächen. *Angewandte Chemie* **2014**, *126* (18), 4813–4816.
[4] Meyer, J.; Reuter, K. Electron-Hole Pairs during the Adsorption Dynamics of O2 on Pd(100): Exciting or Not?. *New Journal of Physics* **2011**, *13* (Aug.), 085010/1-085010/20.

Key Publications (2015)

- Bukas, V. J.; Mitra, S.; Meyer, J.; Reuter, K. Fingerprints of Energy Dissipation for Exothermic Surface Chemical Reactions: O2 on Pd(100). *The Journal of Chemical Physics* **2015**, *143* (3), 34705.
- Rittmeyer, S. P.; Meyer, J.; Inaki, J. J.; Reuter, K. Electronic Friction-Based Vibrational Lifetimes of Molecular Adsorbates: Beyond the Independent-Atom Approximation. *Physical Review Letters* **2015**, *115* (4), 046102/1-046102/5.

2.4 HRSMC Co-operations

Research topic	Co-operating groups	Theme	University
2-D IR of Protein folding	Woutersen/Bolhuis	2.3	UvA
Adaptive QMMM methods	Ensing/Bulo	3	UvA,VU
Applications of chiroptical spectroscopies	Buma/Ariese	2	UvA/VU
Aromaticity in inter/circumstellar ice analogues a combined experimental and theoretical approach	Linnartz/Fonseca Guerra/Bickelhaupt	2.3	UL, VU
Artizymes	Lammertsma/Overhand	1	VU, UL
Calculations on homogeneous catalytic mechanisms	Ehlers/Bouwman	1	UvA, UL
Circular dichroism in plants	Buma/Ariese	2	UvA, VU
Calculations on Multicomponent Syntheses	Bickelhaupt/Orru/Fonseca Guerra	1.3	VU
Chemistry Behind CuII-μ-thiolate and CuI-disulfide complexes	Bouwman/Fonseca Guerra/Bickelhaupt	1.3	VU
Chiral anion-mediated catalysis	Orru/Lammertsma	1	VU
Developing broad spectrum light-harvesting antennas for organic solar cells	Bickelhaupt/Fonseca Guerra/Lammertsma	1.3	VU
Development of device compatible charge separators	Orru/Lammertsma	1	VU
Dutch Compound Library	Orru/Overkleeft/ v.Maarseveen	1	VU, UL, UvA
Early stage dynamics of protein folding	Woutersen/Bolhuis	2.3	UvA
Electrocatalysis of immobilized molecular catalysts for water oxidation	Koper/Reek/Hetterscheid	2.3	UL, UvA
Electronic structure calculations on organometallic complexes	Baerends/Lammertsma	1.3	VU
Electronic structure of phosphinidine complexes	Baerends/Lammertsma	1.3	VU
Enzyme cascade reactions	Wever	1	UvA
Ester hydrogenolysis and (de)hydrogenations using firstrow transition metals	Elsevier/de Bruin/vd Vlugt/Van Maarseveen	1	UvA
Experimental and theoretical studies of molecules of astrochemical interest	Bickelhaupt/Fonseca Guerra/ Linnartz/Ubachs	1.2	VU, UL
Fluorescent organocatalysts	Brouwer/Hiemstra	1.2	UvA
Fragment-oriented rational design of catalysis	Bickelhaupt/Reek	1.3	VU, UvA
Homogenous Catalysis in transition metal complexes	Meijer/Reek/De Bruin	1.3	UvA
Homogeneous vs. heterogeneous electrocatalysis	Koper/Bouwman	1.3	UL
Hydrogenation of Carboxylic Acids with a Homogeneous Cobalt Catalyst	Elsevier/de Bruin	1	UvA
Infrared studies of (di)manganese carbonyl ions	Buma/Ingemann	1.2	UvA
Isotope-labeled peptides	Woutersen/Van Maarseven	1.2	UvA

IR spectroscopy of metal clusters	Bakker/Buma/Oomens/Visscher	2.3	RU, UvA, VU
Light Harvesting Antenna complex	Abrahams/IJdo/Fu/De Groot	1.2	TUD, UL
Light harvesting dyes	Brouwer/Orru/Lammertsma	1.2	UvA, VU
Light Harvesting Molecules	Lammertsma/ Bickelhaupt/ Buma	1.2.3	VU, UvA
Luminescence enhancement of lanthanoid complexes; Orrit/Bouwman	Orrit/Bouwman	1.2	UL
Measuring and simulating chemistry in cometary processes	Bickelhaupt/Linnartz	3.2	VU, UL
Modeling of conformation of peptidomimetics	Orru/Ehlers	1	VU
Molecular separations	Grecea/Dubbeldam	1.3	UvA
Molecular sensing	Grecea/Bouwman/Zhang	1.2	UvA,UL
Non radiative energy transfer in three-component lipid membranes: upconversion followed by FRET	Bonnet/Kennis	1.2	UL, VU
PAHs in the laboratory and in space	Buma/Ubachs/Linnartz	2	UVA, VU, UL
Palladium catalysis, click chemistry involving NHC-triazole compounds	Elsevier/Hiemstra/Van Maarseveen	1	UvA
Pd-Catalyzed Z-Selective Semihydrogenation of Alkynes: Determining the Type of Active Species	Elsevier + de Bruin	1	UvA
Photocatalysis	Brouwer/Reek/Hartl/vdVlugt	1.2	UvA
Photocatalysis	Reek/vd Vlugt/De Groot	1.2	UvA, UL
Photodissociation dynamics of iron complexes	Van Hemert/Lammertsma/Ehlers/Kroes	1.3	UL, VU
Photosynthesis	De Groot/Koper	2.3	UL
Proton conductivity	Grecea/Ensing/Woutersen	1.2.3	UvA
Protons in aqueous environment	Meijer/Ensing/Woutersen	2.3	UvA
Radical copper-phenolate compounds	Bouwman/De Bruin	1.3	UL, UvA
Renewable fuels	Buma/Visscher	1.3	UvA,VU
Selective enzymatic phosphorylation	Hiemstra/Wever	1	UvA
Solar energy conversion	Lammertsma/ Bickelhaupt/Buma	1.2.3	VU, UvA
Spectroscopy (2D-IR)	Reek/vd Vlugt/Woutersen	1.2	UvA
Spectroscopy of chiral molecules	Buma/Janssen	2	UvA, VU
Stimulated Raman in cells	Bonnet, Ariese	1.2	UL, VU
Time-dependent spectroscopy of photocatalytic liposomes	Bonnet/Brouwer	1.2	UL, UvA
TR spectroscopy applied to supramolecular catalysis	Reek/Brouwer	1.2	UvA
Ester hydrogenolysis and (de)hydrogenations using firstrow transition metals	Elsevier/de Bruin/vd Vlugt	1	UvA
Use of phosphatases and sulfatases in enantioselective reactions	Wever	1	UvA
Various Synthetic products	Hiemstra/Orru/ v.Maarseveen	1	UvA, UL
Vibrational circular dichroism	Woutersen/Buma/De Bruin	1.2	UvA

Vibrational circular dichroism: applications and theory	Buma/Visscher	1.3	UvA, VU
Water oxidation catalysis	Buda/de Groot/Koper/Hetterscheid	2.3	UL

2.5 Memberships and awards

Memberships organising committees international meetings

Name staff member	-	**Activity**
Bickelhaupt	-	Member Scientific Committee Girona Seminar, Girona, Spain
	-	Member Interanational Advisory Board, Virtual Conference on Computational Chemistry, Mauritius
Buma	-	Co-chairman of the HRSMC and ESF SILMI Programme Graduate School on "Modern Developments in Spectroscopy", Noordwijk (NL), April 2012 and 2015.
Elsevier	-	Board EUCHEMS conferences Organometallic Chemistry since 2007 Member
Ensing	-	Organizer Winter School for Theoretical Chemistry and Spectroscopy, Han sur Lesse, 2015.
Fonseca Guerra	-	Member International Advisory Board, Virtual Conference on Computational Chemistry, Mauritius
Groot, de	-	Co-organizer Lorentz workshop
Hiemstra	-	Member of the Programme Committee of the 27th European Colloquium on Heterocyclic Chemistry, Amsterdam, July 2016
Linnartz	-	Board member IAU commission 'Laboratory Astrophysics'
	-	Board member international committee of the biannual workshop on infrared plasma spectroscopy
	-	Board member ISWA2016
Maarseveen, van	-	Foreign expert panel member W&T4 (chemistry) Flanders Research Foundation (FWO).
Meijer	-	Coordinating organizer international school ´Understanding Molecular Simulation' 2015
Slootweg	-	Member Organizing Committee of the International Conference on Phosphorus Chemistry 2012 (ICPC 2015)
Timmerman	-	Member of Scientific Advisory Board TIDES-meeting, Oligonucleotide & Peptide Research, Technology & Product Development

Board memberships scientific organisations/academies/awards

Name staff member	-	Activity
Ariese	-	Board Member International Society on Polycyclic Aromatic Compounds
	-	Member of LASERLAB EUROPE working group on future financing
	-	Member of COAST Educational Board
Bickelhaupt	-	Chairman Board HRSMC
	-	Royal Holland Society of Sciences and Humanities (KHMW)
	-	Fellow of the Royal Society of Chemistry (FRSC)
	-	Chairman VU-UvA Education Committee Chemistry
	-	Member Pannel ERC Starting Grant
	-	NWO Astrochemistry program committee
	-	NWO Planetary and Exoplanetary Sciences program committee
	-	Member Management Committee of COST action CM1105 (Functional Metal Complexes that Bind to Biomolecules)
	-	Member of COST action CM1005 (Supramolecular Chemistry in Water)
	-	Member International Advisory Board, Institute of Computational Chemistry and Catalysis, Girona, Spain
	-	Member Advisory Board, Leiden Institute of Chemistry, Leiden, Netherlands
Bolhuis	-	Member FOM BRM programme committee
	-	Director of the Dutch CECAM node
	-	Chair of the CW study group Soft Matter
	-	Co-organized the ESI/CECAM Workshop "From trajectories to reaction coordinates:
	-	making sense of molecular simulation data", September 16-18, 2015, Erwin-Schrödinger-Institute in
	-	Vienna, Austria
Bonnet	-	Board Member CW study group Lipids and Biomembranes
	-	Member Organizing Committee HRSMC Summerschool Photochemistry, Fundamentals and Applications (2016)
Bouwman	-	Board Member Leids Universiteits Fonds (LUF)
	-	Board Member Inorganic Division of EuCheMS
	-	Board Member CW study group Coordination Chemistry & Homogeneous Catalysis
	-	Member NWO-CW TOP/ECHO jury
Brouwer	-	Co-chair IUPAC project Photoluminescence Standards
	-	Member of the sub-committee on Photochemistry IUPAC,
	-	Division III

Brouwer	- Chair IUPAC project Photoluminescence Quantum Yields - Chairman Organizing Committee HRSMC Summerschool Photochemistry, Fundamentals and Applications (1998, 2003, 2008, 2012, 2016) - Member of the Review Group of the project "Application of Cooperative-Excitation into Innovative - Molecular Systems with High-Order Photofunctions", MEXT, Japan, 2014-2018. - Member of the Permanent Steering Committee of the Biannual Conference on Methods and - Applications of Fluorescence: Spectroscopy, Imaging & Probes (MAF:SIP) - Member of IUPAC Sub-commission on Photochemistry - Organizer of LEELIS workshops (Low-Energy Electrons: Lithography, Imaging and Soft matter), - Amsterdam, 2014, 2016 - Chair IUPAC project Measurement of Photoluminescence Quantum Yields - Member of the board of the Study Group Structure and Reactivity (Chemical Sciences, Netherlands - Science Foundation) - Member of board of Works Council of Faculty of Science, University of Amsterdam
Bruin, de	- UvA coordinator new UvA-VU Master Track 'Science for Energy and Sustainability' - Member of the Chemistry Education Committee (OCS) UvA-VU (since 2008). (Co)chair of the committee since 2012 - Member Educational Board NIOK - Member American Chemical Society
Buma	- Member American Chemical Society - Member Senate UvA - Scientific Director HRSMC (since 2008) - Chairman John van Geuns Fonds Foundation - Member and secretary Board Stichting Bèta Plus - Kohler Distinguished Lectureship - Member International Advisory Committee "International Symposium on Molecular Beams", 2017 - Programme manager "Analytical Chemistry and Spectroscopy" of LaserLab Amsterdam (partner of LaserLab Europe). - Member Management team Institute QuantiVision (Innovative Medical Devices Initiative initiated by - ZonMW). - Member Senate of the University of Amsterdam. - Member and secretary Board Stichting Bèta Plus

Dubbeldam	- Organiser Graduate winterschool on - Understanding Molecular Simulation, January 5-16, 2015; Amsterdam.
Elsevier	- Member Board HRSMC (since 2008) - Member Scientific Council NRSC-Catalysis - Scientific Director HRSMC 2002-2007 - Visiting professorship at the Weizman Institute of Science (Israel) - Visiting professorship at ULP Strasbourg and at ENSIACET Toulouse
Ensing	- Member Educational Board HRSMC - Graduate Winterschool on Theoretical Chemistry and Spectroscopy, - December 8-12, 2015 (Han-sur-Lesse, Belgium) - Co-organized the ACMM symposium in honour of Evert-Jan Baerends 70th birthday. - Graduate winterschool on - Understanding Molecular Simulation, January 5-16, 2015; Amsterdam.
Fonseca Guerra	- EU Visiting Professorship at Warsaw University of Technology, Warsaw, Poland
Fernández Ibáñez	- Member of the Organizing Committee, 5th HRSMC Summer School on Organic Synthesis, Summerm2017 - Management Committee Member, EU COST-network C-H Activation in Organic Synthesis (CHAOS) - Member of the Editorial Board of Advances in Chemistry (Organometallic Chemistry section) - -Member of the core team 'Task force Sustainability' UvA - Member of the board Women in FNWI (WiF), University of Amsterdam
Groenen	- Chairman of the "Syllabuscommissie Nieuwe Natuurkunde" - Member of the International Scientific Advisory Board of the Max Planck Institute for Bioinorganic Chemistry (Mülheim, Germany)
Groot, de	- Member of the NWO Advisory Board Maatschappelijk Verantwoord Innoveren - Member of schrijfgroep programmacommissie NWO programme Co2 neutral production of fuels - Member of the committee of recommendation Open Wetlab (de Waag) - Member of the Jury for the Martinus van Marum Prijs - Scientific director Research program BSC (BioSolar Cells) - Member of the Steering committee BSC - Member of the Management Team BSC

Groot, de	- Member of de Raad van Toezicht Stichting Leiden Honours Community - Member of the FCT review panel for evaluation of research unit Natural and Environmental Sciences (Panel 04)
Hiemstra	- Member of "Koninklijke Hollandsche Maatschappij der Wetenschappen" - Chairman Examination Committee Bachelor Scheikunde and Master Chemistry, UvA - Member of the International Advisory Board of the Organic Division of the Czech Chemical Society - Member of the American Chemical Society - Member of the International Society of Heterocyclic Chemistry - Elected Member of the Royal Holland Society of Sciences (KHMW) - Member of the International Advisory Board of the Organic division of the Czech Chemical Society - Member of the Program Committee of the 27th European Colloquium on Heterocyclic Chemistry, - Amsterdam, July 2016 - Member of the Editorial Board of Molecules (Open Access Organic Chemistry Journal) - Chairman of the Examination Committee master Chemistry and bachelor Scheikunde, UvA (until - September 1st 2015) - Chairman of the Research Committee of the HRSMC - Member of the Organizing Committee, 5th HRSMC Summer School on Organic Synthesis, Summer - 2017
Ingemann	- Member of The European Chemistry Thematic Network (on behalf of the Faculty of Science) - Head of the Structure Analysis group at HIMS comprising the instrumental methods: MS, NMR, X-Ray - and EPR - Coordinator of the Master Chemistry Track: Molecular Design, Synthesis and Catalysis
Koper	- Vice-President of the International Society of Electrochemistry - Board Member HRSMC - Board Member NIOK (Netherlands Institute for Catalysis Research) - Member of review panels of NWO, FWO, Austrian Science Foundation - Carl Wagner Memorial Award of the Electrochemical Society - Member of review panels of NWO, FWO

Lammertsma	- Member Educational Board HRSMC - Member of the Board of the Chemistry & Society Section (CMG) of the Royal Dutch Chemical Society (KNCV) - Management Member COST Action CM1302, the European Network on Smart Inorganic Polymers - Member of the Board NWO/CW study group "Coordination Chemistry and Homogeneous Catalysis" - Member of the Board of NWO Chemical Sciences (Gebiedsbestuur) - Member of the Netherlands Initiative on Material Scarcity (NIMS) - Member of the Top Team of the Top Sector Chemistry
Linnartz	- Research coordinator FP7 ITN 'Laboratory Astrochemical Surface Science in Europe' - Coordinator 'solid state part' within the NWO Dutch Astrochemistry Program - Coordinator 'biomarker part' within the NWO PEPSci (Planetary and Exoplanetary Science) program - Vice-chair Division XII of IAU commission 14: working group solids and their surfaces - Board Member European Task Force Laboratory Astrophysics - Chairman education committee astronomy at Leiden Observatory - Member Greenberg fellowshop selection committee - Member EW-VIDI selection committee
Maarseveen, van	- Member of the management committee of EU-COST action CM0905 ORCA "Organocatalysis" - Member of the Board of the NWO-CW study group Design & Synthesis - Expert member, Panel W&T4 Fonds Wetenschappelijk Onderzoek, Flanders, Belgium - Member of the International Advisory Board European Journal of Organic Chemistry - Member of the Organizing Committee, 5th HRSMC Summer School on Organic Synthesis, Summer - 2017
Meijer	- Member, Scientific Council CECAM - Member, UCO UvA - Organiser Graduate winterschool on - Understanding Molecular Simulation, January 5-16, 2015; Amsterdam.
Mutti	- Honorary Research Fellow from The University of Manchester

Orrit	- Member Academia Europaea - Member Review panels for NWO, AERES, DPG, FWO 2011
Orru	- Member Organic Chemistry Section of the Royal Durch Chemical Society (KNCV) - Member of the board of the 'Design & Synthesis' studygroup of NWO-CW
Reek	- Member of the management team of the BioSolar Cells (since 2010) - Member Young Royal Netherlands Academy of Arts and Sciences (KNAW) 2006-2011 - Member of the Royal Netherlands Academy of Arts and Sciences (KNAW) (since 2015) - Member of the management team NIOK (since 2012) - Member of 'Koninklijke Holandsche Maatschappij der Wetenschappen' (since 2013) - Boardmember KNCV since 2009 - Director van 't Hoff Institute for Molecular Science (HIMS) (2013-2017) - Member (Chair 2013-2016) UOC UvA - Director of research priority area sustainable chemistry UvA (since 2013) - Chair of NWO work group Coordination and Catalysis (since 2008) - Scientific director InCatT - Director of research priority area Sustainable Chemistry UvA - Management team NRSCC - Board member KNCV (research)
Reek	- Management team BioSolarCell (Dutch artificial leaf program) - Chair UOC UvA - Member of the World economic form - Steering committee Co van Ledden Hulsebosch Center
Timmerman	- Member of the scientific advisory board of the yearly TIDES-meeting organized in the USA.
Tromp	- Member of the international user committee of the ANKA research facility (Karlsruhe, Germany) (since 2013) - Member of the European Synchrotron User Organisation Committee (since 2013). - Member 'Agentschap voor Innovatie door Wetenschap en Technologie' (IWT) evaluation panel PhD proposals, Belgium (since 2014). - Member of the MAX Laboratory (Lund, Sweden) Program Advisory Committee (since 2012)

Tromp	- Member of the Swiss Light Source Peer Review Panel (2009-current). Chair of the Hard X-ray Committee of the Pair Review Panel (since 2011). - Member of the Scientific Advisory Committee of the SOLEIL synchrotron (since 2014). - Member of BMW Diesel IAS-TUM focus group on 'Electrochemical Interfaces in Batteries' (since 2013) - Member of 12 TUM Faculty Search and Appointment Committees (since 2010) - Member of the American Chemical Society (since 2004) - Member of the KNCV, incl. Dutch Catalysis Society (since 1995) - Member Gesellschaft Deutscher Chemiker e. V., GDCh, German Chemical Society, incl. Deutsche Gesellschaft für Katalyse (since 2011).Member of the Deutscher Hochschulverband DHV (since 2010). - Member of the Royal Society of Chemistry (since 2006). - Member of the International X-ray Absorption Spectroscopy Society (since 2000). - Member of NWO TOP-ECHO review panel - Secretary of the organizing committee of the EuCheMS International Conference on Organometallic - Chemistry 2017 in Amsterdam. - Secretary of the organizing committee of the International Symposium on Homogeneous Catalysis - 2018 in Amsterdam. - Member of the Spectroscopy Village Beamlines Review Committee, Diamond Light Source - Chair of the Peer Review Panel (incl. all sub-committees) of the Swiss Light Source. Chair of the hard Xray panel - Member, Board of Examinations, Chemistry UvA/VU - Member, Advisory Board Technology Center FNWI, UvA - Member, Sounding Board to the Dean, FNWI, UvA - Member, Management Team, COST Action CHAOS
Vreede	- Co-organizer ACMM Symposium, June 25, 2015
Visscher	- Director Amsterdam Center for Multiscale Modeling - Member werkgroep Supercomputers, NWO/NCF - Auditor to the International Treasurer of the European Photochemistry Association
Williams	- Member of the Board of Examiners of the Forensic Science Master. - Member of the FNWI library committee.

Woutersen	- Member of the scientific advisory committee of the Max-Planck-Institut in Mainz - Member of the international organizing committee of the European Conference on Spectroscopy of - Biological Molecules (ECSMB)
Woutersen	- Member of the organizing committee of the Conference on Multi-Dimensional Spectroscopy 2016 (CMDS2106) - Member of the Program Advisory Committee (PAC) of the free- electron laser FELIX
Zhang	- Professor at Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences - Member of EU COST Action CM1403 "Upconversion nanomaterials for biomedical application" - Member of Rare Earth Society of China / Luminescence Branch - Member of academic committee, Centre for Advanced Optoelectronic Functional Materials Research, - Key Laboratory for UV Light-Emitting Materials and Technology of the Ministry of Education, Northeast Normal University - Member of Advisory committee of 3rd International Workshop on Persistent and Photostimulable Phosphors (Arlington, USA) - Chairing research theme "Luminescence Dynamics of spatially confined systems" at CIOMP/CAS

Memberships international editorial boards

Name staff member	**Member of**
Ariese	- Polycyclic Aromatic Compounds
Bickelhaupt	- Chemistry - A European Journal - ChemistryOpen - Chemistry - An Asian Journal - Journal of Computational Chemistry - Physical Chemistry Chemical Physics
Bouwman	- Applied Organometallic Chemistry (advisory board) - European Journal of Inorganic Chemistry (advisory board)
Brouwer	- Member Editorial Board European Journal of Organic Chemistry
Bruin, de	- European Journal of Inorganic Chemistry (Chair Editorial Board) - Organometallics (Editorial Advisory Board) - ACS Catalysis (Editorial Advisory Board).

Buma	-	Research Letters in Physical Chemistry
Buma	-	ChemPhysChem (Editorial Advisory Board).
	-	
Elsevier	-	Collection Czechoslovak Chemical Communications (advisory board)
	-	Editor-in-Chief of Applied Organometallic Chemistry (Wiley)
	-	Magnetic Resonance in Chemistry (advisory board)
Hiemstra	-	Molecules, Open Access Organic Chemistry Journal (Editorial Board)
Koper	-	Catalysis Today
	-	Electrochimica Acta
	-	Journal of Electroanalytical Chemistry
	-	ChemCatChem
	-	ChemElectroChem
	-	ACS Catalysis
Lammertsma	-	Beilstein Journal of Organic Chemistry (advisory board member)
	-	Heteroatom Chemistry (editorial board member)
	-	Organometallics (editorial board member)
Linnartz	-	Editor CAMOP - Physica Scripta
Maarseveen, van	-	European Journal of Organic Chemistry (International Advisory Board)
Orrit	-	Angewandte Chemie
	-	ChemPhysChem
	-	PCCP
	-	Annalen der Physik
Orru	-	Current Organic Chemistry (Advisory Board Member)
	-	Topics in heterocyclic chemistry (volume editor)
Reek	-	European Journal of Inorganic Chemistry (Advisory Board)
	-	ChemPlusChem (Advisory Board)
Timmerman	-	Review Editorial Board of Frontiers in Immunotherapies and Vaccines
Williams	-	The Scientific World Journal
	-	The Open Inorganic Chemistry Journal
Zhang	-	Member of editorial board of Journal of Rare Earths

2.6 The HRSMC Fellowship Programme

In 2015 the HRSMC established a new Fellowship Programme. It provides funding for foreign researchers of postdoc level and higher to visit and collaborate with HRSMC-affiliated research groups, aiming specifically to set up new and challenging research lines. In 2015, there have been two application rounds in April and October.

General outline of the Fellowship Programme:
The HRSMC Fellowship programme aims to support and reinforce high-quality research within the HRSMC. Within the programme, visits by outstanding foreign researchers (postdoc level and higher) to HRSMC-affiliated research groups are financed.
The HRSMC strongly welcomes applications, which

- stimulate cross-fertilization between differently-affiliated HRSMC research groups, involving 2 or more applicants from different groups, and
- support fundamental, not directly application-driven research.

Staff and associated members of the HRSMC with a permanent position can apply. Applications in which staff members of 2 or more different research groups are involved have a higher priority for funding (if other aspects are comparable).

Visits by outstanding, foreign researchers with a minimum of 2 weeks and a maximum of 6 months are supported. Grants can be requested to help to meet the costs of subsistence and travel. The following rates apply:
Subsistence costs: €1750 per month for an experienced researcher or €2000 per month for a full professor.
Travel costs: The maximum amount of grant depends on the country in which the researcher is appointed. For researchers based in Europe the maximum is €500, for researchers based outside Europe €1500. There is no compensation for consumables or other research costs.

Awarded Fellowships – 1st Call, April 2015:

Time-resolved spectroscopic study on functional nanomaterials and/or nano-cavities
Guest: Dr. Pengtao Jing; hosted by Dr. Hong Zhang (UvA) and Dr. Stefania Grecea (UvA).
A visit of 5 months.

Fundamental understanding on gas-surface interaction
Guest: Dr. Arban Uka; hosted by Dr. Ludo Juurlink (UL) and prof. Wybren Jan Buma (UvA).
A visit of 1,5 months.

Unravelling interstellar chemical recipes: solid state formation of proteins, sugars, and fats.
Guest: Dr. Sergio Ioppolo; hosted by prof. dr. Harold Linnartz (UL).
Four one-week visits over a period of one year.

Awarded Fellowships – 2nd Call, October 2015:

Unraveling the mechanism of proton transport in proton-conducting MOFs

Guest: Dr. Saeed Amirjalayer (WWU/CeNTech Münster); hosted by Dr. Bernd Ensing (UvA), Dr. Stefania Grecea (UvA) and Prof. dr. Sander Woutersen (UvA).

An application for 3 months, in the period from 16-11-2015 to 30-04-2017; approximately 6 stays of 15 days.

Palladium-Catalyzed Oxidative Aerobic Isocyanide Insertion – A Mechanistic Study

Guest: Dr. Jordi Poater (University of Barcelona, Spain); hosted by Dr. Eelco Ruijter (VU), Prof. dr. Romano Orru (VU), Prof. dr. Matthias Bickelhaupt (VU).

A visit of 6 months.

3. Education and Research Training

The main mission of the HRSMC is to provide its PhD students with high-level education training. Apart from completing a research project, the PhD students of the HRSMC follow an individual education and training programme. For this purpose the education committee supplies them with a selection of courses, which are announced annually in the study guide on the HRSMC website. The management of the school administers the credit points obtained by the PhD students and presents HRSMC certificates to those students who have fulfilled their education programme. As the validation for HRSMC Schools and Courses and the criteria for the HRSMC certificate were determined in 2006, the Board reassessed this validation and the criteria for the HRSMC certificate. As of March 2014, the new HRSMC Education Programme became valid (see Annex 4.5).

3.1 HRSMC Education Programme

The HRSMC offers PhD students a broad programme of inter-university courses and schools.

HRSMC Courses (2-3 ECTS)

- Molecular Modelling (every two or three years, HRSMC theme 2 and 3)
- Physical Methods in Inorganic Chemistry (biannually, HRSMC theme 1)
- Photophysics, Photochemistry, and Photobiology (every three years, HRSMC theme 2)
- Molecular Simulation (yearly, HRSMC theme 3)
- Synthetic Chemistry problem sessions (HRSMC theme 1)

Character:

- Courses are given at UvA, UL or VU (or in combinations).
- Participants are mostly from HRSMC, a few from other Dutch universities or from Dutch chemical companies. The Molecular Simulation course has a lot of participants from abroad.
- Lecturers are mainly from Holland.

HRSMC Schools (2-3 ECTS)

- Summer School on Photochemistry (every 4 years, HRSMC theme 2)
- Tulip School 'Modern Developments in Spectroscopy' (every 3 years, HRSMC theme 2)
- Summer School 'Synthetic Bio-organic Chemistry' (every 4 years, HRSMC theme 1)
- Autumn School on Metal-organic Chemistry and Catalysis (every 2 years, HRSMC theme 1)

Character:

- More like a conference with lectures, discussion sessions and poster sessions.
- The schools are given at an external location.
- Participants come partly from the HRSMC. Many participants come from other Dutch universities and from abroad.
- Lecturers come mostly from abroad.

Activities of 2015:

- The two weeks HRSMC School *'Molecular Simulation'*, organized under the auspices of CECAM (5-16 January 2015, UvA)
- HRSMC Course *'Physical Methods in Inorganic Chemistry'* (29 January - 6 February 2015, UvA/UL)
- HRSMC TULIP School *'Modern Developments in Spectroscopy*' (14-17 April 2015, De Witte Raef Noordwijk)
- KNCV/HRSMC *'Career Advice Activity'* for PhD students and postdocs (13 October 2015, UL)
- The research groups of Prof. dr. H. Hiemstra (UvA) and Prof. dr. ir. R.V.A. Orru (VU) organized several *'Synthetic Chemistry problem solving sessions'*

Details of courses that were specifically developed for the HRSMC by its members were:

HRSMC School Molecular Simulation – MOLSIM2015
5-16 January 2015, UvA

Organisation: Dr. B. Ensing (UvA), Prof. dr. E.J. Meijer (UvA) and I. Weijer (HRSMC)
HRSMC Lecturers: Prof. dr. P.Bolhuis (UvA), Dr. E.J. Meijer (UvA)
Guest Lecturers: Dr. S. Abeln (VU), Prof. dr. D. Frenkel (AMOLF), Prof. dr. B. Smit, (University of California, Berkeley), Prof. dr. T.H.J. Vlugt (TU Delft)
Participants: 81 participants; 23 MSc students and 58 PhD students (of which 51 participants came from foreign universities and 7 from Dutch universities including 2 HRSMC members)

HRSMC Course Physical Methods in Inorganic Chemistry – PhMIC2015
29 January - 6 February 2015, UvA/UL

Organisation: Prof. dr. E. Bouwman (UL), Dr. S. Bonnet (UL), Prof. dr. B. de Bruin (UvA), Prof. dr. C.J. Elsevier (UvA) Dr. M. Tromp (UvA), I. Weijer (HRSMC) and drs. H.E. Zwaan (HRSMC)
HRSMC Lecturers: Dr. S. Bonnet (UL), Prof. dr. E. Bouwman (UL), Prof. dr. B. de Bruin (UvA), Prof. dr. C.J. Elsevier (UvA), Dr. D.G.H. Hetterscheid (UL), Dr. S. Ingemann Jørgensen (UvA), Dr. L. Juurlink and Dr. Moniek Tromp (UvA)
Guest Lecturers: Dr. H. Kooijman (Shell)
Participants: 33 participants, of which:

- 10 MSc students (9 UvA-VU, 1 UL; 9 students passed the MSc exam)
- 22 PhD students (12 UvA, 7 UL, 3 VU)
- 1 Postdoc (UvA).

HRSMC TULIP School 'Modern Developments in Spectroscopy'
14-17 April 2015, De Witte Raaf Noordwijk

Organisation: Prof. dr. W.J. Buma (UvA), Prof. dr. J. Herek (University of Twente), Prof. dr. M.H.M. Janssen (VU), M.C.H. Smits (HRSMC), I. Weijer (HRSMC) and drs. H.E. Zwaan (HRSMC)

Guest Lecturers: Prof. dr. P. Corkum (National Research Council-Canada, University of Ottawa, Canada), Prof. dr. J. Doyle (Harvard University, USA), Prof. dr. K. Eikema (VU), Prof. dr. J. Enderlein (Universität Göttingen, Germany), Prof. dr. M. Havenith (Ruhr-Universität Bochum, Germany), Prof. dr. D. Nesbitt (University of Colorado, Boulder, USA)

Participants: 48 participants, of which:

- 6 MSc students (5 UvA-VU, 1 UL)
- 42 PhD students (21 Dutch Universities: 4 UvA, 5 UL, 8 VU, 4 Radboud University)

HRSMC 4-day Proposal Writing Course in combination with 1-day Peer Review Course (5-9 October 2015, UL)

Organisation: I. Weijer (HRSMC) and drs. H.E. Zwaan (HRSMC)

Guest Lecturer: Dr. Ulrike Muller (California State University Fresno, USA)

Participants: 1 MSc student, 8 PhD student, 2 Postdoc for the 4-day Course.
2 PhD students extra for the 1-day Course.

KNCV/HRSMC Career Advice Activity for PhD students and postdocs, 13 October 2015, UL - Gorlaeus

With various lectures regarding career possibilities and job-application. In addition, each participant got 40 min. quality time with a career consultant.

Organisation: S. Blanken (KNCV), J. Dijkzeul (UL), R. Weijer (HRSMC) and H. Zwaan (HRSMC)

Participants: 30 (19 HRSMC members)

3.2 Symposium

The annual HRMSC Symposium was held at the VU University Amsterdam on November 5, 2015. The symposium, which was attended by ca. 190 scientists, also included poster sessions with 44 posters, mainly presented by PhD students. The format of previous symposia was also used for this symposium: less posters (about three posters per group selected by the work group leaders) per session, and more and shorter lectures.

The following lectures were given:
Theme 1 'Synthesis, Characterisation, Reactivity and Properties of Molecules'

- Dr. Chris Slootweg (VU)
  Cooperative Lewis Acid/Base Catalysis
- Linda Jongbloed (UvA)
  A NiC-He in Nickel C-H activation
- Luuk Steemers (UvA)
  Research towards the scaffold assisted synthesis of a rotaxane

Theme 2 'Photochemistry and (Laser) Spectroscopy'

- Prof. dr. Sander Woutersen (UvA)
  Water at its weirdest: The strange case of PEG vs. POM
- Aquiles Carattino (UL)
  In situ tuning of gold nanorod plasmon through oxidative cyanide etching
- Adriano Monti (UL)
  Crucial Role of Nuclear Dynamics for Electron Injection in a Dye-Semiconductor Complex

Theme 3 'Theoretical Chemistry'

- Dr. Jörg Meyer (UL)
  Hot or not? - Energy conversion dynamics of chemical processes at surfaces from 1st principles
- Abel de Cozar (VU)
  Aggregation and Cooperative Effects in the Aldol Reaction of Lithium Enolates

Guest Lectures:

- Prof. dr. ir. B.M. (Bert) Weckhuysen (UU)
  Catalytic Materials studied at the Level of Single Particles, Molecules and Atoms
- Lecture Winner Dick Stufkens Prize: Dr. Tatu Kumpulainen (former UvA PhD student; University of Geneva, Switserland)
  Proton-Transfer Reactions in 'Super' Photoacids and Supramolecular Assemblies

3.3 PhD Graduations (in order of graduation date) & first job after PhD Graduation

Rutters, J.P.A.,
Auxiliary mediated synthesis of ring-strained lactams
Promotor: Prof. dr. H. Hiemstra
Co-promotor: Dr. J.H. van Maarseveen
January 13, 2015
Assessor physical and chemical properties at Dutch Board for the Authorisation of Plant Protection Products and Biocides

Bosch, B. van den
Complexes for electro- and photocatalytic proton reduction
Promotor: Prof. dr. J.N.H. Reek
Co-promotor: Prof. dr. S. Woutersen
January 27, 2015
Chief Material Officer, MgAubel/Guest Resarcher TU Delft Experimental MicroMechanics

Mirtschink, A.,
Energy Density Functionals from the Strong-Interaction Limit of Density Functional Theory
January 29, 2015
Promotor: Prof. dr. E. J. Baerends
Co-Promotor: Dr. P. Gori-Giorgi
Post-doctoral Researcher, VU

Ording-Wenker, E.C.M.
Biomimetic redox reactions of the Cu(II) μ-thiolate complex
Promotor: Prof. dr. E. Bouwman
March 11, 2015
Programme Manager, NWO

Janssen, G.V.
Enantioselective synthesis of diverse compounds using asymmetric catalysis and chiral auxiliairies.
Promotor: Prof. dr. ir. R.V.A. Orru
Co-promotor Prof. dr. K. Lammertsma
April 28, 2015
Postdoctoral Researcher, Antoni van Leeuwenhoek

Loop, van der, T.F.
Hydrogen-bond dynamics and proton transfer in nanoconfinement
Promotor: Prof. dr. S. Woutersen
Co-promotor: Prof. dr. H.J. Bakker
June 15, 2015
Management Consultant, Financial Risk Capgemini Consulting

Kumpulainen, T.
Proton-transfer reactions in "super" photoacids and supramolecular assemblies
Promotor: Prof. dr. A.M. Brouwer
Co-promotor: Prof. dr. S. Woutersen
May 21, 2015
Postdoctoral Researcher, Université de Genève

Meuzelaar, H.
New light on protein folding: Unraveling folding and unfolding mechanisms using time-resolved and two-dimensional vibrational spectroscopy
Promotor: Prof. dr. S. Woutersen
Co-Promotor: Dr. J. Vreede
June 30, 2015
Lecturer in Chemistry, Hogeschool Inholland

Sluijter, S.N.
Multidentate Di-N-heterocyclic carbene ligands for transition metal catalyzed hydrogenation reactions
Promotor: Prof. dr. C.J. Elsevier
Co-Promotor: Dr.ir. J.I. van der Vlugt
September 18, 2015
Project Manager Chemical Innovation at MatrixIC & Port of Amsterdam

Hooijschuur, J.H.
Raman Spectroscopy as a Potential Method for the Detection of Life Signatures
Promotor: Prof. dr. G.R. Davies
Co-Promotores Prof. dr. C. Gooijer
Dr. F. Ariese
September 24, 2015
R&D Specialist Raman Spectroscopy and Service Specialist Analysis, ASaP BV

Diaz Morales, O.A.
Catalysis of the electrochemical water oxidation to oxygen
Promotor: Prof. dr. M.T.M. Koper,
Co-Promotor: Dr. F. Calle-Vallejo
November 19, 2015
Postdoctoral researcher, Stockholm University

Shen, J.
Electrocatalytic reduction of CO2 and nitrate on immobilized metal porphyrins
Promotor: Prof. dr. M.T.M. Koper
Co-promotor: Dr. D.G.H. Hetterscheid
December 9, 2015

Den Dunnen, A.
Surface-structure dependencies in catalytic reactions
Promotor: Prof. dr. M.T.M. Koper
Co-Promotor: Dr. L.B.F. Juurlink
December 9, 2015
Postdoctoral Researcher, Guest, Leiden University

Monti, A.
Taking control of charge transfer : strategic design for solar cells
Promotor: Prof. Dr. Huub J. M. de Groot
Copromotor: Dr. Francesco Buda
December 21, 2015

Kortlever, R.G.H.
Selective and efficient electrochemical CO2 reduction on nanostructured catalysts
Promotor Prof. dr. M.T.M. Koper
Co-promotor: Dr. L.B.F. Juurlink
December 22, 2015
Postdoctoral Researcher, Caltech

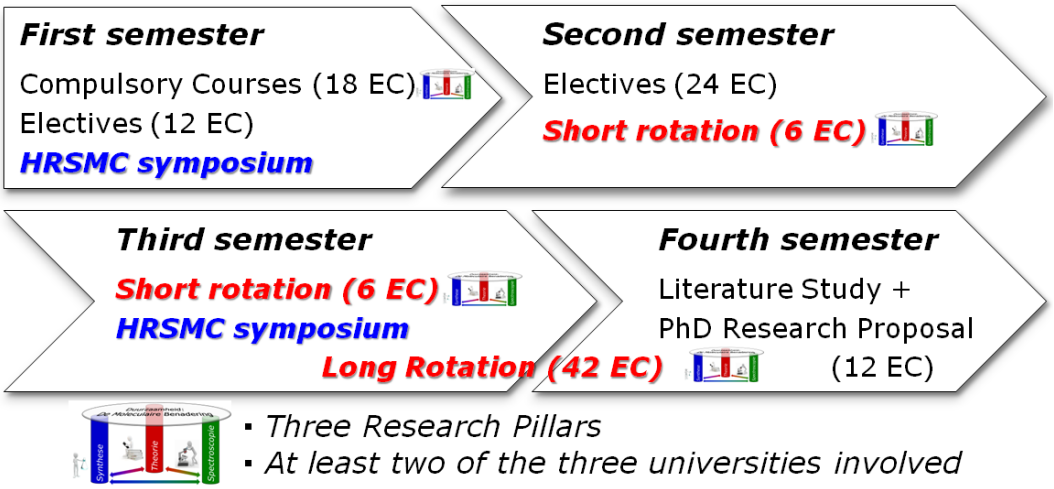
3.4 HRSMC Excellence Master 'Sustainability: the Molecular Approach'

Apart from providing and organizing an outstanding educational programme for PhD students which is also accessible to (advanced) MSc students, the HRSMC has been elected in 2012 as one of the thirteen Graduate Schools to receive substantial funding from NWO. With this funding the HRSMC can offer young PhD students the opportunity to develop their own research ideas within the framework of the programme *"Sustainability, the Molecular Approach"*. The funding is part of NWO's Graduate Programme and aims to develop Dutch PhD Educational Programmes. On December 31, 2015 nine MSc students participated in this Excellence Program and three students graduated in the period of August-October 2015.
As already mentioned in the preface, in 2015, the HRSMC has granted two proposals for PhD research written by chemistry students Hans de Bruijn (appointed at the Leiden University) and Kaj van Vliet (appointed at the University of Amsterdam).

General outline of the programme:
The interuniversity HRSMC Excellence Master 'Sustainability: the Molecular Approach' prepares talented chemistry students for a scientific career. Researchers of the University of Amsterdam (UvA), the VU University Amsterdam (VU) and Leiden University (the HRSMC partners) composed a unique, demanding and interdisciplinary programme characterised by strong integration of theory, spectroscopy and synthesis. Only the best 10 percent of the chemistry students are eligible for the programme. A crucial part is the preparation of a proposal for PhD research to be performed by the students themselves. Four proposals are rewarded with an actual PhD position, financed through the Graduate Programme of the Netherlands Organisation for Scientific Research (NWO).

The students are getting more guidance from a special committee mentoring the selected students during the different stages of this Top Master Track (e.g. progress and choice of internships). This special 'Advisory Committee' consists of Dr. Eelco Ruijter (VU), Dr. Sylvestre Bonnet (UL) and Dr. Bernd Ensing (UvA, also member of the HRSMC Education Committee).

The two-year HRSMC Honours Master Programme "*Sustainability: The Molecular Approach*" consists of the following programme:



On December 31, 2015 eight MSc students participated in this the HRSMC Excellence programme Sustainability, the Molecular Approach", of which nine students started in September 2015, four students in September 2014 and one in September 2013 (other students from this cohort are graduated).

Two PhD proposals selected in HRSMC/NWO excellence programme

In 2015, the HRSMC has granted two proposals for PhD research written by chemistry students Hans de Bruijn (UL) (*An experimental and theoretical study of the hydroaminomethylation of internal olefins to linear amines with a Co-based catalytic system*; supervisors Prof. dr. E. Bouwman (Leiden) and Prof. dr. F.M. Bickelhaupt (VU Amsterdam) and Kaj van Vliet (VU) (*Creative Advances in visible light photoredox catalysis*; supervisors Prof. dr. B. de Bruin (UvA) and Prof. A.M. Brouwer (UvA)). Both students, who received their master's degree with honours (cum laude), wrote their proposal as part of the special HRSMC master's programme for talented chemistry students. They started their PhD research in November 2015, financed by the Netherlands Organisation for Scientific Research NWO.

Both students presented their proposal for a broad panel of experts, in which Prof. dr. G. van Koten (UU), Prof. dr. R. van Santen (TUE) and Prof. dr. D. Wiersma (RUG) acted as advisory non-HRSMC members. According to the panel both proposals excelled not only in academic quality but also in their interdisciplinary and interuniversity approach, illustrative of both the Excellence Master and the HRSMC research school.

4. Annexes

4.1 Annex 1 - HRSMC Organisation

Organisation Structure
The interuniversity research school HRSMC is a cooperation between the University of Amsterdam (UvA), the Vrije Universiteit Amsterdam (VU) and Leiden University (UL), UvA being the university in charge of the HRSMC ('penvoerder'). The HRSMC organisation structure consists of:

Scientific Director and Managing Staff
- Prof. dr. W.J. Buma (UvA), Scientific Director
- Drs. H.E. Zwaan-Van der Plas, Executive Secretary
- Mrs R. Weijer, Administration Officer
- Mrs M.C.H. Smits-Weijers, Administration Officer

Board
- Prof. dr. F.M. Bickelhaupt (VU, chairman)
- Prof. dr. C.J. Elsevier (UvA)
- Prof. dr. M. Koper (UL)

The scientific director and executive secretary of the HRSMC prepare and attend the meetings of the Board.

Research Committee (OZC)
- Dr. F. Buda (UL, research theme 2/3)
- Prof. dr. H. Hiemstra (chairman, UvA, research theme 1)
- Dr. F. Ariese (VU, research theme 2)

Education Committee (OWC)
- Dr. B. Ensing (UvA, research theme 3)
- Prof. dr. K. Lammertsma (VU, chairman, research theme 1)
- Dr. L. Juurlink (UL, research theme 2)
- E. Schippers, MSc (UvA, research theme 1, PhD student)

External Advisory Committee (WAR)
- Prof. dr. W.J. Briels (TU-Twente)
- Prof. dr. E. Drent (SRTCA, UL)
- Dr. R. Hage (Catexel)
- Prof. dr. J. Reedijk (UL)
- Prof. dr. J.W. Verhoeven (emeritus UvA)
- Prof. dr. J.G. de Vries (Leibniz Institute for Catalysis, Rostock, Germany/RUG)

PhD Platform

- S. Askes, MSc; PhD student in the Metals in Catalysis, Biomimetics & Inorganic Materials Group of Prof. dr. E. Bouwman at the UL;
- T. van der Loop, MSc and H. Meuzelaar, MSc; PhD students in the Molecular Photonics Group of Prof. dr. W.J. Buma and Prof. dr. A.M. Brouwer at the UvA;
- E. Schippers, MSc and C. te Grotenhuis, MSc; PhD students in the group of Homogeneous, Supramolecular and Bio-inspired catalysis of Prof. dr. J.N.H. Reek and Prof. dr. B. de Bruin at the UvA
- J.H. Hooijschuur, MSc; PhD student in the Biomolecular Spectroscopy Group of Dr. F. Ariese at the VU;
- F. Zaccaria, MSc; PhD student in the Theoretical Chemistry Group of Prof. dr. Matthias Bickelhaupt and Prof. dr. L. Visscher at the VU.
- D. Boom, MSc and J. Borger, MSc; PhD students in the Organophosphorus, Organometallic and Computational Chemistry Group of Dr. C. Slootweg at VU.

4.2 Annex 2 - Financial Account 2015

Income		**Expenses**	
Contribution UvA 2015 - faculty[1]	150.000	Donation HIMS Institute[1]	150.000
Contribution UvA 2015 - HIMS[1]	150.000	Personnel Costs	80.854
Interest	535	Fellowship Programme[2]	43.357
Tulip School Spectroscopy	39.197	Tulip School Spectroscopy	46.541
		Symposium	10.043
		Cursus Ulrike Muller	6.655
		Bureau Costs	1.463
		Graduate Programme[3]	1.159
		Dick Stufkens PhD prize	1.000
		Annual Report 2014	846
		Board	538
		Courses	404
		Other	458
	€ 339.732		**€ 343.317**

Income minus Expenses[4] −**€ 3.585**

Estimation for expenses HRSMC-NWO Graduate Programme, the personnel costs for the appointment of two PhD students for November and December 2015:
€ 16.667 (2/48 x 2 x 200 keuro).
These costs are compensated by the NWO grant received in 2012[3].

1) As of 2014, a new agreement between the VSNU (Association of universities in the Netherlands) and SODOLA (the Dutch network of accredited research schools in all fields of academic research) has become applicable for the funding of Research Schools. Based on this agreement, as of 2015, the HRSMC should get funding of 300 KEuro. Instead of 50 kEuro from the faculty and 5 kEuro from the HIMS Institute, the contribution of the faculty is raised to 150 kEuro and 150 kEuro for the HIMS Institute. As this increase for the HIMS Institute would strongly affect HRSMC affiliated research groups from the UvA/HIMS Institute, the HRSMC Board decided to donate 150 kEuro to the HIMS Institute.

2) Is the total sum of: € 12.857,- for the visits that already took place in 2015 as a result of the awarded Fellowships in 2015 and € 30.500,- as a reservation of the awarded Fellowships in 2015 who will take place in the coming years.

3) For the HRSMC-NWO Graduate Programme 'Sustainability: The Molecular Approach', the HRSMC received **800 kEuro** for the appointment of 4 PhD students in 2012. The first two PhD students, Hans de Bruijn and Kaj van Vliet, have been appointed in November 2015 (see chapter 3.4).

4) This expected deficit is compensated by past reservations.

4.3 Annex 3 - - Staff and Temporary Personnel 2015

Theme	Name Group		Name			Function		
1	Biocatalysis (UvA, HIMS)		Wever	R.		Emeritus		
			Mutti	F.		HGL		
			Wever	R.		HGL Guest		
			Böhmer	W.		PhD	01/09/2015	01/09/2019
			Knaus			PD	01/01/2015	01/01/2019
			Tseliou	V.		PhD	01/10/2015	01/10/2019
			Vilim	J.		PhD	01/10/2015	01/10/2019
			Hartog	A.F.		OBP		
			Pham			OBP		
1	Heterogeneous Catalysis and Sustainable Chemistry (UvA, HIMS) (SusCat)		Rothenberg	H.G.		HGL		
			Grecea	S.		UD		
			Shiju	N.R.		UD		
			Yan	N.		Tenure Tracker		
			Alberts	A.H.		PD	01/01/2014	01/01/2015
			Eisenberg			PhD	01/01/2015	01/01/2019
			Guo			PhD	01/01/2015	01/01/2019
			Narani	D.		PD	01/06/2015	31/05/2016
			Pandey	J.		PD	01/07/2015	30/06/2016
			Prinsen	P.L.K.		PD	01/02/2014	31/01/2016
			Solomon Raja	E.G.K.		PD	01/07/2014	30/06/2016
			Gao	Y.		PhD	01/01/2014	01/01/2018
			Gheorghe	A.		PhD	01/01/2016	01/01/2020
			Rees			PhD	01/01/2015	01/01/2019
			Santacroce	V.		PhD	15/09/2014	15/03/2016
			Tang	Y.		PhD	01/10/2015	01/10/2019
			Zhang	W.		PhD	01/10/2015	01/10/2019
			Collignon	P.F.		OBP		
			Geels	N.J.		OBP		
			Mittelmeijer-Hazele	M.		OBP/PD		
1	Homogeneous, and Bio-Inspired Catalysis (UvA, HIMS) (HOMCAT)	S	Bruin	B.	de	HGL		
			Reek	J.N.H.		HGL		
			Zwaan	B.	van de	HGL BZ		
			Tromp	M.		Tenure Tracker		
			Vlugt	J.I.	van de	UD		

Hartl	F.	WP Guest	01/04/2005	31/12/2099
Das	B.G.	PD	01/07/2015	30/06/2016
Detz	R.J.	PD Guest	01/09/2012	01/09/2016
Devillard		PhD	01/01/2015	01/01/2019
Dzik	W.I.	PD	01/11/2011	01/11/2016
Gonell Gomez	S.	PD	01/05/2015	30/04/2016
Kluwer	A.M.	PD Guest		01/01/2016
Li	P.	PD	01/07/2012	01/01/2015
Mathew	S.	PD	01/09/2015	01/09/2016
Pascui	A.E.	PD	01/01/2014	30/06/2015
Raoufmoghaddam	S.	PD	01/02/2014	01/02/2016
Wang	Q.	PD	01/01/2014	01/12/2015
Wang	X.	PD	01/05/2014	01/05/2015
Bagh		PhD	01/01/2015	01/01/2019
Bai	S.	Bursaal AIO	01/09/2015	01/09/2019
Becker	R.	PhD	01/03/2012	01/03/2016
Boer	S.Y. de	PhD	15/08/2011	15/08/2015
Bosch	B. van den	PhD Guest	01/05/2014	01/02/2015
Boulens	P.A.	PhD Guest	01/04/2013	01/10/2015
Broere	D.L.J.	PhD	15/05/2012	15/05/2016
Chirila	A.	PhD	01/09/2012	01/09/2016
Coskuner	B.	PhD Guest	01/01/2012	01/01/2016
Daubignard	J.J.M.	PhD Guest	01/01/2015	01/01/2016
Daubignard	J.J.M.	PhD	01/01/2011	01/01/2015
Goswami	M.	PhD	01/08/2013	01/09/2017
Hartendorp	A.P.T.	PhD	01/09/2015	01/09/2019
Hessels	J.	PhD	01/10/2015	01/10/2019
Jacobs	I.	PhD Guest	01/03/2013	01/09/2015
Jans	A.C.H.	PhD	15/03/2014	15/09/2015
Jongbloed	L.S.	PhD	15/02/2012	15/02/2016
Jongkind	L.J.	PhD	01/09/2014	01/09/2018
Koelewijn	J.M.	PhD	01/02/2011	01/02/2015
Kuijpers	P.F.	PhD	01/10/2012	01/10/2016
La Rosa	A.	PD	01/01/2016	01/01/2017
Leenders	S.H.A.M.	PhD	01/10/2011	01/10/2015
Martin	D.J.	PD	01/10/2015	01/10/2016
Nurttila	S.S.	PhD	01/06/2014	01/06/2018
Oldenhof	S.	PhD Guest	01/10/2014	01/03/2015
Oudsen	J.P.H.	PhD	01/09/2015	01/09/2019
Plessius	R.	PhD	01/10/2015	01/10/2019

		Rebreyend	C.		PhD	01/08/2013	01/08/2017
		Saha	B.		PhD Guest	01/09/2014	01/03/2015
		Schippers	E.C.F.		PhD	01/11/2013	01/11/2017
		Subbiah	V.		PhD	01/01/2015	01/01/2015
		Sun	B.		PhD	01/10/2015	01/10/2019
		Tang	Z.		PhD	01/01/2011	01/01/2015
		Te Grotenhuis	C.		PhD	01/08/2013	01/08/2017
		Venderbosch	B.		PhD	01/11/2015	01/11/2019
		Vreeken	V.		PhD	01/05/2012	15/05/2016
		Watering	F.F.	vd	PhD	01/11/2012	01/11/2016
		Zaffaroni	R.		PhD NWO	01/12/2012	01/12/2016
		Ait El Maate	F.		OBP		
		Burg	A.M.	vd	OBP		
		Duin-Berteling	E.		OBP		
		Geels	N.J.		OBP		
		Mahabiersing	C.		OBP		
1	Metals in Catalysis, Biomimetics & Inorganic Materials (UL, LIC) (MCBIM)	Drent	E.		Emeritus		
		Reedijk	J.		Emeritus		
		Bouwman	E.		HGL		
		Bonnet	S.B.		Tenure Tracker		
		Hetterscheid	D.G.H.		Tenure Tracker		
		IJdo	D.J.W.		WP Guest	01/04/2009	31/12/2016
		Gloaguen	Y.		PD	15/05/2013	29/02/2016
		Higgins	S.L.H.		PD	01/09/2013	31/12/2016
		Siewert	B.		PD	01/09/2013	31/12/2016
		Terrade	F.G.		PD	19/05/2014	18/05/2015
		Askes	S.H.C.		PhD	01/10/2012	01/10/2016
		Bruijn	H.	de	PhD	01/11/2015	01/11/2019
		Busemann	A.		PhD	08/12/2014	08/12/2018
		Cuello-Garibo			PhD	17/06/2013	17/06/2017
		Dijkman	T.	van	PhD	01/08/2011	31/07/2015
		Geest	E.	van	PhD	01/09/2015	01/09/2019
		Gezer	G.		PhD	15/07/2013	15/07/2017
		Guijt	M.C.		PhD	01/09/2013	01/09/2017
		Hopkins			PhD	01/01/2015	01/01/2019
		Jiang	F.		PhD	01/04/2014	01/04/2018
		Kottrup	K.		PhD	01/07/2013	01/07/2017
		Lameijer	L.N.		PhD	01/07/2013	01/07/2017

		Langerman			PhD	01/01/2015	01/01/2019
		Limburg	B.		PhD	01/06/2011	31/05/2015
		Liu	X.		PhD	21/09/2012	21/09/2016
		Luo	S.		PhD	01/09/2013	01/09/2017
		Meijer	M.S.		PhD	01/01/2014	01/01/2016
		Rixel	V.	van	PhD	01/02/2013	01/02/2017
		Sk	A.		PhD	01/05/2015	01/05/2019
		Smits	N.		PhD	01/01/2016	01/01/2020
		Brussel	J.J.M.	van	OBP		
		Dijk	J.A.P.P.	van	OBP		
		Snellenberg	Y		SECR		
1	Molecular Inorganic Chemistry (UvA, HIMS)	Oskam	A.		Emeritus		
		Vrieze	K.		Emeritus		
		Elsevier	C.J.		HGL		
		Korstanje	T.J.		PD	01/09/2013	01/09/2015
		Sluijter	S.N.		PhD	01/06/2011	01/06/2015
		Ernsting	J.M.		OBP		
1	Organic and Organometallic Chemistry (VU, EMS)	Lammertsma	K.		Emeritus		
		Grossmann	T.N.		HGL		
		Ehlers	A.W.		UD		
		Slootweg	J.C.		UD		
		Joost	M.G.		PD	15/12/2014	01/01/2016
		Aydin			PhD	01/01/2015	01/01/2019
		Blom			PhD	01/01/2015	01/01/2019
		Boom	D.H.A.		PhD	01/11/2013	01/11/2017
		Boon	L.J.P.	van der	PhD	16/12/2011	16/12/2015
		Borger	J.E.		PhD	15/12/2013	15/12/2016
		Enter			PhD	01/01/2015	01/01/2019
		Habraken	E.R.M.		PhD	15/12/2014	15/12/2018
		Hendriks			PhD	01/01/2015	01/01/2019
		Holtrop	f.		PhD	01/09/2015	01/09/2019
		Holtrop	F.		PhD	01/01/2015	31/12/2019
		Krachko	T.		PhD	01/09/2013	01/09/2017
		Mens			PhD	01/01/2015	01/01/2019
		Nicolas	E.C.		PhD	01/08/2013	01/08/2016
		Rong	M.K.		PhD	15/12/2010	01/01/2015
		Boer	M.	de	OBP		
		Jong	G.B.	de	OBP		
		Smits-Weijers	M.C.H.		SECR		
		Rombouts	J.A.		PhD	01/05/2011	01/09/2015

1	Synthetic and Chemistry (VU, EMS)	Orru	R.V.A.		HGL		
		Ruijter	E.		UD		
		Braun	J.		PhD	11/11/2014	11/11/2018
		Cioc	R.		PhD	15/11/2012	15/11/2016
		Collet			PhD	01/01/2015	01/01/2019
		Estévez Closas	V.		PhD	01/05/2013	01/05/2017
		Graaff	C.		PhD	15/08/2011	15/08/2015
		Heijden	G.	van de	PhD	01/11/2012	01/11/2016
		Kraakman			PhD	01/01/2015	01/01/2019
		Laan			PhD	01/01/2015	01/01/2019
		Lint	M.J.	van	PhD	01/01/2011	01/01/2015
		Mampuys	P.		PhD	01/09/2013	01/09/2017
		Saya	J.M.		PhD	01/12/2014	01/12/2018
		Schaapkens			PhD	01/01/2015	01/01/2019
		Schaik			PhD	01/01/2015	01/01/2019
		Vicente Garcia	E.		PhD	01/03/2013	01/03/2017
		Janssen	A.C.		OBP		
1	Synthetic Organic Chemistry (UvA, HIMS)	Hiemstra	H.		HGL		
		Maarseveen	J.H.	van	HGL		
		Timmerman	P.		HGL BZ		
		Maarseveen	J.H.	van	UHD		
		Fernández-Ibáñez	M.A.		Tenure Tracker		
		Ingemann Jørgense	S.		UD		
		Kanner	C.B.		WP Guest	01/03/2010	01/03/2015
		Valderas Cortina	C.		PD	01/05/2015	31/07/2016
		Naksomboon	K.		PhD	01/09/2015	01/09/2019
		Popovic	S.		PhD	01/02/2010	01/06/2015
		Richelle	G.J.J.		PhD	01/11/2013	01/11/2017
		Steemers	L.		PhD	01/01/2012	01/01/2016
		Streefkerk	D.E.		PhD	01/06/2014	01/06/2018
		Wijsman	L.		PhD	01/09/2015	28/02/2019
		Žari			PhD	01/11/2014	31/03/2015
		Bieraugel	H.		OBP Guest		
		Klein Nijenhuis	R.		OBP		
		Wanner	M.J.		OBP		
		Zuidinga	E.		OBP		
2	Biomolecular Spectroscopy (VU, EMS)	Ariese	F.		UHD		
		Gooijer	C.		Emeritus		
		Zwan	G.	van de	Gepensioneerd	01/06/2012	31/12/2099

		Hoorn	C.	van		01/07/2012	01/07/2016
		Mooij	B.		PhD	01/10/2015	01/10/2019
		Moester	M.J.B.		PhD	01/01/2011	01/01/2015
		Zada	L.		PhD	01/11/2014	01/11/2018
2	Biophysical Organic Chemistry (UL, LIC)	Groot	H.J.M.	de	HGL		
		Alia	A.		UD		
		Buda	F.		UD		
		Ganapathy	S.		PD	15/05/2012	13/11/2016
		Miloslavina	Y.		PD	01/02/2012	31/01/2015
		Thomas	B.		PD	31/01/2012	16/07/2016
		Augustijn	D.		PhD	01/08/2014	31/07/2018
		Miloslavina	Y.		PD	02/01/2012	31/01/2015
		Monti	A.		PhD	01/06/2011	30/09/2015
		Roy	U.		PhD	01/01/2012	31/01/2016
		Ruiter	J.M.	de	PhD	01/09/2013	06/12/2017
		Schadewijk	R.	van	PhD	01/02/2014	31/01/2018
		Sevink	G.J.A.		PhD	01/01/2016	31/12/2099
		Sun	Z.		PhD	02/09/2014	31/08/2018
		Sai sankar Gupta			OBP		
		Velden	E.	van de	SECR		
2	Laboratory Astrophysics Astrochemistry (UL, LION)	Linnartz	H.V.J.		HGL		
		Doney	K.D.		PhD	07/01/2014	30/06/2018
	Molecular Nano Spins (UL, LION) (MONOS)	Groenen	E.J.J.		Emeritus		
		Völker	S.L.		Emeritus		
		Orrit	M.		HGL		
		Gast	P.		UD		
		Huber	M.		UD		
		Azarkh	M.		PD	01/03/2012	31/12/2015
		Ebrahami Pour Fa	S.		PD	01/08/2013	01/07/2015
		Caldarola			PhD	01/01/2015	01/01/2019
		Carattino	A.		PhD	01/02/2013	01/02/2016
		Hou	L.		PhD	15/08/2012	15/08/2016
		Kumar	P.		PhD	15/06/2012	15/06/2016
		Nami	F.		PhD	01/03/2012	01/03/2016
		Panarelli	E.G.		PhD	01/06/2014	01/06/2018

		Pradhan	B.		PhD	01/02/2014	31/01/2018
		Verhart	N.R.		PhD	09/07/2012	09/07/2016
		Zhang	W.		PhD	01/09/2014	31/08/2018
		Zurlo	E.		PhD	01/02/2015	31/01/2019
		Leeuwen	H.C.M. va		SECR		
2	Molecular Photonics (UvA, HIMS) (MOLPHOT)	Schenk	H.		Emeritus		
		Verhoeven	J.W.		Emeritus		
		Aalders	M.C.G.		HGL BZ		
		Bakker	H.J.		HGL		
		Brouwer	A.M.		HGL		
		Buma	W.J.		HGL		
		Oomens	J.		HGL BZ		
		Woutersen	S.		HGL-BZ		
		Zhang	H.		UD		
		Jing	P.		HRSMC-fellow	01/08/2015	01/01/2015
		Rijs	A.M.		Ass. Prof		
		Williams	R.M.		UD		
		Bakker	J.M.		WP Guest	01/01/1994	31/12/2099
		Sitters	R.		WP Guest	01/01/2013	01/01/2015
		Bloem	R.		PD	03/07/2015	31/12/2015
		Dijk	C.N.	van	PD	01/07/2011	01/10/2019
		Nicu	V.P.		PD	01/06/2015	01/06/2019
		Ottoson	N.E.		PD	01/02/2015	01/06/2015
		Petrignani	A.		Postdoc	01/01/2015	01/01/2018
		Shen	S.		PD	01/05/2015	01/05/2016
		Chen	H.C.		PhD Guest	01/09/2011	01/09/2016
		Cota	R.O.		PhD	01/06/2015	01/06/2019
		Ding	Y.		PhD Guest	01/02/2013	01/04/2015
		Gutierrez Cota	R.O.		PhD	01/06/2015	01/06/2019
		Haitjema	J.		PhD	15/09/2015	15/09/2019
		Koenis	M.A.J.		PhD	01/09/2015	01/09/2019
		Kumpulainen	T.		PhD Guest	01/10/2014	01/04/2015
		Loop	T.F.	van der	PhD Guest	01/11/2014	01/06/2015
		Lugier	O.C.M.		PhD Guest	20/03/2015	01/07/2015
		Maltseva	E.		PhD	01/08/2012	01/08/2016
		Martens			PhD	01/01/2015	01/01/2019
		Meuzelaar	H.		PhD	01/10/2014	01/07/2015
		Petrova	D.		PhD	01/04/2015	01/04/2019
		Raeisolsadati	M.		PhD	01/11/2012	01/01/2015

		Oskouei					
		Rocha Martins	B.M.		PhD	01/11/2014	01/11/2018
		Roeters	S.J.		PhD	15/10/2011	15/10/2015
		Strazdaite	S.		PhD Guest	01/11/2011	01/11/2015
		Strudwick	B.H.		PhD	01/08/2014	01/08/2015
		Suhina	T.		PhD	01/09/2012	01/09/2016
		Zhang	Y.		PhD	01/01/2015	01/01/2019
		Zheng	D.		PhD	01/09/2014	01/09/2018
		Talavera Ormeno	C.		Guest	01/09/2014	01/02/2015
		Bakker	B.H.		OBP		
		Bebelaar	D.		OBP		
		Groeneveld	M.M.		OBP Guest		
		Hilbers	M.F.		OBP		
		Ramesdonk	H.J.	van	OBP Guest		
		Reinders	P.P.		OBP		
		Sanders	H.J.		OBP		
2	Surface Chemistry and Catalysis (UL, LIC)	Kleijn	A.W.		HGL BZ		
		Koper	M.T.M.		HGL		
		Fu	W.T.		UD		
		Groot	I.M.N.		Tenure Tracker		
		Heering	H.A.		Research Fell	01/04/2012	31/10/2015
		Hetterscheid	D.G.H.		Tenure Tracker		
		Juurlink	L.B.F.		Ass. Prof		
		Calle Vallejo	F.		PD (Veni)	01/04/2015	30/03/2018
		Figueiredo	M.		PD	01/11/2014	30/04/2017
		Göttle	A.		PD	01/09/2014	14/03/2017
		Huang	Y.		PD	16/10/2013	31/03/2017
		Walsh	A.J.		PD	01/06/2014	17/08/2016
		Auras	S.		PhD	15/12/2015	15/12/2019
		Badan	C.		PhD	16/07/2012	31/07/2017
		Birdja	Y.Y.		PhD	16/12/2013	15/12/2017
		Bremmer			PhD	01/10/2013	30/09/2017
		Cao	K.		PhD	01/09/2014	31/08/2018
		Chen			PhD	01/09/2015	31/08/2019
		D'Agostini	S.		PhD	01/12/2014	30/11/2018
		Den Dunnen	A.		PhD	01/02/2011	01/05/2015
		Diaz Morales	O.A.		PhD	01/06/2011	31/08/2016

		Dijk	B.		PhD	01/01/2016	31/12/2020
		Ham	C.J.M.	vd	PhD	01/09/2013	31/08/2017
		Hersbach	T.		PhD	01/10/2014	30/09/2018
		Jacobse	L.		PhD	16/09/2013	16/09/2017
		Kolb	M.J.		PhD	01/01/2012	01/05/2016
		Kortlever	R.G.H.		PhD	16/11/2011	15/11/2015
		Ledezma Yanez	I.D.		PhD	28/11/2011	31/05/2016
		Lent	R.	van	PhD	01/05/2014	30/04/2018
		Mom			PhD	01/01/2013	31/12/2016
		Perez Gallent	E.		PhD	16/11/2013	15/11/2017
		Plas	M.	vd	PhD	22/04/2014	23/04/2018
		Rossius	S.G.H.		PhD	01/11/2011	30/11/2016
		Shen	J.		PhD Guest	17/11/2011	16/11/2015
		Spronsen			PhD	01/01/2012	31/03/2016
		Vos	J.		PhD	01/05/2015	30/04/2019
		Dijkzeul	J.C.M.		SECR		
		Tapan	N.A.		Guest	01/01/2015	01/01/2015
3	Computational Chemistry (UvA, HIMS)	Bolhuis	P.G.		HGL		
		Meijer	E.J.		Hgl		
		Lowe	C.		UHD		
		Dubbeldam	D.		UD		
		Ensing	B.		UD		
		Vreede	J.		UD		
		Cruz Cabeza			PD	01/10/2011	22/02/2015
		Ni	R.		PD	01/09/2012	31/08/2017
		Rudavskyi	A.		PD	01/10/2015	01/10/2016
		Sun	D.		PD	21/10/2013	21/10/2015
		Swenson	D.W.H.		PD	01/01/2012	01/01/2015
		Brandeburgo	W.		PhD	15/01/2011	15/01/2015
		Brotzakis	Z.F.		PhD	01/09/2012	01/09/2016
		Burtch	N.C.		PhD	01/06/2015	01/09/2015
		Diaz Leines	G.		PhD Guest	01/05/2014	01/05/2015
		Govindarajan	N.		PhD	01/01/2016	31/12/2020
		Heinen	J.		PhD	01/09/2014	31/08/2018
		Homsi Brandenbu	W.		PhD	15/01/2011	15/01/2015
		Kumar	A.		PhD	01/09/2010	31/01/2016
		Newton	A.C.		PhD	15/04/2012	15/04/2016
		Nowosielski	M.		PhD	15/04/2011	15/04/2015
		Putenkhalatil	R.C.		PhD	01/01/2016	31/12/2020

		Tiwari		PhD	01/01/2015	01/01/2019
		Torres Knoop	A.	PhD	01/03/2012	01/03/2016
		Vijaykumar	A.	PhD Guest	01/06/2013	01/06/2017
3	Theoretical Chemi (VU, EMS)	Baerends	E.J.	Emeritus		
		Bickelhaupt	F.M.	HGL		
		Gori Giorgi	P.	HGL		
		Visscher	L.	HGL		
		Fonseca Guerra	C.	UD		
		Gori Giorgi	P.	UD		
		Gritsenko	O.V.	UD		
		Infante	I. A. C.	UD		
		Cosseddu	S.M.	PD	01/02/2015	01/02/2017
		Giesbertz	K.J.H.	PD	09/01/2012	09/01/2015
		Heshmat	M.	PD	02/02/2013	02/02/2015
		Kazaryan	A.K.	PD	01/01/2014	04/01/2015
		Lani	G.	PD	01/04/2013	01/04/2016
		Malet Giralt	F.	PD	01/03/2012	01/06/2016
		Paragi	G.T.	PD	01/05/2013	01/02/2016
		Wagner	L.O.	PD	01/11/2013	01/11/2015
		Boughlala	Z.	PhD	01/08/2013	01/08/2017
		Cózar		PhD	01/01/2015	01/01/2019
		de Cózar Ruano	A.	PD	01/09/2015	01/09/2017
		Franchini	M.	PhD	01/01/2014	01/01/2016
		Gangarapu		PhD	01/01/2015	01/01/2019
		Giarrusso		PhD	01/10/2015	01/10/2015
		Grossi		PhD	01/09/2015	01/09/2019
		Handzik	M.	PhD	01/01/2015	01/01/2019
		Hernandez Fernandez	F.	PhD	01/01/2016	01/06/2016
		Juliaci Rocha		PhD	01/01/2015	01/01/2019
		Lopez Tariva	P.	PhD	01/01/2016	31/12/2020
		López-Tarifa		PhD	01/01/2015	01/01/2019
		Lubbe	S. van der	PhD	01/01/2016	31/12/2020
		Meer	R. van	PhD	01/01/2011	01/01/2015
		Mulder	J.R.	PhD	01/10/2011	01/10/2015
		Sun	X	PhD	01/11/2014	01/11/2018
		Vuckovic	S.	PhD	01/01/2013	01/01/2017
		Zaccaria	F.	PhD	01/09/2014	01/09/2018
		Zapata		PhD	01/01/2015	01/01/2019
	Theoretical Chemistry	Meyer	J.	Dr	01/01/2015	31/12/2099
		Nattino	F.	PD	01/01/2015	01/01/2017

	(UL)						
		Nattino	F.		PhD	01/11/2015	01/11/2019
		Rasti	S.		PhD	01/01/2016	31/12/2020
		Seal	S.		PhD	01/01/2016	01/01/2020
		Spiering	P.		PhD	01/09/2015	01/09/2019
1,2,3	Excellence Master	Abad Torres	J.			01/09/2015	01/09/2016
		Bouwens	T.			01/01/2014	01/01/2019
		Brinck	S.C.	ten		01/09/2013	01/09/2015
		Bruijn	H.	de		01/01/2014	01/09/2015
		Doorn	I.	van		01/01/2015	01/01/2017
		Heuvel	N.	vd		01/09/2015	01/09/2017
		Keijer	T.			01/09/2015	01/09/2017
		Klein	D.			01/09/2015	31/12/2019
		Landman	I.			01/01/2014	01/01/2019
		Opdam	L.			01/09/2015	01/09/2017
		Schaap	I.L.			01/10/2013	01/10/2017
		Venne	M.			01/09/2013	01/09/2016
		Vliet	K.M.	van		01/09/2013	01/10/2015
	WAR	Briels	W.		WARlid	Tot 5/11/2015	
		Hage	R.		WARlid		
		Reedijk	J.		WARlid		
		Verhoeven	J.W.		WARlid		
		Vogt	E.		WAR		
		Vries	J.G.	de	WARlid	Tot 5/11/2015	

4.4 Annex 4 – Publications

Biocatalysis (UvA, HIMS)
Dr. F. Mutti

Holzer, A. K.; Hiebler, K.; Mutti, F. G.; Simon, R. C.; Kroutil, W.; Lauterbach, L.; Lenz, O.; Kroutil, W. Asymmetric Biocatalytic Amination of Ketones at the Expense of NH3 and Molecular Hydrogen. *Organic letters* **2015**, *17* (10), 2431–2433.

Knaus, T.; Mutti, F. G.; Humphreys, L. D.; Turner, N. J.; Scrutton, N. S. Systematic Methodology for the Development of Biocatalytic Hydrogen-Borrowing Cascades: Application to the Synthesis of Chiral α-Substituted Carboxylic Acids from α-Substituted A,β-Unsaturated Aldehydes. *Organic & biomolecular chemistry* **2015**, *13* (1), 223–233.

Mutti, F. G.; Knaus, T.; Scrutton, N. S.; Breuer, M.; Turner, N. J. Conversion of Alcohols to Enantiopure Amines through Dual-Enzyme Hydrogen-Borrowing Cascades. *Science (New York, N.Y.)* **2015**, *349* (6255), 1525–1529.

Heterogeneous Catalysis and Sustainable Chemistry (UvA, HIMS)
Prof. dr.G. Rothenberg[1], Dr. S. Grecea, Dr. N.R. Shiju, Dr. N. Yan

Beerthuis, R.; Granollers, M.; Brown, D. R.; Salavagione, H. J.; Rothenberg, G.; Shiju, N. R. Catalytic Acetoxylation of Lactic Acid to 2-Acetoxypropionic Acid, En Route to Acrylic Acid. *RSC Advances* **2015**, *5* (6), 4103–4108.

Beerthuis, R.; Rothenberg, G.; Shiju, N. R. Catalytic Routes towards Acrylic Acid, Adipic Acid and ε-Caprolactam Starting from Biorenewables. *Green Chemistry* **2015**, *17* (3), 1341–1361.

Ferbinteanu, M.; Cimpoesu, F.; Tanase, S. Metal-Organic Frameworks with D-F Cyanide Bridges: Structural Diversity, Bonding Regime, and Magnetism. *Structure and Bonding (Berlin, Germany)* **2015**, *163* (Lanthanide Metal-Organic Frameworks), 185–229.

Gao, Y.; Broersen, R.; Hageman, W.; Yan, N.; Mittelmeijer-Hazeleger, M. C.; Rothenberg, G.; Tanase, S. High Proton Conductivity in Cyanide-Bridged Metal-Organic Frameworks: Understanding the Role of Water. *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **2015**, *3* (44), 22347–22352.

Lankelma, M.; de Boer, J.; Ferbinteanu, M.; Dantas Ramos, A. L.; Tanasa, R.; Rothenberg, G.; Tanase, S.; de, B. J.; Ferbinteanu, M.; Ramos, A. L. D.; et al. A Novel One-Dimensional Chain Built of Vanadyl Ions and Pyrazine-2,5-Dicarboxylate. *Dalton transactions (Cambridge, England : 2003)* **2015**, *44* (25), 11380–11387.

Liu, X.; Akerboom, S.; Bouwman, E.; de, J. M.; Meijerink, A.; Mutikainen, I.; Tanase, S.; Jong, M. de; Mutikainen, I.; Tanase, S.; et al. Mixed-Lanthanoid Metal-Organic Framework for Ratiometric Cryogenic Temperature Sensing. *Inorganic chemistry* **2015**, *54* (23), 11323–11329.

Strassberger, Z.; Prinsen, P.; Klis, F. van der; Es, D. S. van; Tanase, S.; Rothenberg, G. Lignin Solubilisation and Gentle Fractionation in Liquid Ammonia. *Green Chemistry* **2015**, *17* (1), 325–334.

Yan, N.; Zeng, Y.; Shalchi, B.; Wang, W.; Gao, T.; Rothenberg, G.; Luo, J. Discovery and Understanding of the Ambient-Condition Degradation of Doped Barium Cerate Proton-Conducting Perovskite Oxide in Solid Oxide Fuel Cells. *Journal of the Electrochemical Society* **2015**, *162* (14), F1408–F1414.

Vreeken, V.; Siegler, M. A.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. C-H Activation of Benzene by a Photoactivated Ni(II)(azide): Formation of a Transient Nickel Nitrido Complex. *Angewandte Chemie (International ed. in English)* **2015**, *54* (24), 7055–7059.

Homogeneous, Supramolecular and Bio-Inspired Catalysis (UvA, HIMS)
Prof. dr. B. de Bruin[1], Prof. dr. J.N.H. Reek[1], Dr. M. Tromp, Dr. Ir. J.I. van der Vlugt

Berben, L. A.; de Bruin, B.; Heyduk, A. F.; de, B. B.; Heyduk, A. F. Non-Innocent Ligands. *Chemical Communications (Cambridge, United Kingdom)* **2015**, *51* (9), 1553–1554.

Broere, D. L. J.; Metz, L. L.; de Bruin, B.; Reek, J. N. H.; Siegler, M. A.; van der Vlugt, J. I. Redox-Active Ligand-Induced Homolytic Bond Activation. *Angewandte Chemie International Edition* **2015**, *54* (5), 1516–1520.

García-Simón, C.; Gramage-Doria, R.; Raoufmoghaddam, S.; Parella, T.; Costas, M.; Ribas, X.; Reek, J. N. H. Enantioselective Hydroformylation by a Rh-Catalyst Entrapped in a Supramolecular Metallocage. *Journal of the American Chemical Society* **2015**, *137* (7), 2680–2687.

Geer, A. M.; Serrano, A. L.; de Bruin, B.; Ciriano, M. A.; Tejel, C.; de, B. B.; Ciriano, M. A.; Tejel, C. Terminal Phosphanido Rhodium Complexes Mediating Catalytic P-P and P-C Bond Formation. *Angewandte Chemie (International ed. in English)* **2015**, *54* (2), 472–475.

Gorlin, Y.; Siebel, A.; Piana, M.; Huthwelker, T.; Jha, H.; Monsch, G.; Kraus, F.; Gasteiger, H. A.; Tromp, M. Operando Characterization of Intermediates Produced in a Lithium-Sulfur Battery. *Journal of the Electrochemical Society* **2015**, *162* (7), A1146–A1155.

Goswami, M.; Lyaskovskyy, V.; Domingos, S. R.; Buma, W. J.; Woutersen, S.; Troeppner, O.; Ivanović-Burmazović, I.; Lu, H.; Cui, X.; Zhang, X. P.; et al. Characterization of Porphyrin-Co(III)-"Nitrene Radical" Species Relevant in Catalytic Nitrene Transfer Reactions. *Journal of the American Chemical Society* **2015**, *137* (16), 5468–5479.

Grundner, S.; Markovits, M. A. C.; Li, G.; Tromp, M.; Pidko, E. A.; Hensen, E. J. M.; Jentys, A.; Sanchez-Sanchez, M.; Lercher, J. A.; Olah, G. A.; et al. Single-Site Trinuclear Copper Oxygen Clusters in Mordenite for Selective Conversion of Methane to Methanol. *Nature Communications* **2015**, *6*, 7546.

Jongbloed, L. S.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. Facile Synthesis and Versatile Reactivity of an Unusual Cyclometalated Rhodium(I) Pincer Complex. *Chemistry - A European Journal* **2015**, *21* (19), 7297–7305.

Korstanje, T. J.; Ivar van der Vlugt, J.; Elsevier, C. J.; de Bruin, B. Hydrogenation of Carboxylic Acids with a Homogeneous Cobalt Catalyst. *Science* **2015**, *350* (6258).

Lichtenberg, C.; Viciu, L.; Vogt, M.; Rodriguez-Lugo, R. E.; Adelhardt, M.; Sutter, J.; Khusniyarov, M. M.; Meyer, K.; de, B. B.; Bill, E.; et al. Low-Valent Iron: An Fe(I) Ate Compound as a Building Block for a Linear Trinuclear Fe Cluster. *Chemical Communications (Cambridge, United Kingdom)* **2015**, *51* (73), 13890–13893.

Lichtenberg, C.; Viciu, L.; Adelhardt, M.; Sutter, J. J.; Meyer, K.; de, B. B.; Grutzmacher, H.; de Bruin, B.; Gruetzmacher, H. Low-Valent Iron(i) Amido Olefin

Complexes as Promotors for Dehydrogenation Reactions. *Angewandte Chemie (International ed. in English)* **2015**, *54* (19), 5766–5771.

Nasalevich, M. A.; Becker, R.; Ramos-Fernandez, E. V.; Castellanos, S.; Veber, S. L.; Fedin, M. V.; Kapteijn, F.; Reek, J. N. H.; van der Vlugt, J. I.; Gascon, J.; et al. Co@NH $_2$ -MIL-125(Ti): Cobaloxime-Derived Metal–organic Framework-Based Composite for Light-Driven H $_2$ Production. *Energy Environ. Sci.* **2015**, *8* (1), 364–375.

Oldenhof, S.; Lutz, M.; de Bruin, B.; Ivar van der Vlugt, J.; Reek, J. N. H.; Raynal, M.; Ballester, P.; Vidal-Ferran, A.; Leeuwen, P. W. N. M. van; Raynal, M.; et al. Dehydrogenation of Formic Acid by Ir–bisMETAMORPhos Complexes: Experimental and Computational Insight into the Role of a Cooperative Ligand. *Chem. Sci.* **2015**, *6* (2), 1027–1034.

Pronk, M.; de Kreuk, M. K.; de Bruin, B.; Kamminga, P.; Kleerebezem, R.; van Loosdrecht, M. C. M.; de, K. M. K.; de, B. B.; Kamminga, P.; Kleerebezem, R.; et al. Full Scale Performance of the Aerobic Granular Sludge Process for Sewage Treatment. *Water Research* **2015**, *84*, 207–217.

Rebreyend, C.; de Bruin, B.; de, B. B. Photolytic N2 Splitting: A Road to Sustainable NH3 Production?. *Angewandte Chemie (International ed. in English)* **2015**, *54* (1), 42–44.

Scheibel, M. G.; Abbenseth, J.; Kinauer, M.; Wurtele, C.; Schneider, S.; Heinemann, F. W.; de, B. B.; Wuertele, C.; de Bruin, B.; Schneider, S. Homolytic N-H Activation of Ammonia: Hydrogen Transfer of Parent Iridium Ammine, Amide, Imide, and Nitride Species. *Inorganic Chemistry* **2015**, *54* (19), 9290–9302.

Schwab, M. M.; Himmel, D.; Kratzert, D.; Radtke, V.; Weis, P.; Krossing, I.; Kacprzak, S.; Weber, S.; Ray, K.; Scheidt, E.-W.; et al. Ni(cod)2][Al(OR(F))4], a Source for Naked Nickel(I) Chemistry. *Angewandte Chemie (International ed. in English)* **2015**, *54* (49), 14706–14709.

Thomas, R.; Kas, J.; Glatzel, P.; Al Samarai, M.; de Groot, F. M. F.; Alonso Mori, R.; Kavčič, M.; Zitnik, M.; Bucar, K.; Rehr, J. J.; et al. Resonant Inelastic X-Ray Scattering of Molybdenum Oxides and Sulfides. *The Journal of Physical Chemistry C* **2015**, 150126100226006.

Vreeken, V.; de, B. B.; Reek, J. N. H.; van, der V. J. I.; Siegler, M. A.; Lutz, M.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. C-H Activation of Benzene by a Photoactivated NiII(azide): Formation of a Transient Nickel Nitrido Complex. *Angewandte Chemie (International ed. in English)* **2015**, *54* (24), 7055–7059.

Vreeken, V.; Siegler, M. A.; de Bruin, B.; Reek, J. N. H.; Lutz, M.; van der Vlugt, J. I. C-H Activation of Benzene by a Photoactivated Ni(II)(azide): Formation of a Transient Nickel Nitrido Complex. *Angewandte Chemie (International ed. in English)* **2015**, *54* (24), 7055–7059.

Metals in Catalysis, Biomimetics & Inorganic Materials (UL, LIC)

Prof. dr. E. Bouwman[1], Dr. S. Bonnet, Dr. D. Hetterscheid

Askes, S. H. C.; Bonnet, S. Up-Converting Vesicles such as Liposomes and Polymerosomes and Uses in Triplet-Triplet Annihilation Upconversion in in Vivo Phototherapy., April 30, 2015.

Askes, S. H. C.; Kloz, M.; Bruylants, G.; Kennis, J. T. M.; Bonnet, S. Triplet-Triplet Annihilation Upconversion Followed by FRET for the Red Light Activation of a

Photodissociative Ruthenium Complex in Liposomes. *Physical chemistry chemical physics : PCCP* **2015**, *17* (41), 27380–27390.

Askes, S. H. C.; Lopez, M. N.; Harkes, R.; Koning, R. I.; Koster, B.; Schmidt, T.; Kros, A.; Bonnet, S.; Mora, N. L.; Harkes, R.; et al. Imaging the Lipid Bilayer of Giant Unilamellar Vesicles Using Red-to-Blue Light Upconversion. *Chemical Communications (Cambridge, United Kingdom)* **2015**, *51* (44), 9137–9140.

Bedoui, S.; Nicolazzi, W.; Zheng, S.; Bonnet, S.; Molnar, G.; Bousseksou, A. Impact of Single Crystal Properties on Nucleation and Growth Mechanisms of a Spin Transition. *Polyhedron* **2015**, *87*, 411–416.

Bonnet, S. Upconverting Lipid Vesicles for the Red Light Activation of Anticancer Metallodrugs. In *Abstracts of Papers, 250th ACS National Meeting & Exposition, Boston, MA, United States, August 16-20, 2015*; American Chemical Society, 2015; p INOR-51.

Bonnet, S. Shifting the Light Activation of Metallodrugs to the Red and Near-Infrared Region in Anticancer Phototherapy. *Comments on Inorganic Chemistry* **2015**, *35* (4), 179–213.

Kong, L.; Askes, S. H. C.; Bonnet, S.; Kros, A.; Campbell, F. Temporal Control of Membrane Fusion through Photolabile PEGylation of Liposome Membranes. *Angewandte Chemie, International Edition* **2016**, *55* (4), 1396–1400.

Limburg, B.; Bouwman, E.; Bonnet, S. Catalytic Photoinduced Electron Transport across a Lipid Bilayer Mediated by a Membrane-Soluble Electron Relay. *Chemical communications (Cambridge, England)* **2015**, *51* (96), 17128–17131.

Liu, X.; Akerboom, S.; Askes, S. H. C.; Mutikainen, I.; Bouwman, E. A Novel Coordination Network of Tb(III) with 2-Hydroxy-Trimesic Acid Showing Very Intense Photoluminescence. *Inorganic Chemistry Communications* **2015**, *61*, 60–63.

Liu, X.; Akerboom, S.; Bouwman, E.; de, J. M.; Meijerink, A.; Mutikainen, I.; Tanase, S. Mixed-Lanthanoid Metal-Organic Framework for Ratiometric Cryogenic Temperature Sensing. *Inorganic chemistry* **2015**, *54* (23), 11323–11329.

Liu, X.; Siegler, M. A.; Bouwman, E. Ratiometric Thermometer Based on a Lanthanoid Coordination Polymer. *European Journal of Inorganic Chemistry* **2016**, Ahead of Print.

Ording-Wenker, E. C. M.; Siegler, M. A.; Bouwman, E. Coordination of New Disulfide Ligands to CuI and CuII: Does a CuIIμ-Thiolate Complex Form?. *Inorganica Chimica Acta* **2015**, *428*, 193–202.

Ording-Wenker, E. C. M.; Siegler, M. A.; Lutz, M.; Bouwman, E. Catalytic Catechol Oxidation by Copper Complexes: Development of a Structure-Activity Relationship. *Dalton Transactions* **2015**, *44* (27), 12196–12209.

van Dijkman, T. F.; de Bruijn, H. M.; Siegler, M. A.; Bouwman, E. Bright Cyan Phosphorescence of a (Phosphane)copper(I) Complex of the Tri-Hydrido-Pyrazolylborate Ligand H3B(3,5-Ph2Pz)-. *European Journal of Inorganic Chemistry* **2015**, *2015* (32), 5387–5394.

Van Dijkman, T. F.; Siegler, M. A.; Bouwman, E. Highly Tunable Fluorinated Trispyrazolylborates [HB(3-CF3-5-{4-RPh}pz)3]- (R = NO2, CF3, Cl, F, H, OMe and NMe2) and Their copper(I) Complexes. *Dalton Transactions* **2015**, *44* (48), 21109–21123.

Van Rixel, V. H. S.; Busemann, A.; Gottle, A. J.; Bonnet, S.; van Rixel, V. H. S.; Busemann, A.; Goettle, A. J.; Bonnet, S. Preparation, Stability, and Photoreactivity of Thiolato Ruthenium Polypyridyl Complexes: Can Cysteine Derivatives Protect Ruthenium-Based Anticancer Complexes?. *Journal of Inorganic Biochemistry* **2015**, *150*, 174–181.

Molecular Inorganic Chemistry (UvA, HIMS)
Prof. dr. C.J. Elsevier[1]

Drost, R. M.; Broere, D. L. J.; Hoogenboom, J.; de Baan, S. N.; Lutz, M.; de Bruin, B.; Elsevier, C. J. Allylpalladium(II) Histidylidene Complexes and Their Application in Z-Selective Transfer Semihydrogenation of Alkynes. *European Journal of Inorganic Chemistry* **2015**, *2015* (6), 982–996.

Drost, R. M.; Rosar, V.; Dalla Marta, S.; Lutz, M.; Demitri, N.; Milani, B.; de Bruin, B.; Elsevier, C. J. Pd-Catalyzed Z-Selective Semihydrogenation of Alkynes: Determining the Type of Active Species. *ChemCatChem* **2015**, *7* (14), 2095–2107.

Korstanje, T. J.; van, der V. J. I.; Elsevier, C. J.; de, B. B.; van der Vlugt, J. I.; Elsevier, C. J.; de Bruin, B. Hydrogenation of Carboxylic Acids with a Homogeneous Cobalt Catalyst. *Science (Washington, DC, United States)* **2015**, *350* (6258), 298–302.

Sluijter, S. N.; Jongkind, L. J.; Elsevier, C. J. Synthesis of BINAM-Based Chiral Di-1,2,3-Triazolylidene Complexes and Application of the Di-NHC Rh(I) Catalyst in Enantioselective
Hydrosilylation. *European Journal of Inorganic Chemistry* **2015**, *2015* (18), 2948–2955.

Organic and Organometallic Chemistry (VU, EMS)
Prof. dr. K. Lammertsma, Dr. A.W. Ehlers, Dr. J.C. Slootweg

Borger, J. E.; Ehlers, A. W.; Lutz, M.; Slootweg, J. C.; Lammertsma, K. Stabilization and Transfer of the Transient [Mes*P4](-) Butterfly Anion Using BPh3. *Angewandte Chemie (International ed. in English)* **2016**, *55* (2), 613–617.

Devillard, M.; Nicolas, E.; Ehlers, A. W.; Backs, J.; Mallet-Ladeira, S.; Bouhadir, G.; Slootweg, J. C.; Uhl, W.; Bourissou, D. Dative Au→Al Interactions: Crystallographic Characterization and Computational Analysis. *Chemistry - A European Journal* **2015**, *21* (1), 74–79.

Fustier, M.; Le Goff, X.-F. X.-F.; Lutz, M.; Slootweg, J. C.; Mezailles, N.; Mézailles, N. Scandium Carbene Complexes: Synthesis of Mixed Alkyl, Amido, and Phosphido Derivatives. *Organometallics* **2015**, *34* (1), 63–72.

Janssen, G. V.; Vicente-García, E.; Vogel, W.; Slootweg, J. C.; Ruijter, E.; Lammertsma, K.; Orru, R. V. A. Stereoselective Synthesis of β-Sulfinylamino Isocyanides and 2-Imidazolines. *European Journal of Organic Chemistry* **2014**, *2014* (18), 3762–3766.

Mulder, J. R.; Guerra, C. F.; Slootweg, J. C.; Lammertsma, K.; Bickelhaupt, F. M. Substituent Effects on the Optical Properties of Naphthalenediimides: A Frontier Orbital Analysis across the Periodic Table. *Journal of computational chemistry* **2016**, *37* (2), 304–313.

Reinert, A.; Ehlers, A.; Alff, C. Operational Control of Solid Oxide Fuel Cells., January 14, 2015.

Stark, E. A.; Van, H. T. J.; Charquero-Ballester, M.; Parsons, C. E.; McManners, H.; Ehlers, A.; Stein, A.; Kringelbach, M. L. Post-Traumatic Stress Influences the Brain Even in the Absence of Symptoms: A Systematic, Quantitative Meta-Analysis of Neuroimaging Studies. *Neuroscience and biobehavioral reviews* **2015**, *56*, 207–221.

Van Dijk, T.; Bakker, M. S.; Holtrop, F.; Nieger, M.; Slootweg, J. C.; Lammertsma, K.; van, D. T.; Bakker, M. S.; Holtrop, F.; Slootweg, J. C.; et al. Base-Stabilized Nitrilium Ions as Convenient Imine Synthons. *Organic letters* **2015**, *17* (6), 1461–1464.

Van Dijk, T.; Burck, S.; Rosenthal, A. J.; Nieger, M.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K. Synthesis and Coordination Chemistry of Iminophosphanes. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2015**, *21* (26), 9328–9331.

Van, Dijk. T.; Burck, S.; Rosenthal, A. J.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K.; Nieger, M.; van Dijk, T.; Burck, S.; Rosenthal, A. J.; et al. Synthesis and Coordination Chemistry of Iminophosphanes. *Chemistry - A European Journal* **2015**, *21* (26), 9328–9331.

Synthetic and Bio-organic Chemistry (VU, EMS)

Prof. dr. ir. R.V.A. Orru, Dr. E. Ruijter

Bouwman, S.; Orru, R. V. A.; Ruijter, E. Stereoselective Synthesis of Fluorinated Aminoglycosyl Phosphonates. *Organic & biomolecular chemistry* **2015**, *13* (5), 1317–1321.

Cioc, R. C.; van der Niet, D. J. H.; Janssen, E.; Ruijter, E.; Orru, R. V. A.; One-Pot Synthesis of N-Substituted β-Amino Alcohols from Aldehydes and Isocyanides. *Chemistry - A European Journal* **2015**, *21* (21), 7808–7813.

De Graaff, C.; Bensch, L.; van Lint, M. J.; Ruijter, E.; Orru, R. V. A.; de, G. C.; Bensch, L.; van, L. M. J.; Ruijter, E.; Orru, R. V. A. IBX-Mediated Oxidation of Unactivated Cyclic Amines: Application in Highly Diastereoselective Oxidative Ugi-Type and Aza-Friedel-Crafts Reactions. *Organic & biomolecular chemistry* **2015**, *13* (40), 10108–10112.

De Graaff, C.; Bensch, L.; Boersma, S. J.; Cioc, R. C.; van, L. M. J.; Janssen, E.; Orru, R. V. A.; Ruijter, E.; Turner, N. J.; de Graaff, C.; et al. Asymmetric Synthesis of Tetracyclic Pyrroloindolines and Constrained Tryptamines by a Switchable Cascade Reaction. *Angewandte Chemie (International ed. in English)* **2015**, *54* (47), 14133–14136.

Kruithof, A.; Ruijter, E.; Orru, R. V. A. Synthesis of Heterocycles by Formal Cycloadditions of Isocyanides. *Chemistry, an Asian journal* **2015**, *10* (3), 508–520.

Synthetic Organic Chemistry (UvA, HIMS)

Prof. dr. H. Hiemstra[1], Prof. dr. J.H. van Maarseveen, Prof. dr. P. Timmerman, Dr. M.Á. Fernández-Ibáñez, Dr. S. Ingemann

Breman, A. C.; Telderman, S. E. M.; van, S. R. P. M.; Scott, J. I.; van, M. J. H.; Ingemann, S.; Hiemstra, H.; van Santen, R. P. M.; Scott, J. I.; van Maarseveen, J. H.; et al. Cinchona Alkaloid Catalyzed Sulfa-Michael Addition Reactions Leading to Enantiopure β-Functionalized Cysteines. *The Journal of organic chemistry* **2015**, *80* (21), 10561–10574.

Rodenko, B.; Wanner, M. J.; Alkhaldi, A. A. M.; Ebiloma, G. U.; Barnes, R. L.; Kaiser, M.; Brun, R.; McCulloch, R.; Koomen, G.-J.; de Koning, H. P. Targeting the Parasite's DNA with Methyltriazenyl Purine Analogs Is a Safe, Selective, and Efficacious Antitrypanosomal Strategy. *Antimicrobial agents and chemotherapy* **2015**, *59* (11), 6708–6716.

Ruiz-Olalla, A.; Wurdemann, M. A.; Wanner, M. J.; Ingemann, S.; van, M. J. H.; Hiemstra, H.; Wuerdemann, M. A.; Wanner, M. J.; Ingemann, S.; van Maarseveen, J.

H.; et al. Organocatalytic Enantioselective Pictet-Spengler Approach to Biologically Relevant 1-Benzyl-1,2,3,4-Tetrahydroisoquinoline Alkaloids. *The Journal of organic chemistry* **2015**, *80* (10), 5125–5132.

Saya, J. M.; Vos, K.; Kleinnijenhuis, R. A.; van, M. J. H.; Ingemann, S.; Hiemstra, H.; van Maarseveen, J. H.; Ingemann, S.; Hiemstra, H. Total Synthesis of Aquatolide. *Organic letters* **2015**, *17* (15), 3892–3894.

Smeenk, L. E. J.; Timmers-Parohi, D.; Benschop, J. J.; Puijk, W. C.; Hiemstra, H.; van Maarseveen, J. H.; Timmerman, P. Reconstructing the Discontinuous and Conformational β1/β3-Loop Binding Site on hFSH/hCG by Using Highly Constrained Multicyclic Peptides. *Chembiochem : a European journal of chemical biology* **2015**, *16* (1), 91–99.

Wassenaar, J.; Detz, R. J.; de, B. S. Y.; Reek, J. N. H.; Lutz, M.; van, M. J. H.; Hiemstra, H.; de Boer, S. Y.; Lutz, M.; van Maarseveen, J. H.; et al. Enantioselective Synthesis of Tunable Chiral Clickphine P,N-Ligands and Their Application in Ir-Catalyzed Asymmetric Hydrogenation. *The Journal of organic chemistry* **2015**, *80* (7), 3634–3642.

Biomolecular Spectroscopy (VU, EMS)
Dr. F. Ariese

Dutta, A.; Gautam, R.; Chatterjee, S.; Sikdar, S. K.; Umapathy, S.; Ariese, F.; Sikdar, S. K.; Umapathy, S. Ascorbate Protects Neurons against Oxidative Stress: A Raman Microspectroscopic Study. *ACS chemical neuroscience* **2015**, *6* (11), 1794–1801.

Gautam, R.; Samuel, A.; Sil, S.; Chaturvedi, D.; Dutta, A.; Ariese, F.; Umapathy, S. Raman and Mid-Infrared Spectroscopic Imaging: Applications and Advancements. *Current Science* **2015**, *108* (3), 341–356.

Hooijschuur, J.-H.; Verkaaik, M. F. C.; Davies, G. R.; Ariese, F. Raman Spectroscopy for Future Planetary Exploration: Photodegradation, Self-Absorption and Quantification of Carotenoids in Microorganisms and Mineral Matrices. *Journal of Raman Spectroscopy* **2015**, *46* (10), 856–862.

Iping, P. I. E.; Esmonde-White, F. W. L.; de, W. W.; Morris, M. D.; Ariese, F.; Iping Petterson, I. E.; Esmonde-White, F. W. L.; de Wilde, W.; Morris, M. D.; Ariese, F. Tissue Phantoms to Compare Spatial and Temporal Offset Modes of Deep Raman Spectroscopy. *The Analyst* **2015**, *140* (7), 2504–2512.

Kumar, V. R.; Rajkumar, N.; Ariese, F.; Umapathy, S. Direct Observation of Thermal Equilibrium of Excited Triplet States of 9,10-Phenanthrenequinone. A Time-Resolved Resonance Raman Study. *Journal of Physical Chemistry A* **2015**, *119* (40), 10147–10157.

Periyasamy, V.; Sil, S.; Dhal, G.; Ariese, F.; Umapathy, S.; Pramanik, M. Experimentally Validated Raman Monte Carlo Simulation for a Cuboid Object to Obtain Raman Spectroscopic Signatures for Hidden Material. *Journal of Raman Spectroscopy* **2015**, *46* (7), 669–676.

Van Hoorn, C. H.; Ariese, F.; Iannuzzi, D.; Mank, A. J. G. Using Ferrule-Top Opto Mechanical Probes as a New Tool in VCSEL Reliability Experiments. *Optics express* **2015**, *23* (23), 30318–30328.

Verkaaik, M. F. C.; Hooijschuur, J.-H.; Davies, G. R.; Ariese, F.; Hooijschuur, J.-H.; Davies, G. R. Raman Spectroscopic Techniques for Planetary Exploration: Detecting Microorganisms through Minerals. *Astrobiology* **2015**, *15* (8), 697–707.

Zanni, M.; Jemmis, E. D.; Aravamudhan, S.; Pallipurath, A.; Arunan, E.; Schnedermann, C.; Mishra, A. K.; Warren, M.; Hirst, J. D.; John, F.; et al. Time and Space Resolved Methods: General Discussion. *Faraday Discussions* **2015**, *177*, 263–292.

Biophysical Organic Chemistry (UL, LIC)
Prof. dr. H.J.M. de Groot, Dr. Alia, Dr. F. Buda

Faez, S.; Verhart, N. R.; Markoulides, M.; Buda, F.; Gourdon, A.; Orrit, M. Design and Synthesis of Aromatic Molecules for Probing Electric Fields at the Nanoscale. *Faraday Discuss.* **2015**, *184*, 251–262.

Faez, S.; Verhart, N. R.; Markoulides, M.; Buda, F.; Gourdon, A.; Orrit, M. Design and Synthesis of Aromatic Molecules for Probing Electric Fields at the Nanoscale. *Faraday Discuss.* **2015**, *184* (Single-Molecule Microscopy and Spectroscopy), 251–262.

Monti, A.; de, G. H. J. M.; Buda, F.; Negre, C. F. A.; Batista, V. S.; Rego, L. G. C. Crucial Role of Nuclear Dynamics for Electron Injection in a Dye-Semiconductor Complex. *J. Phys. Chem. Lett.* **2015**, *6* (12), 2393–2398.

Monti, A.; Negre, C. F. A.; Batista, V. S.; Rego, L. G. C.; de Groot, H. J. M.; Buda, F. Crucial Role of Nuclear Dynamics for Electron Injection in a Dye-Semiconductor Complex. *J. Phys. Chem. Lett.* **2015**, *6* (12), 2393–2398.

Laboratory Astrophysics and Astrochemistry (UL, LION)
Prof. dr. H. Linnartz

Bacalla, X.; Zhao, D.; Salumbides, E. J.; Haddad, M. A.; Linnartz, H.; Ubachs, W. The B2Π-X2Π Electronic Origin Band of 13C6H. *Journal of Molecular Spectroscopy* **2015**, *308–309*, 41–44.

Bossa, J.-B.; Paardekooper, D. M.; Isokoski, K.; Linnartz, H. Methane Ice Photochemistry and Kinetic Study Using Laser Desorption Time-of-Flight Mass Spectrometry at 20 K. *Physical Chemistry Chemical Physics* **2015**, *17* (26), 17346–17354.

Bossa, J.-B.; Maté, B.; Fransen, C.; Cazaux, S.; Pilling, S.; Rocha, W. R. M.; Ortigoso, J.; Linnartz, H.; Accolla M., C. E. . D. F. et al; Ayotte P., S. S. S. . S. K. P. et al; et al. POROSITY AND BAND-STRENGTH MEASUREMENTS OF MULTI-PHASE COMPOSITE ICES. *The Astrophysical Journal* **2015**, *814* (1), 47.

Cazaux, S.; Bossa, J.-B.; Linnartz, H.; Tielens, A. G. G. M. Pore Evolution in Interstellar Ice Analogues: Simulating the Effects of Temperature Increase. *Astronomy & Astrophysics* **2015**, *573* (Pt. 1), A16/1-A16/7.

Cook, A. M.; Ricca, A.; Mattioda, A. L.; Bouwman, J.; Roser, J.; Linnartz, H.; Bregman, J.; Allamandola, L. J. Photochemistry of Polycyclic Aromatic Hydrocarbons in Cosmic Water Ice: The Role of PAH Ionization and Concentration. *Astrophysical Journal* **2015**, *799* (1), 14/1-14/20.

Doney, K. D.; Zhao, D.; Linnartz, H. High-Resolution Infrared Spectrum of Triacetylene: The v5 State Revisited and New Vibrational States. *Journal of Molecular Spectroscopy* **2015**, *316*, 54–63.

Fedoseev, G.; Cuppen, H. M.; Ioppolo, S.; Lamberts, T.; Linnartz, H. Experimental Evidence for Glycolaldehyde and Ethylene Glycol Formation by Surface Hydrogenation of CO Molecules under Dense Molecular Cloud Conditions. *Monthly Notices of the Royal Astronomical Society* **2015**, *448* (2), 1288–1297.

Fedoseev, G.; Ioppolo, S.; Zhao, D.; Lamberts, T.; Linnartz, H. Low-Temperature Surface Formation of NH3 and HNCO: Hydrogenation of Nitrogen Atoms in CO-Rich

Interstellar Ice Analogues. *Monthly Notices of the Royal Astronomical Society* **2014**, *446* (1), 439–448.

Fedoseev, G.; Ioppolo, ‹ S; Linnartz, H. Deuterium Enrichment of Ammonia Produced by Surface N+H/D Addition Reactions at Low Temperature. *MNRAS* **2015**, *446*, 449–458.

Haddad, M. A.; Zhao, D.; Linnartz, H.; Ubachs, W. The Electronic Spectra of Long Carbon-Chain (13)C2nH/D Molecules for (). *Molecular Physics* **2015**, *113* (15–16), 2063–2072.

Lamberts, T.; Ioppolo, S.; Cuppen, H. M.; Fedoseev, G.; Linnartz, H. Thermal H/D Exchange in Polar Ice - Deuteron Scrambling in Space. *Monthly Notices of the Royal Astronomical Society* **2015**, *448* (4), 3820–3828.

Ligterink, N. F. W.; Paardekooper, D. M.; Chuang, K.-J.; Both, M. L.; Cruz-Diaz, G. A.; van Helden, J. H.; Linnartz, H. Controlling the Emission Profile of an H 2 Discharge Lamp to Simulate Interstellar Radiation Fields. *Astronomy & Astrophysics* **2015**, *584*, A56.

Linnartz, H.; Ioppolo, S.; Fedoseev, G. Atom Addition Reactions in Interstellar Ice Analogues. *International Reviews in Physical Chemistry* **2015**, *34* (2), 205–237.

Zhao, D.; Galazutdinov, G. A.; Linnartz, H.; Krelowski, J. Detection of OH+ in Translucent Interstellar Clouds: New Electronic Transitions and Probing the Primary Cosmic Ray Ionization Rate. *Astrophysical Journal, Letters* **2015**, *805* (2), 1–5.

Zhao, D.; Galazutdinov, G. A.; Linnartz, H.; Krelowski, J. Mercapto Radical (SH) in Translucent Interstellar Clouds. *Astronomy & Astrophysics* **2015**, *579* (Pt. 1), L1/1-L1/4.

Zhen, J.; Castellanos, P.; Paardekooper, D. M.; Ligterink, N.; Linnartz, H.; Nahon, L.; Joblin, C.; Tielens, A. G. G. M. Laboratory Photo-Chemistry of PAHs: Ionization versus Fragmentation. *Astrophysical Journal, Letters* **2015**, *804* (1), 1–6.

Molecular Nano-Optics and Spins (UL, LION)

Prof. dr. E.J.J. Groenen, Prof. dr. M. Orrit, Dr. P. Gast, Dr. M. I. Huber

Azarkh, M.; Groenen, E. J. J. Simulation of Multi-Frequency EPR Spectra for a Distribution of the Zero-Field Splitting. *Journal of Magnetic Resonance* **2015**, *255*, 106–113.

Azarkh, M.; Groenen, E. J. J. Temperature Determination by EPR at 275 GHz and the Detection of Temperature Jumps in Aqueous Samples. *The journal of physical chemistry. B* **2015**, *119* (42), 13416–13421.

Faez, S.; Orrit, M.; Lahini, Y.; Weidlich, S.; Weidlich, S.; Wondraczek, K.; Zeisberger, M.; Schmidt, M. A.; Garmann, R. F.; Manoharan, V. N.; et al. Fast, Label-Free Tracking of Single Viruses and Weakly Scattering Nanoparticles in a Nanofluidic Optical Fiber. *ACS nano* **2015**, *9* (12), 12349–12357.

Hashemi Shabestari, M.; Kumar, P.; Segers-Nolten, I. M. J.; Claessens, M. M. A. E.; van Rooijen, B. D.; Subramaniam, V.; Huber, M. Three Long-Range Distance Constraints and an Approach Towards a Model for the α-Synuclein-Fibril Fold. *Applied Magnetic Resonance* **2015**, *46* (4), 369–388.

Hou, L.; Yorulmaz, M.; Verhart, N. R.; Orrit, M. Explosive Formation and Dynamics of Vapor Nanobubbles around a Continuously Heated Gold Nanosphere. *New Journal of Physics* **2015**, *17* (Jan.), 13050.

Khatua, S.; Yuan, H.; Orrit, M. Enhanced-Fluorescence Correlation Spectroscopy at Micro-Molar Dye Concentration around a Single Gold Nanorod. *Physical chemistry chemical physics : PCCP* **2015**, *17* (33), 21127–21132.

Kumar, P.; Segers-Nolten, I. M. J.; Schilderink, N.; Subramaniam, V.; Huber, M. Parkinson's Protein α-Synuclein Binds Efficiently and with a Novel Conformation to Two Natural Membrane Mimics. *PloS one* **2015**, *10* (11), e0142795.

Mance, D.; Gast, P.; Huber, M.; Baldus, M.; Ivanov, K. L. The Magnetic Field Dependence of Cross-Effect Dynamic Nuclear Polarization under Magic Angle Spinning. *Journal of Chemical Physics* **2015**, *142* (23), 234201/1-234201/10.

Mathies, G.; Gast, P.; Chasteen, N. D.; Luck, A. N.; Mason, A. B.; Groenen, E. J. J. Exploring the Fe(III) Binding Sites of Human Serum Transferrin with EPR at 275 GHz. *Journal of biological inorganic chemistry : JBIC : a publication of the Society of Biological Inorganic Chemistry* **2015**, *20* (3), 487–496.

Navarro, P.; Bocquet, F. C.; Deperasińska, I.; Pirug, G.; Tautz, F. S.; Orrit, M. Electron Energy Loss of Terrylene Deposited on Au(111): Vibrational and Electronic Spectroscopy. *The Journal of Physical Chemistry C* **2015**, *119* (1), 277–283.

Orrit, M. Single-Molecule Chemistry Is More than Superresolved Fluorescence Microscopy. *Angewandte Chemie (International ed. in English)* **2015**, *54* (28), 8004–8005.

Reinisch, G.; Huber, M.; Zweymuller, K. A. Low-Carbon Metal-on-Metal Articulations for Hip Arthroplasties--Evaluation of Wear and Histology after 11 to 17 Years. *Zeitschrift fur Orthopadie und Unfallchirurgie* **2015**, *153* (4), 392–398.

Scarpelli, F.; Arrieta, A. L.; Gast, P.; Groenen, E. J. J.; Milikisyants, S.; Murphy, M. E. P.; Huber, M. A Single-Crystal EPR Study at 95 GHz of the Type-2 Copper Site of Nitrite Reductase from Alcaligenes Faecalis. *Applied Magnetic Resonance* **2015**, *46* (4), 411–420.

Schilder, J.; Liu, W.-M.; Kumar, P.; Overhand, M.; Huber, M.; Ubbink, M. Protein Docking Using an Ensemble of Spin Labels Optimized by Intra-Molecular Paramagnetic Relaxation Enhancement. *Physical chemistry chemical physics : PCCP* **2016**, *18* (8), 5729–5742.

Stachon, T.; Seitz, B.; Huber, M.; Zawada, M.; Szentmary, N.; Bischoff, M.; Langenbucher, A. Growth Factors and Interleukins in Amniotic Membrane Tissue Homogenate. *Klinische Monatsbla.ovrddot.tter fu.ovrddot.r Augenheilkunde* **2015**, *232* (7), 858–862.

Son, van, S. M.; van, der W. M.; Huber, M.; Lindhoud, S.; van, M. C. P. M. Double Electron-Electron Spin Resonance Tracks Flavodoxin Folding. *The journal of physical chemistry. B* **2015**, *119* (43), 13507–13514.

Yuan, H.; Gaiduk, A.; Siekierzycka, J. R.; Fujiyoshi, S.; Matsushita, M.; Nettels, D.; Schuler, B.; Seidel, C. A. M.; Orrit, M. Temperature-Cycle Microscopy Reveals Single-Molecule Conformational Heterogeneity. *Physical chemistry chemical physics : PCCP* **2015**, *17* (9), 6532–6544.

Molecular Photonics (UvA, HIMS)

Prof. dr. A.M. Brouwer, Prof. dr. W.J. Buma, Prof. dr. S. Woutersen,

Dr. R. M. Williams, Dr. H. Zhang, Prof. dr. J. Oomens (Radboud University)

Balkowski, G.; Szemik-Hojniak, A.; Buma, W. J.; Zhang, H.; Deperasinska, I.; Poisson, L.; Mestdagh, J. M.; Piani, G.; Oberda, K. Ultrafast Excited-State Dynamics of a Cyano-Substituted "Proton Sponge". *Journal of Physical Chemistry A* **2015**, *119* (46), 11233–11240.

Chen, H.-C.; Hetterscheid, D. G. H.; Williams, R. M. R. M.; van der Vlugt, J. I.; Reek, J. N. H.; Brouwer, A. M. Platinum(II)-Porphyrin as a Sensitizer for Visible-Light Driven Water Oxidation in Neutral Phosphate Buffer. *Energy & Environmental Science* **2015**, *8* (3), 975–982.

Chen, H.-C.; Hsu, C.-P.; Reek, J. N. H.; Williams, R. M.; Brouwer, A. M. Highly Soluble Benzo[ghi]perylenetriimide Derivatives: Stable and Air-Insensitive Electron Acceptors for Artificial Photosynthesis. *ChemSusChem* **2015**, *8* (21), 3639–3650.

Ding, Y.; Hong, X.; Liu, Y.; Ding, Y.; Aalders, M. C. G.; Wu, F.; Zhang, Y.; Liu, X.; Zhang, H.; de, J. E. M. L. D.; et al. Interplay between Static and Dynamic Energy Transfer in Biofunctional Upconversion Nanoplatforms. *The journal of physical chemistry letters* **2015**, *6* (13), 2518–2523.

Domingos, S. R.; Buma, W. J.; Woutersen, S.; Domingos, S. R.; Hartl, F. Elucidating the Structure of Chiral Molecules by Using Amplified Vibrational Circular Dichroism: From Theory to Experimental Realization. *Chemphyschem : a European journal of chemical physics and physical chemistry* **2015**.

Du, W.; Cruz-Cabeza, A. J.; Woutersen, S.; Davey, R. J.; Yin, Q. Can the Study of Self-Assembly in Solution Lead to a Good Model for the Nucleation Pathway? The Case of Tolfenamic Acid. *Chemical Science* **2015**, *6* (6), 3515–3524.

Goswami, M.; Lyaskovskyy, V.; Domingos, S. R.; Buma, W. J.; Woutersen, S.; de, B. B.; Troeppner, O.; Ivanovic-Burmazovic, I.; Lu, H.; Cui, X.; et al. Characterization of Porphyrin-Co(III)-'Nitrene Radical' Species Relevant in Catalytic Nitrene Transfer Reactions. *Journal of the American Chemical Soc*
iety **2015**, *137* (16), 5468–5479.

Hennig, R.; Heidrich, J.; Saur, M.; Schmueser, L.; Roeters, S. J.; Hellmann, N.; Woutersen, S.; Bonn, M.; Weidner, T.; Markl, J.; et al. IM30 Triggers Membrane Fusion in Cyanobacteria and Chloroplasts. *Nature Communications* **2015**, *6*, 7018.

Huerta-Viga, A.; Amirjalayer, S.; Domingos, S. R.; Meuzelaar, H.; Rupenyan, A.; Woutersen, S. The Structure of Salt Bridges between Arg+ and Glu- in Peptides Investigated with 2D-IR Spectroscopy: Evidence for Two Distinct Hydrogen-Bond Geometries. *Journal of Chemical Physics* **2015**, *142* (21), 212444/1-212444/8.

Kiawi, D. M.; Bakker, J. M.; Oomens, J.; Buma, W. J.; Jamshidi, Z.; Visscher, L.; Waters, L. B. F. M. Water Adsorption on Free Cobalt Cluster Cations. *Journal of Physical Chemistry A* **2015**, *119* (44), 10828–10837.

Kumpulainen, T.; Bakker, B. H.; Brouwer, A. M. Complexes of a Naphthalimide Photoacid with Organic Bases, and Their Excited-State Dynamics in Polar Aprotic Organic Solvents. *Physical chemistry chemical physics : PCCP* **2015**, *17* (32), 20715–20724.

Kumpulainen, T.; Bakker, B. H.; Hilbers, M.; Brouwer, A. M. Synthesis and Spectroscopic Characterization of 1,8-Naphthalimide Derived "Super" Photoacids. *The journal of physical chemistry. B* **2015**, *119* (6), 2515–2524.

Le, V. H.; Inai, M.; Williams, R. M.; Kan, T. Ecteinascidins. A Review of the Chemistry, Biology and Clinical Utility of Potent Tetrahydroisoquinoline Antitumor Antibiotics. *Natural product reports* **2015**, *32* (2), 328–347.

Ligare, M. R.; de, V. M. S.; Rijs, A. M.; Berden, G.; Oomens, J.; KabelaiÐ^{2}c, M.; Nachtigallova, D.; Oomens, J.; Oomens, J. Resonant Infrared Multiple Photon Dissociation Spectroscopy of Anionic Nucleotide Monophosphate Clusters. *The journal of physical chemistry. B* **2015**, *119* (25), 7894–7901.

Liu, X.; Chen, H.-C.; Kong, X.; Zhang, Y.; Tu, L.; Chang, Y.; Wu, F.; Wang, T.; Reek, J. N. H.; Brouwer, A. M.; et al. Near Infrared Light-Driven Water Oxidation in a Molecule-Based Artificial Photosynthetic Device Using an Upconversion Nano-Photosensitizer. *Chemical Communications (Cambridge, United Kingdom)* **2015**, *51* (65), 13008–13011.

Mackie, C. J.; Candian, A.; Petrignani, A.; Tielens, A. G. G. M.; Huang, X.; Maltseva, E.; Buma, W. J.; Oomens, J.; Lee, T. J. The Anharmonic Quartic Force Field Infrared Spectra of Three Polycyclic Aromatic Hydrocarbons: Naphthalene, Anthracene, and Tetracene. *The Journal of chemical physics* **2015**, *143* (22), 224314.

Maltseva, E.; Petrignani, A.; Candian, A.; Mackie, C. J.; Huang, X.; Lee, T. J.; Tielens, A. G. G. M.; Oomens, J.; Buma, W. J. High-Resolution IR Absorption Spectroscopy of Polycyclic Aromatic Hydrocarbons: The Realm of Anharmonicity. *arXiv.org, e-Print Archive, Astrophysics* **2016**, 1–13.

Martens, J. K.; Grzetic, J.; Berden, G.; Oomens, J. Gas-Phase Conformations of Small Polyprolines and Their Fragment Ions by IRMPD Spectroscopy. *International Journal of Mass Spectrometry* **2015**, *377*, 179–187.

McMahon, S.; Amirjalayer, S.; Buma, W. J.; Halpin, Y.; Long, C.; Rooney, A. D.; Woutersen, S.; Pryce, M. T. An Investigation into the Photochemistry Of, and the Electrochemically Induced CO-Loss From, [(CO)5MC(OMe)Me](M = Cr or W) Using Low-Temperature Matrix Isolation, Picosecond Infrared Spectroscopy, Cyclic Voltammetry, and Time-Dependent Density Functional . *Dalton Transactions* **2015**, *44* (35), 15424–15434.

Meuzelaar, H.; Panman, M. R.; Woutersen, S. Guanidinium-Induced Denaturation by Breaking of Salt Bridges. *Angewandte Chemie, International Edition* **2015**, *54* (50), 15255–15259.

Panman, M. R.; van Dijk, C. N.; Meuzelaar, H.; Woutersen, S. Communication: Nanosecond Folding Dynamics of an Alpha Helix: Time-Dependent 2D-IR Cross Peaks Observed Using Polarization-Sensitive Dispersed Pump-Probe Spectroscopy. *Journal of Chemical Physics* **2015**, *142* (4), 041103/1-041103/4.

Rijs, A.; Oomens, J. While Obviously Not the Natural Environment of Biological Molecules, the Gas Phase Provides the Ultimate Degree of Isolation. Introduction. *Topics in current chemistry* **2015**, *364*, v–vii.

Gas-Phase IR Spectroscopy and Structure of Biological Molecules; Rijs, A. M., Oomens, J., Eds.; Topics in Current Chemistry; Springer International Publishing: Cham, 2015; Vol. 364.

Rijs, A. M.; Oomens, J. IR Spectroscopic Techniques to Study Isolated Biomolecules; 2014; pp 1–42.

Suhina, T.; Weber, B.; Carpentier, C. E.; Lorincz, K.; Schall, P.; Bonn, D.; Brouwer, A. M. Fluorescence Microscopy Visualization of Contacts between Objects. *Angewandte Chemie (International ed. in English)* **2015**, *54* (12), 3688–3691.

Tan, E. M. M.; Amirjalayer, S.; Smolarek, S.; Vdovin, A.; Buma, W. J.; Zerbetto, F. Fast Photodynamics of Azobenzene Probed by Scanning Excited-State Potential Energy Surfaces Using Slow Spectroscopy. *Nature communications* **2015**, *6*, 5860.

Tros, M.; Woutersen, S. Polarization-Modulation Setup for Ultrafast Infrared Anisotropy Experiments to Study Liquid Dynamics. *Optics Letters* **2015**, *40* (11), 2607–2609.

Yamaguchi, T.; Hilbers, M. F.; Reinders, P. P.; Kobayashi, Y.; Brouwer, A. M.; Abe, J. Nanosecond Photochromic Molecular Switching of a Biphenyl-Bridged Imidazole Dimer Revealed by Wide Range Transient Absorption Spectroscopy. *Chemical communications (Cambridge, England)* **2015**, *51* (7), 1375–1378.

Surface Chemistry and Catalysis (UL, LIC)

Prof. dr. M. Koper[1], Dr. W.T. Fu, Dr. I.M.N. Groot, Dr. D. Hetterscheid, Dr. L.B.F. Juurlink

Badan, C.; Koper, M. T. M.; Juurlink, L. B. F. How Well Does Pt(211) Represent Pt[n(111) × (100)] Surfaces in Adsorption/Desorption?. *Journal of Physical Chemistry C* **2015**, *119* (24), 13551–13560.

Badan, C.; Koper, M. T. M.; Juurlink, L. B. F. How Well Does Pt(211) Represent Pt[*N* (111) × (100)] Surfaces in Adsorption/Desorption? *The Journal of Physical Chemistry C* **2015**, *119* (24), 13551–13560.

Calle-Vallejo, F.; Tymoczko, J.; Colic, V.; Vu, Q. H.; Pohl, M. D.; Morgenstern, K.; Loffreda, D.; Sautet, P.; Schuhmann, W.; Bandarenka, A. S. Finding Optimal Surface Sites on Heterogeneous Catalysts by Counting Nearest Neighbors. *Science* **2015**, *350* (6257), 185–189.

Calle-Vallejo, F.; Díaz-Morales, O. A.; Kolb, M. J.; Koper, M. T. M. Why Is Bulk Thermochemistry a Good Descriptor for the Electrocatalytic Activity of Transition Metal Oxides? *ACS Catalysis* **2015**, *5* (2), 869–873.

Calle-Vallejo, F.; Loffreda, D.; Koper, M. T. M.; Sautet, P. Introducing Structural Sensitivity into Adsorption–energy Scaling Relations by Means of Coordination Numbers. *Nature Chemistry* **2015**, *7* (5), 403–410.

Chen, C.-H.; Jacobse, L.; McKelvey, K.; Lai, S. C. S.; Koper, M. T. M.; Unwin, P. R. Voltammetric Scanning Electrochemical Cell Microscopy: Dynamic Imaging of Hydrazine Electro-Oxidation on Platinum Electrodes. *Analytical Chemistry* **2015**, *87* (11), 5782–5789.

Chen, H.-C.; Hetterscheid, D. G. H.; Williams, R. M. R. M.; van der Vlugt, J. I.; Reek, J. N. H.; Brouwer, A. M. Platinum(II)-Porphyrin as a Sensitizer for Visible-Light Driven Water Oxidation in Neutral Phosphate Buffer. *Energy & Environmental Science* **2015**, *8* (3), 975–982.

Chen, T.; Li, H.; Ma, H.; Koper, M. T. M. Surface Modification of Pt(100) for Electrocatalytic Nitrate Reduction to Dinitrogen in Alkaline Solution. *Langmuir* **2015**, *31* (10), 3277–3281.

den Dunnen, A.; van der Niet, M. J. T. C.; Badan, C.; Koper, M. T. M.; Juurlink, L. B. F.; den, D. A.; van, der N. M. J. T. C.; Badan, C.; Koper, M. T. M.; Juurlink, L. B. F. Long-Range Influence of Steps on Water Adsorption on Clean and D-Covered Pt Surfaces. *Physical chemistry chemical physics : PCCP* **2015**, *17* (13), 8530–8537.

den Dunnen. A.; Wiegman, S.; Jacobse, L.; Juurlink, L. B. F.; Dunnen, A.; Wiegman, S.; Jacobse, L.; Juurlink, L. B. F.; den Dunnen, A.; Wiegman, S.; et al. Reaction Dynamics of Initial O2 Sticking on Pd(100). *Journal of Chemical Physics* **2015**, *142* (21), 214708/1-214708/7.

Diaz-Morales, O.; Ledezma-Yanez, I.; Koper, M. T. M.; Calle-Vallejo, F. Guidelines for the Rational Design of Ni-Based Double Hydroxide Electrocatalysts for the Oxygen Evolution Reaction. *Acs Catalysis* **2015**, *5*.

Farber, R. G.; Killelea, D. R.; Juurlink, L. B.; Kolb, M. J. Water Adsorption on Pt(111) and Stepped Pt Surfaces. In *Abstracts, Joint 41st Great Lakes and 46th Central Regional Meeting of the American Chemical Society, Grand Rapids, MI, United States, May 27-30*; American Chemical Society, 2015; p JGLCRM-248.

Fu, W. T.; IJdo, D. J. W. New Rhombohedral Pyrochlores Ca2Ln3Sb3O14 (Ln=lanthanide and Y): Space Group Revised. *Journal of Solid State Chemistry* **2015**, *229*, 330–335.

Hetterscheid, D. In Situ Characterization of Molecular Water Oxidation Catalysts. In *Abstracts of Papers, 250th ACS National Meeting & Exposition, Boston, MA, United States, August 16-20, 2015*; American Chemical Society, 2015; p INOR-374.

Jacobse, L.; den Dunnen, A.; Juurlink, L. B. F.; den, D. A.; Juurlink, L. B. F.; Dunnen, A.; Juurlink, L. B. F. The Molecular Dynamics of Adsorption and Dissociation of O2 on Pt(553). *Journal of Chemical Physics* **2015**, *143* (1), 14703.

Juurlink, L. B. F. F.; Koper, M. T. M. M.; Nieuwenhuys, B. E. Fifty Years of Heterogeneous Catalysis and Surface Science at Leiden University. *Catalysis Today* **2015**, *244*, 1–2.

Kas, R.; Kortlever, R.; Yılmaz, H.; Koper, M. T. M.; Mul, G. Manipulating the Hydrocarbon Selectivity of Copper Nanoparticles in CO_2 Electroreduction by Process Conditions. *ChemElectroChem* **2015**, *2* (3), 354–358.

Kortlever, R.; Balemans, C.; Kwon, Y.; Koper, M. T. M. Electrochemical CO2 Reduction to Formic Acid on a Pd-Based Formic Acid Oxidation Catalyst. *Catalysis Today* **2015**, *244*, 58–62.

Kortlever, R.; Peters, I.; Koper, S.; Koper, M. T. M. Electrochemical CO_2 Reduction to Formic Acid at Low Overpotential and with High Faradaic Efficiency on Carbon-Supported Bimetallic Pd–Pt Nanoparticles. *ACS Catalysis* **2015**, *5* (7), 3916–3923.

Kwon, Y.; Birdja, Y. Y.; Raoufmoghaddam, S.; Koper, M. T. M. Electrocatalytic Hydrogenation of 5-Hydroxymethylfurfural in Acidic Solution. *ChemSusChem* **2015**, *8* (10), 1745–1751.

Kwon, Y.; de Jong, E.; van der Waal, J. K.; Koper, M. T. M. Selective Electrocatalytic Oxidation of Sorbitol to Fructose and Sorbose. *ChemSusChem* **2015**, *8* (6), 970–973.

Matveev, A. V.; Kaichev, V. V.; Saraev, A. A.; Gorodetskii, V. V.; Knop-Gericke, A.; Bukhtiyarov, V. I.; Nieuwenhuys, B. E. Oxidation of Propylene over Pd(551): Temperature Hysteresis Induced by Carbon Deposition and Oxygen Adsorption. *Catalysis Today* **2015**, *244*, 29–35.

Monzó, J.; Malewski, Y.; Kortlever, R.; Vidal-Iglesias, F. J.; Solla-Gullón, J.; Koper, M. T. M.; Rodriguez, P. Enhanced Electrocatalytic Activity of Au@Cu Core@shell Nanoparticles towards CO_2 Reduction. *J. Mater. Chem. A* **2015**, *3* (47), 23690–23698.

Seitz, L. C.; Hersbach, T. J. P.; Nordlund, D.; Jaramillo, T. F. Enhancement Effect of Noble Metals on Manganese Oxide for the Oxygen Evolution Reaction. *The Journal of Physical Chemistry Letters* **2015**, *6* (20), 4178–4183.

Shen, J.; Birdja, Y. Y.; Koper, M. T. M. Electrocatalytic Nitrate Reduction by a Cobalt Protoporphyrin Immobilized on a Pyrolytic Graphite Electrode. *Langmuir* **2015**, *31* (30), 8495–8501.

Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y. Y.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I.; Schouten, K. J. P.; Mul, G.; Koper, M. T. M. Electrocatalytic Reduction of Carbon Dioxide to Carbon Monoxide and Methane at an Immobilized Cobalt Protoporphyrin. *Nature Communications* **2015**, *6*, 8177.

Tymoczko, J.; Calle-Vallejo, F.; Čolić, V.; Schuhmann, W.; Bandarenka, A. S. Evaluation of the Electrochemical Stability of Model Cu-Pt(111) Near-Surface Alloy Catalysts. *Electrochimica Acta* **2015**, *179*, 469–474.

Van Spronsen, M. A.; van Baarle, G. J. C.; Herbschleb, C. T.; Frenken, J. W. M.; Groot, I. M. N. High-Pressure
Operando STM Studies Giving Insight in CO Oxidation and NO Reduction over Pt(1 1 0). *Catalysis Today* **2015**, *244*, 85–95.

Computational Chemistry (UvA, HIMS)

Prof. dr. P.G. Bolhuis, Prof. dr. E.J. Meijer, Dr. B. Ensing,
Dr. D. Dubbeldam, Dr. J. Vreede

Balaji, S. P.; Ramdin, M.; Vlugt, T. J. H.; Gangarapu, S.; Zuilhof, H.; Torres-Knoop, A.; Dubbeldam, D.; Zuilhof, H.; Goetheer, E. L. V; Ramdin, M.; et al. Simulating the Reactions of CO2 in Aqueous Monoethanolamine Solution by Reaction Ensemble Monte Carlo Using the Continuous Fractional Component Method. *Journal of Chemical Theory and Computation* **2015**, *11* (6), 2661–2669.

Balestra, S. R. G.; Hamad, S.; Ruiz-Salvador, A. R.; Dominguez Garcia, V.; Merkling, P. J.; Dubbeldam, D.; Calero, S. Understanding Nanopore Window Distortions in the Reversible Molecular Valve Zeolite RHO. *Chemistry of Materials* **2015**, *27* (16), 5657–5667.

Bolhuis, P. G.; Dellago, C. Practical and Conceptual Path Sampling Issues. *European Physical Journal: Special Topics* **2015**, *224* (12), 2409–2427.

Brotzakis, P.; Kumar, A.; Bolhuis, P. G. Dynamics of Water at Protein Surfaces. In *Abstracts of Papers, 250th ACS National Meeting & Exposition, Boston, MA, United States, August 16-20, 2015*; American Chemical Society, 2015; p PHYS-332.

Bueno-Perez, R.; Gutierrez-Sevillano, J. J.; Merkling, P. J.; Calero, S.; Dubbeldam, D.; Merkling, P. J.; Calero, S. Separation of Amyl Alcohol Isomers in ZIF-77. *ChemPhysChem* **2015**, *16* (13), 2735–2738.

Bueno-Perez, R.; Martin-Calvo, A.; Gomez-Alvarez, P.; Gutierrez-Sevillano, J.-J.; Merkling, P.; Vlugt, T.; Van Erp, T. S.; Dubbeldam, D.; Calero, S. Enantioselective Adsorption in Zeolites and Metal-Organic Frameworks. In *Abstracts of Papers, 249th ACS National Meeting & Exposition, Denver, CO, United States, March 22-26, 2015*; American Chemical Society, 2015; p PHYS-52.

Burtch, N. C.; Dubbeldam, D.; Walton, K. S. Investigating Water and Framework Dynamics in Pillared MOFs. *Molecular Simulation* **2015**, *41* (16–17), 1379–1387.

Burtch, N. C.; Torres-Knoop, A.; Foo, G. S.; Leisen, J.; Sievers, C.; Ensing, B.; Dubbeldam, D.; Walton, K. S.; Torres-Knoop, A.; Ensing, B.; et al. Understanding DABCO Nanorotor Dynamics in Isostructural Metal-Organic Frameworks. *Journal of Physical Chemistry Letters* **2015**, *6* (5), 812–816.

De Wispelaere, K.; Ghysels, A.; Van, S. V.; De, W. K.; Ensing, B.; Meijer, E. J.; Ensing, B.; Ghysels, A.; Meijer, E. J.; et al. Complex Reaction Environments and Competing Reaction Mechanisms in Zeolite Catalysis: Insights from Advanced Molecular Dynamics. *Chemistry - A European Journal* **2015**, *21* (26), 9385–9396.

Du, W.; Bolhuis, P. G. Equilibrium Kinetic Network of the Villin Headpiece in Implicit Solvent. *Biophysical journal* **2015**, *108* (2), 368–378.

Evers, C. H. J.; Luiken, J. A.; Bolhuis, P. G.; Kegel, W. K. Programming Self-Assembly of Virus-like Shells via Colloidal Bond Hybridization. *arXiv.org, e-Print Archive, Condensed Matter* **2015**, 1–18.

Homsi Brandeburgo, W.; van der Post, S. T.; Meijer, E. J.; Ensing, B.; Homsi, B. W.; van, der P. S. T.; Meijer, E. J.; Ensing, B. On the Slowdown Mechanism of Water Dynamics around Small Amphiphiles. *Physical Chemistry Chemical Physics* **2015**, *17* (38), 24968–24977.

Luiken, J. A.; Bolhuis, P. G. Primary Nucleation Kinetics of Short Fibril-Forming Amyloidogenic Peptides. *Journal of Physical Chemistry B* **2015**, *119* (39), 12568–12579.

Luiken, J. A.; Bolhuis, P. G. Prediction of a Stable Associated Liquid of Short Amyloidogenic Peptides. *Physical Chemistry Chemical Physics* **2015**, *17* (16), 10556–10567.

Luna-Triguero, A.; Vicent-Luna, J. M.; Dubbeldam, D.; Gomez-Alvarez, P.; Calero, S. Understanding and Exploiting Window Effects for Adsorption and Separations of Hydrocarbons. *Journal of Physical Chemistry C* **2015**, *119* (33), 19236–19243.

Newton, A. C.; Groenewold, J.; Kegel, W. K.; Bolhuis, P. G. Rotational Diffusion Affects the Dynamical Self-Assembly Pathways of Patchy Particles. *Proceedings of the National Academy of Sciences of the United States of America* **2015**, *112* (50), 15308–15313.

Ni, R.; Kleijn, J. M.; Abeln, S.; Stuart, M. A. C.; Bolhuis, P. G. The Competition between Surface Adsorption and Folding of Fibril-Forming Polypeptides. *arXiv.org, e-Print Archive, Condensed Matter* **2015**, 1–6.

Ni, R.; Stuart, M. A. C.; Bolhuis, P. G. Tunable Long Range Forces Mediated by Self-Propelled Colloidal Hard Spheres. *Physical Review Letters* **2015**, *114* (1), 18302/1-18302/5, 5 .

Ramdin, M.; Balaji, S. P.; Torres-Knoop, A.; Dubbeldam, D.; Willem de Loos, T.; Vlugt, T. J. H. Solubility of Natural Gas Species in Ionic Liquids and Commercial Solvents: Experiments and Monte Carlo Simulations. *Journal of Chemical & Engineering Data* **2015**, *60* (10), 3039–3045.

Singhal, K.; Vreede, J.; Bolhuis, P. G.; Mashaghi, A.; Tans, S. J. The Trigger Factor Chaperone Encapsulates and Stabilizes Partial Folds of Substrate Proteins. *PLoS computational biology* **2015**, *11* (10), e1004444.

Torres-Knoop, A.; Balestra, S. R. G.; Krishna, R.; Calero, S.; Dubbeldam, D. Entropic Separations of Mixtures of Aromatics by Selective Face-to-Face Molecular Stacking in One-Dimensional Channels of Metal-Organic Frameworks and Zeolites. *ChemPhysChem* **2015**, *16* (3), 532–535.

Torres-Knoop, A.; Dubbeldam, D. Exploiting Large-Pore Metal-Organic Frameworks for Separations through Entropic Molecular Mechanisms. *ChemPhysChem* **2015**, *16* (10), 2046–2067.

Torres-Knoop, A.; Heinen, J.; Krishna, R.; Dubbeldam, D. Entropic Separation of Styrene/Ethylbenzene Mixtures by Exploitation of Subtle Differences in Molecular Configurations in Ordered Crystalline Nanoporous Adsorbents. *Langmuir : the ACS journal of surfaces and colloids* **2015**, *31* (12), 3771–3778.

Trinh, T. T.; Tran, K.-Q.; Zhang, X.-Q.; van Santen, R. A.; Meijer, E. J.; van, S. R. A.; Meijer, E. J. The Role of a Structure Directing Agent Tetramethylammonium Template in the Initial Steps of Silicate Oligomerization in Aqueous Solution. *Physical Chemistry Chemical Physics* **2015**, *17* (34), 21810–21818.

Van den Ende, J. A.; Smets, M. M. H.; de Jong, D. T.; Brugman, S. J. T.; Ensing, B.; Tinnemans, P. T.; Meekes, H.; Cuppen, H. M. Do Solid-to-Solid Polymorphic Transitions in DL-Norleucine Proceed through Nucleation?. *Faraday Discussions* **2015**, *179* (Nucleation--A Transition State to the Directed Assembly of Materials), 421–436.

Vijaykumar, A.; Bolhuis, P. G.; ten Wolde, P. R. Combining Molecular Dynamics with Mesoscopic Green's Function Reaction Dynamics Simulations. *Journal of Chemical Physics* **2015**, *143* (21), 214102/1-214102/12.

Zeiler, R. N. W.; Bolhuis, P. G. Exposure of Thiol Groups in the Heat-Induced Denaturation of β-Lactoglobulin. *Molecular Simulation* **2015**, *41* (10–12), 1006–1014.

Zhu, J.; Vreede, J.; Hospes, M.; Arents, J.; Kennis, J. T. M.; van Stokkum, I. H. M.; Hellingwerf, K. J.; Groot, M. L.; van, S. I. H. M.; Hellingwerf, K. J.; et al. Short Hydrogen Bonds and Negative Charge in Photoactive Yellow Protein Promote Fast Isomerization but Not High Quantum Yield. *Journal of Physical Chemistry B* **2015**, *119* (6), 2372–2383.

Theoretical Chemistry (VU, EMS)

Prof. dr. F.M. Bickelhaupt[1], Prof. dr. L. Visscher, Dr. C. Fonseca Guerra, Prof. dr. P. Gori Giorgi, Dr. O. Gritsenko

Bickelhaupt, F. M.; Sola, M.; Fernandez, I.; Solà, M.; Fernández, I. Understanding the Reactivity of Endohedral Metallofullerenes: C78 versus Sc3N@C78. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2015**, *21* (15), 5760–5768.

Crawford, T. D.; Kumar, A.; Hannon, K. P.; Hofener, S.; Visscher, L. Frozen-Density Embedding Potentials and Chiroptical Properties. *Journal of Chemical Theory and Computation* **2015**, *11* (11), 5305–5315.

Dairaku, T.; Furuita, K.; Sato, H.; Šebera, J.; Yamanaka, D.; Otaki, H.; Kikkawa, S.; Kondo, Y.; Katahira, R.; Matthias Bickelhaupt, F.; et al. Direct Detection of the Mercury-Nitrogen Bond in the Thymine-Hg(II)-Thymine Base-Pair with (199)Hg NMR Spectroscopy. *Chemical communications (Cambridge, England)* **2015**, *51* (40), 8488–8491.

Dairaku, T.; Furuita, K.; Sato, H.; Sebera, J.; Yamanaka, D.; Otaki, H.; Kikkawa, S.; Kondo, Y.; Katahira, R.; Matthias Bickelhaupt, F.; et al. Direct Detection of the Mercury-Nitrogen Bond in the Thymine-HgII-Thymidine Base-Pair with 199Hg NMR Spectroscopy. *Chemical Communications (Cambridge, United Kingdom)* **2015**, *51* (40), 8488–8491.

Devarajan, D.; Gustafson, S. J.; Bickelhaupt, F. M.; Ess, D. H. Is There a Need to Discuss Atomic Orbital Overlap When Teaching Hydrogen-Halide Bond Strength and Acidity Trends in Organic Chemistry?. *Journal of Chemical Education* **2015**, *92* (2), 286–290.

Dumont, E.; Drsata, T.; Guerra, C. F.; Lankas, F. Insights into the Structure of Intrastrand Cross-Link DNA Lesion-Containing Oligonucleotides: G[8-5m]T and G[8-5]C from Molecular Dynamics Simulations. *Biochemistry* **2015**, *54* (5), 1259–1267.

Gavara, R.; Aguilo, E.; Fonseca Guerra, C.; Rodriguez, L.; Lima, J. C.; Fonseca, G. C.; Lima, J. C. Thermodynamic Aspects of Aurophilic Hydrogelators. *Inorganic Chemistry* **2015**, *54* (11), 5195–5203.

Goesten, M. G.; Fonseca Guerra, C.; Kapteijn, F.; Gascon, J.; Bickelhaupt, F. M. Six-Coordinate Group 13 Complexes: The Role of D Orbitals and Electron-Rich Multi-Center Bonding. *Angewandte Chemie, International Edition* **2015**, *54* (41), 12034–12038.

Guillaumes, L.; Simon, S.; Fonseca Guerra, C. The Role of Aromaticity, Hybridization, Electrostatics, and Covalency in Resonance-Assisted Hydrogen Bonds of Adenine-Thymine (AT) Base Pairs and Their Mimics. *ChemistryOpen* **2015**, *4* (3), 198.

Hering, F.; Nitsch, J.; Paul, U.; Steffen, A.; Bickelhaupt, F. M.; Radius, U.; Herrmann, W. A.; Jahnke, M. C.; Hahn, F. E.; Diez-Gonzalez, S.; et al. Bite-Angle Bending as a Key for Understanding Group-10 Metal Reactivity of D ^{10} -[M(NHC) $_2$] Complexes with Sterically Modest NHC Ligands. *Chem. Sci.* **2015**, *6* (2), 1426–1432.

Kazaryan, A.; Baerends, E. J. Ligand Field Effects and the High Spin-High Reactivity Correlation in the H Abstraction by Non-Heme Iron(IV)-Oxo Complexes: A DFT Frontier Orbital Perspective. *ACS Catalysis* **2015**, *5* (3), 1475–1488.

Kazaryan, A.; van Santen, R.; Baerends, E. J.; van, S. R.; Baerends, E. J. Light-Induced Water Splitting by Titanium-Tetrahydroxide: A Computational Study. *Physical chemistry chemical physics : PCCP* **2015**, *17* (31), 20308–20321.

Kiawi, D. M.; Bakker, J. M.; Oomens, J.; Buma, W. J.; Jamshidi, Z.; Visscher, L.; Waters, L. B. F. M. Water Adsorption on Free Cobalt Cluster Cations. *The journal of physical chemistry. A* **2015**, *119* (44), 10828–10837.

Muck, F. M.; Baus, J. A.; Nutz, M.; Burschka, C.; Tacke, R.; Poater, J.; Bickelhaupt, F. M.; Bickelhaupt, F. M. Reactivity of the Donor-Stabilized Silylenes [iPrNC(Ph)NiPr]2 Si and [iPrNC(NiPr2)NiPr]2 Si: Activation of CO2 and CS2. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2015**, *21* (46), 16665–16672.

Muck, F. M.; Kloss, D.; Baus, J. A.; Burschka, C.; Bertermann, R.; Tacke, R.; Poater, J.; Fonseca, G. C.; Bickelhaupt, F. M.; Bickelhaupt, F. M. Stable Four-Coordinate Guanidinatosilicon(IV) Complexes with SiN3El Skeletons (El = S, Se, Te) and Si=El Double Bonds. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2015**, *21* (40), 14011–14021.

Mueck, F. M.; Baus, J. A.; Nutz, M.; Burschka, C.; Poater, J.; Bickelhaupt, F. M.; Tacke, R. Reactivity of the Donor-Stabilized Silylenes [iPrNC(Ph)NiPr]2Si and [iPrNC(NiPr2)NiPr]2Si: Activation of CO2 and CS2. *Chemistry - A European Journal* **2015**, *21* (46), 16665–16672.

Mueck, F. M.; Kloss, D.; Baus, J. A.; Burschka, C.; Bertermann, R.; Poater, J.; Fonseca Guerra, C.; Bickelhaupt, F. M.; Tacke, R. Stable Four-Coordinate Guanidinatosilicon(IV) Complexes with SiN3El Skeletons (El=S, Se, Te) and Si[n.63742]El Double Bonds. *Chemistry - A European Journal* **2015**, *21* (40), 14011–14021.

Roos, G.; Fonseca Guerra, C. C.; Bickelhaupt, F. M. How the Disulfide Conformation Determines the Disulfide/thiol Redox Potential. *Journal of Biomolecular Structure and Dynamics* **2015**, *33* (1), 93–103.

Ruger, R.; van, L. E.; Lu, Y.; Ruger, R.; Visscher, L.; Frenzel, J.; Heine, T.; Rueger, R.; van Lenthe, E.; Lu, Y.; et al. Efficient Calculation of Electronic Absorption Spectra by Means of Intensity-Selected Time-Dependent Density Functional Tight Binding. *Journal of chemical theory and computation* **2015**, *11* (1), 157–167.

Schluns, D.; Klahr, K.; Muck-Lichtenfeld, C.; Visscher, L.; Neugebauer, J.; Schluens, D.; Klahr, K.; Mueck-Lichtenfeld, C.; Visscher, L.; Neugebauer, J.; et al. Subsystem-DFT Potential-Energy Curves for Weakly Interacting Systems. *Physical chemistry chemical physics : PCCP* **2015**, *17* (22), 14323–14341.

Sinha, I.; Fonseca Guerra, C.; Müller, J. A Highly Stabilizing silver(I)-Mediated Base Pair in Parallel-Stranded DNA. *Angewandte Chemie (International ed. in English)* **2015**, *54* (12), 3603–3606.

Sosa Carrizo, E. D.; Bickelhaupt, F. M.; Fernandez, I. Factors Controlling β-Elimination Reactions in Group 10 Metal Complexes. *Chemistry - A European Journal* **2015**, *21* (41), 14362–14369.

Sosa, C. E. D.; Fernandez, I.; Sosa, C. E. D.; Bickelhaupt, F. M.; Bickelhaupt, F. M. Factors Controlling β-Elimination Reactions in Group 10 Metal Complexes. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2015**, *21* (41), 14362–14369.

Stasyuk, O. A.; Szatylowicz, H.; Fonseca Guerra, C.; Krygowski, T. M. Theoretical Study of Electron-Attracting Ability of the Nitro Group: Classical and Reverse Substituent Effects. *Structural Chemistry* **2015**, *26* (4), 905–913.

Talbot, A.; Devarajan, D.; Gustafson, S. J.; Fernandez, I.; Bickelhaupt, F. M.; Ess, D. H. Activation-Strain Analysis Reveals Unexpected Origin of Fast Reactivity in Heteroaromatic Azadiene Inverse-Electron-Demand Diels-Alder Cycloadditions. *Journal of Organic Chemistry* **2015**, *80* (1), 548–558.

Teodoro, T. Q.; Haiduke, R. L. A.; Dammalapati, U.; Knoop, S.; Visscher, L. The Ground-State Potential Energy Curve of the Radium Dimer from Relativistic Coupled Cluster Calculations. *Journal of Chemical Physics* **2015**, *143* (8), 084307/1-084307/7.

Teodoro, T. Q.; Haiduke, R. L. A.; Visscher, L. Nuclear Electric Quadrupole Moment of Potassium from the Molecular Method. *Physical Review A: Atomic, Molecular, and Optical Physics* **2015**, *91* (3–A), 032516/1-032516/4.

van Weerdenburg, B. J. A.; Engwerda, A. H. J.; Eshuis, N.; Longo, A.; Banerjee, D.; Tessari, M.; Guerra, C. F.; Rutjes, F. P. J. T.; Bickelhaupt, F. M.; Feiters, M. C.; et al. Computational (DFT) and Experimental (EXAFS) Study of the Interaction of [Ir(IMes)(H)2(L)3] with Substrates and Co-Substrates Relevant for SABRE in Dilute Systems. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2015**, *21* (29), 10482–10489.

Vellé, A.; Cebollada, A.; Ruiz, S.; Fonseca Guerra, C.; Sanz Miguel, P. J. Crystallographic and Computational Study on Cationic Triply Hydrogen-Bonded Nucleobases without Direct Anionic Stabilization. *Crystal Growth & Design* **2015**, *15* (12), 5873–5878.

Wang, J.; Baerends, E. J. Real-Space Representation of Electron Correlation in π-Conjugated Systems. *The Journal of chemical physics* **2015**, *142* (20), 204311/1-204311/12.

Wolters, L. P.; Bickelhaupt, F. M. The Activation Strain Model and Molecular Orbital Theory. *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2015**, *5* (4), 324–343.

Wolters, L. P.; Bickelhaupt, F. M. Selective C-H and C-C Bond Activation: Electronic Regimes as a Tool for Designing d10 MLn Catalysts. *Chemistry - An Asian Journal* **2015**, *10* (10), 2272–2282.

Wolters, L. P.; Koekkoek, R.; Bickelhaupt, F. M. Role of Steric Attraction and Bite-Angle Flexibility in Metal-Mediated C-H Bond Activation. *ACS Catalysis* **2015**, *5* (10), 5766–5775.

Wolters, L. P.; Smits, N. W. G.; Guerra, C. F. Covalency in Resonance-Assisted Halogen Bonds Demonstrated with Cooperativity in N-Halo-Guanine Quartets. *Physical chemistry chemical physics : PCCP* **2015**, *17* (3), 1585–1592.

Theoretical Chemistry (UL, LIC)

Dr. J. Meyer

Bukas, V. J.; Mitra, S.; Meyer, J.; Reuter, K. Fingerprints of Energy Dissipation for Exothermic Surface Chemical Reactions: O2 on Pd(100). *The Journal of Chemical Physics* **2015**, *143* (3), 34705.

Rittmeyer, S. P.; Meyer, J.; Inaki, J. J.; Reuter, K. Electronic Friction-Based Vibrational Lifetimes of Molecular Adsorbates: Beyond the Independent-Atom Approximation. *Physical Review Letters* **2015**, *115* (4), 046102/1-046102/5.

4.5 Annex 5 – The HRSMC Education Programme

The management of the school administers the credit points obtained by the PhD students and presents HRSMC certificates to those students who have fulfilled their education programme with a minimum of 15 ECTS.

ECTS system	1 ECTS = 28 h
Literature research, Paper (see remarks for explanation) and Colloquium (see remarks for explanation)	6, all three together
HRSMC school	2-3
HRSMC course	2-3
External course of + 1 week	1-3, the validation of the responsible organization will be used.
Course on didactics	1-2
Presenting a poster at an (inter)national conference	1
Giving a lecture at an (inter)national conference	2
2x attendance of a guest lecture and a scientific discussion	10 attendances=1 EC
Research in another laboratory (preferring outside Holland)	max. 6
Minimum	**15**

Remarks:

- Every PhD needs to follow at least one HRSMC course and one HRSMC school for the HRSMC certificate. If there is no HRSMC school or course available supporting the aspects of the PhD research, an external course can be chosen instead (but for 95% of the PhD student this is not necessary). The other items are optional: for the certificate it is not 'a must' to do a course on didactics or a research in another laboratory, but when this is done a maximum of 6 ECTS can be given for this activity.
- The Han-sur-Lesse Winter school 'Theoretical Chemistry & Spectroscopy' is not organized by the HRSMC, but many HRSMC staff members are involved. Therefore, this course is considered as a HRSMC school for the HRSMC certificate.
- A colloquium is a presentation, which a PhD gives at the beginning (normally after 3-6 months). A PhD researcher presents his/her research plans and gives a general background of the project. This colloquium can be based on the paper.
- A paper should not be confused with a scientific article. A paper is a document, which a PhD researcher normally makes at the beginning of his/her research. This paper includes items like:
  - The general background of the research project
  - The plans a PhD researcher has for the first years of his/her research project
- When the following Courses and Schools were followed with a validation of 3 EC according to the old rating (instead of 2 according to the new validation):
  - HRSMC Course: Physical Methods in Inorganic Chemistry (2011, 2013)
  - HRSMC Summer School on Photochemistry (2012)
  - HRSMC Tulip School 'Modern Developments in Spectroscopy' (2012)
  - HRSMC Summer School Synthetic Bio-organic Chemistry (2013)
  - HRSMC Autumn School Advanced Metal-Organic Chemistry (2012)

For each of these Courses with a validation of 3 EC instead of 2, one extra EC should be done for the total ECs for the certificate.
E.g. if you have followed the 2012 Tulip School for 3 EC, you should have 16 ECs in total.

15 points is a minimum and can, of course, be exceeded.