KNCV Computational and Theoretical Chemistry (CTC) Spring Symposium

Nijmegen

2023

Program

10:00	**Welcome**	
10:10	Ioana Ilie (UvA) *Effects of biological therapeutics on the dynamics of the cellular prion protein*	Chair: Trevor Hamlin (VU)
10:30	Andrea Giuntoli (Groningen) *Energy Renormalization: dynamics-focused coarse-graining across the glass transition*	
	Posters	
12:00	Paul Geerlings (Vrije Universiteit Brussel) *Introducing External Electric and Magnetic Fields , Mechanical Forces and Pressure in Conceptual Density Functional Theory*	Chair: Jörg Meyer (Leiden)
12:30	Klaas Giesbertz (VU)	
12:50	Vesna Erić (RUG) *Spectral Signatures Unravel Energy Transfer Pathways in Supramolecular Aggregates*	
	Lunch and posters	
13:45	General Assembly / ALV	
14:20	Marc de Wergifosse (UCLouvain) *Simplified quantum chemistry methods for large systems*	Chair: Thanja Lamberts (Leiden)
14:40	Francesca Grisoni (TU/e) *Chemical language models for de novo drug design*	
15:00	Menno Bokdam (Twente) *Looking inside 'dynamic solids' using on-the-fly machine learning force fields*	
	Tea	
15:50	Katharina Doblhoff-Dier (Leiden) *Getting electrochemical barriers right: What we can learn from band alignments, dielectric constants and capacitance measurements*	Chair: David Picconi (Groningen)
16:10	Lucas de Azevedo Santos (VU) *Intermolecular Covalent Interactions*	
16:25	Closing	
	Drinks	

Effects of biological therapeutics on the dynamics of the cellular prion protein

Ioana Ilie

Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands
i.m.ilie@uva.nl

Prion diseases are associated with the conversion of the cellular prion protein (PrPC) into a pathogenic conformer. A proposed therapeutic approach to avoid the pathogenic transformation is to develop monoclonal antibodies that bind to PrPC and stabilize its structure. Here, I investigate the influence of POM1 and POM6, two monoclonal antibodies, on the flexibility and the interaction with the membrane of PrPC by molecular dynamics simulations. Results show that antibody binding limits the range of orientations of the GD with respect to the membrane and decreases the distance between PrPC and membrane. Furthermore, the GD flexibility (Ilie & Caflisch 2022) and the interactions of the flexible tail and the GD are modulated differently by the two antibodies (Ilie et al. 2022). Additionally, I introduce a novel computationally-based approach towards the design of peptides that could modulate the activity of the cellular prion protein.

Energy Renormalization: dynamics-focused coarse-graining across the glass transition

Andrea Giuntoli

Zernike Institute, Groningen, The Netherlands
a.giuntoli@rug.nl

Coarse-grained models of molecular and polymeric systems are useful to overcome the spatiotemporal limitations of all-atom simulations. However, they are typically calibrated to capture the underlying atomistic structure and present accelerated dynamics. This is a critical issue in the modeling of glass-forming systems, where the thermomechanical properties stem from the dynamics of relaxation phenomena. The Energy Renormalization scheme builds temperature-dependent parametrizations of coarse-grained force fields to capture the relaxation dynamics of glass-formers across the glass transition temperature. It is based on the universal Generalized Entropy Theory for glass-formers and the connections between picosecond dynamics and segmental relaxation times. I will present the development of this modeling technique from the early theoretical efforts to the recent streamlined workflow, which allows to quickly generate chemically accurate, dynamically consistent coarse-grained models for glass-forming melts. I will finally show recent developments of these ideas applied to a crosslinked epoxy resin, extending the scheme from thermoplastics to thermosets with the inclusion of a generalizable Machine Learning parametrization strategy.

Chemical language models for de novo drug design

Francesca Grisoni

Eindhoven University of Technology, Institute for Complex Molecular Systems, Dept. Biomedical Engineering, Eindhoven, Netherlands
f.grisoni@tue.nl

Artificial intelligence (AI) is fueling computer-aided molecule discovery. Chemical language models (CLMs) constitute a recent addition to the chemist's toolkit for AI-driven drug design. CLMs can be used to generate novel molecular structures in the form of strings without relying on human-engineered assembly rules. By taking inspiration from natural language processing, CLMs have shown able to learn "syntax" rules for molecule generation, and to implicitly capture "semantic" molecular features, such as physicochemical properties, bioactivity, and chemical synthesizability. This talk will illustrate some successful applications of CLMs to design novel bioactive compounds from scratch in the context of drug (and molecule) discovery, at the interface between theory and wet-lab experiments.

Introducing External Electric and Magnetic Fields , Mechanical Forces and Pressure in Conceptual Density Functional Theory

Paul Geerlings

Research Group of General Chemistry (ALGC), Vrije Universiteit Brussel, (VUB), Pleinlaan 2, 1050, Brussels, Belgium
pgeerlin@vub.ac.be

A brief introduction is given on the passage from Density Functional Theory (DFT) to Conceptual DFT (CDFT)[1,2,3] and the basics of CDFT highlighting among others the fundamental role of the $E=E[N,v]$ functional and the response functions $(\partial m\delta m'E/\partial Nm\ \delta v(r1)\ldots.\delta v(rm'))(n=m+m')$ when interpreting/predicting chemical reactivity. The extension of the functional is discussed with external electric (ε), [4] and magnetic (B) fields[5,6], mechanical forces (F) [7,8] and pressure (p) [9], coping with recent trends in experimental chemistry using electric fields as effective effectors of chemical change, mechanochemistry and high-pressure chemistry. New response functions are introduced, their evaluation for atoms, diatomics and in some cases small polyatomics being performed in a finite field approach. Particular attention will be devoted to periodicity as leitmotiv, to symmetry breaking (ε), segmented property curves and polarity inversion (B), reactivity/potential energy surface intricacies (F), electronic volume, autoionization and bonding characteristics (p).[10]

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Simplified quantum chemistry methods for large systems

Marc de Wergifosse

Theoretical Chemistry Group Molecular Chemistry, Materials and Catalysis Division (MOST), Institute of Condensed Matter and Nanosciences, Louvain-la-Neuve, Belgique
marc.dewergifosse@uclouvain.be

The high computational costs and steep scaling limit the scope of ab initio electronic structure calculations. Excited-state calculations are currently limited to systems up to a few hundred of atoms. By providing better balance between cost and accuracy, simplified quantum chemistry (sQC)[1] methods extend the predictive power of quantum chemistry (QC) to large systems. Among some recent applications, we were able to provide a new all-atom quantum chemistry methodology to compute the second-harmonic generation (SHG) and two-photon absorption (2PA) of fluorescent proteins[2,3] and fluorescent organic nanoparticles4. In this talk, I will shortly review recent method developments[1] that I did within the simplified time-dependent density functional theory (sTD-DFT), I will also introduce the eXact integral sTD-DFT (XsTD-DFT) method, and outline future challenges for sQC methods.

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Looking inside ‘dynamic solids’ using on-the-fly machine learning force fields

Menno Bokdam

University of Twente
m.bokdam@utwente.nl

Ab intio based Molecular Dynamics (MD) is known for its high accuracy, but also for its unfeasible demand for computational power when going beyond one thousand atoms and picosecond time scales. In recent years, several important approaches have been developed that have enabled a very successful application of machine learning in this field. These advances are so substantial that it could mean "the end of ab initio MD"*. I will introduce our implementation of on-the-fly learning in a commonly used Density Functional Theory software package, and focus on the potential that the method has for research in condensed matter physics. Examples from the (in)organic halide perovskites where we have simulated observables that would have been impossible using conventional methods will be presented. The common denominator of a much larger class of ‘dynamic solids’ is their anharmonic lattice dynamics and wide variety of rare-events. Large thermodynamic ensembles must be simulated with MD to obtain, for example: phase transition temperatures and melting points, phonon bandstructures, X-ray spectra and thermal conductivity. We observe a qualitative and quantitative agreement between experiment and theory on several temperature depended NMR experimental observables. This leads us to suspect that the simulated trajectories of crystal structure provide a realistic insight into the ionic dynamics of these perovskites.

* G. Csányi, Quote from keynote, Psi-K conference ‘22

Getting electrochemical barriers right: What we can learn from band alignments, dielectric constants and capacitance measurements

Katharina Doblhoff-Dier

Leiden Institue of Chemsitry, Leiden University, Leiden, The Netherlands
k.doblhoff-dier@lic.leidenuniv.nl

Reaction barriers are at the core of every reaction as they define the reaction kinetics. Correctly predicting reaction barriers is therefore relevant if we want to predict reaction rates and determine the dominant reaction pathways. However, if computing accurate reaction barriers is already a challenge in heterogeneous catalysis, the problems only get worse when looking at electrochemical reactions. In the latter case, we have to deal not only with the inaccuracy of typical DFT calculations, but also with the influence of the electrolytic environment and the (surface-near) profile of the potential field. In this talk, I will discuss our recent effort to get a better grip on these factors of influence. My talk will thus touch on the accuracy of DFT and what we can learn about possible improvements to our exchange-correlation functionals by comparing RPA and G0W0 calculations to DFT, as well as on studies of the electrochemical double layer, which are key to determine surface-near potential profiles. My story will bring us past band alignments and whether they are right or wrong, past dielectric constants and whether old wisdom holds true, and past century old theories of the double layer capacity and why a new century may bring a new theory.

HOAX: A Hyperparameter Optimization Algorithm Explorer for Neural Networks

Albert Thie, Maximilian F.S.J. Menger, Shirin Faraji

Zernike Institute for Advanced Materials, Faculty of Science and Engineering, University of Groningen
a.s.thie@rug.nl

Computational chemistry has become an important tool to predict and understand molecular properties and reactions. Even though recent years have seen a significant growth in new algorithms and computational methods that speed up quantum chemical calculations, the bottleneck for trajectory-based methods to study photo-induced processes is still the huge number of electronic structure calculations. In this work, we present an innovative solution, in which the amount of electronic structure calculations is drastically reduced, by employing machine learning algorithms and methods borrowed from the realm of artificial intelligence. However, applying these algorithms effectively requires finding optimal hyperparameters, which remains a challenge itself. Here we present an automated user-friendly framework, HOAX, to perform the hyperparameter optimization for neural networks, which bypasses the need for a lengthy manual process. The neural network generated potential energy surfaces (PESs) reduces the computational costs compared to the ab initio-based PESs. We perform a comparative investigation on the performance of different hyperparameter optimiziation algorithms, namely grid search, simulated annealing, genetic algorithm, and bayesian optimizer in finding the optimal hyperparameters necessary for constructing the well-performing neural network in order to fit the PESs of small organic molecules. Our results show that this automated toolkit not only facilitate a straightforward way to perform the hyperparameter optimization but also the resulting neural networks-based generated PESs are in reasonable agreement with the ab initio-based PESs.

Exploring the Interaction Between CN radicals and Interstellar Ices

Joan Enrique-Romero (1), Thanja Lamberts (1,2)

1. Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, Leiden, The Netherlands
2. Leiden Observatory, Leiden University, Leiden, The Netherlands
j.enrique.romero@lic.leidenuniv.nl

The formation of HCN and HNC in the interstellar medium may occur on the surfaces of interstellar icy dust particles through the hydrogenation of CN radicals [e.g., Lefloch et al. 2021]. These molecules are essential for astronomers to understand the properties of the regions they study. They are also significant for astrochemists and astrobiologists, as they may play a crucial role in the formation of more complex C- and N-bearing species [e.g., Woon 2002; Theulé et al. 2011; Lee and Choe 2017; Mendoza et al. 2018]. However, the CN radical is known to form hemibonded complexes with water, adding complexity to its surface chemical evolution [Rimola et al. 2018].

Our ongoing computational chemistry study explores the interaction between CN radicals and the two most abundant types of interstellar ice: water and carbon monoxide. We use benchmarking calculations and investigate whether multireference effects are important to treat adsorption phenomena accurately. Additionally, we examine the CN radical's ability to form hemibonded complexes with water and CO, which directly affects the binding energy distributions of CN radicals on each ice type and has far-reaching implications for their chemical evolution.

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Excitonic energy transfer dynamics in photosystem II complexes

Hoang Long Nguyen, Thanh Nhut Do, Kai Zhong, Thomas L. C. Jansen, Jasper Knoester, Howe Siang Tan
Nanyang Technological University & University of Groningen
long.nguyen@rug.nl

The process of excitonic energy transfer (EET) is utilized in photosynthetic protein complexes to facilitate light harvesting. Light energy is transported among the complexes and eventually arrives at the reaction center. Using structure-based calculation, the possible EET pathways can be obtained and used to support the experimental observations.

Frozen carbon chains on interstellar ices – cyanoacetylene hydrogenation in dense molecular clouds

Marten Raaphorst, Thanja Lamberts

Leiden Institute of Chemistry, Leiden University
m.t.raaphorst@lic.leidenuniv.nl

Cyanopolyynes are a class of molecules consisting of a highly unsaturated carbon chain and a nitrile group with the general molecular formula HCnN (n=3, 5, 7, 9, …). These molecules have been observed in most astronomical environments, ranging from Saturn's moon Titan to the Taurus molecular cloud. Their high carbon content may link cyanopolyynes to the formation of more complex organic compounds, such as fatty acids and possibly polycyclic aromatic hydrocarbons. Cyanopolyynes are efficiently formed in the gas phase, but in molecular clouds and prestellar cores they are expected to freeze out on dust grains that are covered with H2O or CO ice. The subsequent surface chemistry, e.g., the adsorption and reaction pathways, have so far not been quantitatively studied. As a first step towards investigating this chemistry, we study the hydrogenation of the smallest cyanopolyyne: cyanoacetylene (HC3N). We report the reaction energies and activation barriers of the five possible product channels of the reaction H + HC3N. Additionally, we present a benchmark of the energies obtained with various exchange-correlation functionals and compared the results to CCSD(T) calculations. Next steps include the investigation of subsequent hydrogenation reactions and the inclusion of surface (ice) molecules.

Spectral Signatures Unravel Energy Transfer Pathways in Supramolecular Aggregates

Vesna Erić, Thomas la Cour Jansen

University of Groningen, Zernike Institute for Advanced Materials, Groningen, The Netherlands
v.eric@rug.nl

Chlorosomes from green sulfur bacteria are supramolecular aggregates acclaimed for the most efficient light capture and energy transfer among natural light-harvesting antennas. To unravel the molecular mechanism responsible for this efficiency, we provide a microscopic description of the energy landscape and its dependence on slow and fast nuclear degrees of freedom, focusing on the role of hydrogen bonding. Our results reveal the importance of the interplay of exciton delocalization over hundreds of molecules and molecular fluctuations for establishing the robustness of the energy transfer process on the sub-picosecond time scale. Additionally, simulations of polarization-resolved two-dimensional electronic spectra correlate the changes in the arrangements of chromophores within chlorosomes with energy transfer pathways manifesting distinct anisotropy decays. We expect that understanding molecular mechanisms ensuring the efficiency of natural light-harvesting complexes may inspire novel designs for application in molecular optoelectronics.

Intermolecular Covalent Interactions

Lucas de Azevedo Santos, Trevor A. Hamlin, F. Matthias Bickelhaupt

Department of Theoretical Chemistry, Amsterdam Institute for Molecular and Life Sciences, Amsterdam Center for Multiscale Modeling, Vrije Universiteit Amsterdam, Amsterdam, The Netherlands
l.deazevedosantos@vu.nl

Pnictogen (PnB), chalcogen (ChB), halogen (XB), and hydrogen (HB) bonds are intermolecular interactions of the type DmZ•••A, where Z = Pn, Ch, X, H.[1,2,3] These intermolecular interactions play a crucial role in chemical reactivity, supramolecular materials, and drug design.[4] Typically, the σ-hole model is invoked to rationalize the unexpected attraction between two partially negatively charged atoms and the geometry of these intermolecular interactions.[5] This model posits that the DmZ•••A complexes are bound and linear due to a Coulombic attraction between a positive electrostatic potential on the molecular surface of the bond donor (DmZ) and the negative, point charge-like bond acceptor (A). We show how this treatment of atoms and molecules is oversimplified and unphysical.[6] Not the Coulombic interactions, but the steric Pauli repulsion is the driving force preventing the bending of the bond acceptor away from D–Z•••A linearity. In fact, the Coulombic interactions favor (not oppose) bending. The cohesion in these interactions furthermore receives a major contribution from HOMO–LUMO orbital interactions. Therefore, we suggest abandoning the term non-covalent interactions for such bonds and instead using the designation intermolecular covalent interactions (ICI).

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An efficient time-domain implementation of the multichromophoric Förster resonant energy transfer method

Kai Zhong, Hoang Long Nguyen, Thanh Nhut Do, Howe-Siang Tan, and Jasper Knoester, Thomas L. C. Jansen

University of Groningen
k.zhong@rug.nl

We present a new time-domain method for calculating energy transfer based on the combination of Multichromophoric Förster Resonance Energy Transfer theory and the Numerical Integration of the Schrödinger Equation method. The method was first tested on model systems, demonstrating agreement with the reference data. We further applied the new method to the Light-Harvesting 2 (LH2) complex, which is a harvesting structure found in purple bacteria. LH2 consists of two concentric rings of bacteriochlorophyll molecules. The so-called B850 ring contains twice as many chromophores as the B800 ring. We use the overdamped Brownian oscillator to describe the dynamic disorder originating from environmental fluctuations and the TrESP coupling model to determine the interactions between chromophores. We calculated the spectra and the transfer rate between the two rings and compared them with experimental results, finding good agreement with the experiment. Our results demonstrate that our new method accurately describes the energy transfer rate for biologically relevant multichromophoric systems. At the same time, we find the method to be more efficient computationally - especially for slow processes. We foresee that the method can be applied to efficiently calculate multi-dimensional spectra of extensive multichromophoric systems in the future.

Modelling ultrafast charge-transfer in organic photovoltaic materials from first-principles: the role of quantum vibrations, environment disorder and light pulse shape

Elisa Palacino-Gonzalez and Thomas la Cour Jansen

Zernike Institute for Advanced Materials, University of Groningen, 9747AG, Nijenborgh 4, Groningen, The Netherlands
E-mail e.palacino.gonzalez@rug.nl

We introduce a first-principles modeling [1] of the ultrafast charge separation dynamics and spectroscopy at the donor-acceptor heterojunction of the P3HT:PCBM organic photovoltaic (OPV) blend. Our approach combines Molecular Dynamics (MD) simulations to describe the blend environment [2] with TDDFT calculations to construct a Merrifield-type Hamiltonian after photoexcitation. The timeresolved spectroscopic observables are then evaluated using the response function-based NISE [3] package (Numerical Integration of the Schrodinger Equation) and compared with available experimental measurements to further validate the model and understand the underlying dynamics. The predicted spectra nicely reproduce the available experimental data [4]. The origin of the line broadening is analyzed in terms of the conformational disorder. This reveals for instance the importance of the torsional different regions of the donor P3HT polymer chains, allowing an identification of the homogeneous and inhomogeneous spectral broadening. Subsequently, the light-induced dynamics of the charge separation in the photovoltaic blend are simulated quantum mechanically with an explicit treatment of the photoexcitation pulses and vibronic effects from specific intramolecular modes. Dissipation rates are computed from the spectral densities derived from the MD trajectory, which allows a realistic description interaction of the bath blend environment with the system. Last, we study the effect of frequency-chirped pulses [5] on the ultrafast charge-transfer dynamics on a reduced dimensionality model derived from our first-principles simulations. The analysis of the electronic wavepackets describing the photoinduced dynamics reveals that chirped-pulses can be used to manipulate the observables associated to the charge-transfer. Our study delivers a complete firstprinciples picture of the electronic and vibrational coherence dynamics characterizing ultrafast charge transfer in prototypical OPVs, emphasizing the role of the vibrational modes controlling the process and the explicit effect of different excitation conditions in the laser fields, suggesting a potential strategy for driving the charge-transfer process towards higher efficiencies.

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How to become the chosen one: Deterministic tweezer loading of ultracold molecules

Etienne F. Walraven, Michael R. Tarbutt, Tijs Karman

Institute for Molecules and Materials, Radboud University, Nijmegen
etienne.walraven@ru.nl

Molecules at microkelvin temperatures may become versatile building blocks for, among other things, quantum simulation and quantum computing. These quantum devices can be built using an array of optical tweezers, where each tweezer must contain a single molecule. The question then arises how to go from having a gas of cold molecules to deterministically loading single molecules into these tweezers. With this poster we show how to perform efficient loading of such a setup by investigation of molecular collisions in this ultracold regime using quantum scattering calculations.

Why are the methine bridge substituents in cyanine dyes not innocent?

Natália P. Neme, Thomas la Cour Jansen and Remco W.A. Havenith

University of Groningen
n.paz.neme@rug.nl

In this study, we investigate the photophysical properties of a cyanine dye analogue by performing first-principles calculations based on Density Functional Theory (DFT) and Time Dependent-DFT. These cationic systems are subject of numerous theoretical and experimental investigations due to their versatile applications in science, technology, medicine and engineering [1]. This diversity is due to the different ways to tune the photophysical properties of this group of dyes, such as by modifying their end groups and chain's length [2]. The vinylene shift is experimentally known for these molecules, and it consists of a bathochromic (red) shift of approximately 100 nm of the 0-0 vibronic transition when a vinyl group is added to the polymethine chain. Our study revealed that the saturated moiety of the cyclopentane ring added to the chain interacts with the conjugated pi-system of the cyanine, leading to a smaller HOMO-LUMO gap. Besides being reported experimentally as responsible for the stability and rigidity of the molecule [3], the chain's ring affects also its photophysical properties. We demonstrate the origin of this interaction and how it can be used to fine tune the absorption energy of this class of dyes.

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Molecular Dynamic Simulation of the Human and Bacterial subclass of decarboxylase Enzymes, in the premises of Parkinson's Disease

Panagiotis Kelefiotis Stratidakis, Kiana Gholamjani Moghaddam, Sahar El Aidy and Shirin Faraji

Zernike Institute for Advanced Materials, University of Groningen, Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen
p.kelefiotis.stratidakis@rug.nl

Humans have a subclass of aromatic amino acid decarboxylase enzymes, dopa decarboxylases, which convert levodopa to dopamine. Since levodopa is the main treatment of Parkinson's disease, inhibitors are co-administered with levodopa to avoid its breakdown by dopa decarboxylase before it reaches the site of action. Bacteria, that can be found in the gut, has an equivalent enzyme, tyrosine decarboxylase, which converts tyrosine to tyramine and recently was shown to also convert levodopa to dopamine and, in turn, to interfere with Parkinson's Disease treatment. This results in loss of function of the medication because the most commonly used human dopa decarboxylase inhibitors show little to no efficacy towards the bacterial tyrosine decarboxylase. Nonetheless, it remains obscure the discrepancy in the binding site of the inhibitors on the human versus the bacterial dopa/tyrosine decarboxylases. To this end, Molecular Dynamics (MD) simulations are currently applied on the crystal structures available for both the human and bacterial enzymes. Structural and functional differences are studied and compared among the different enzymes.

Hydrodeoxygenation reaction over Mo2C catalyst: mechanism and descriptor identification

Raghavendra Meena [1,2], Harry Bitter [1], Han Zuilhof [2], Guanna Li [1,2]

[1] Biobased Chemistry and Technology, Wageningen University, The Netherlands
[2] Laboratory of Organic Chemistry, Wageningen University, The Netherlands
raghavendra.meena@wur.nl

With rapidly increasing applications of catalysis, the design and discovery of cheap and-efficient catalysts are crucial. One of the most important applications of catalysis is in biomass valorisation. Platinum group metals (PGMs) are well known for catalysing biobased feedstock to obtain value-added chemicals. However, PGMs are scarce, expensive, and susceptible to poisoning by impurities present in the bulk. Therefore, viable alternatives like transition metal carbides (TMCs) have been studied. In this work, we studied a unique reaction pathway for hydrodeoxygenation (HDO) of butyric acid over molybdenum carbide, β-Mo2C (101) surface, which is crucial in biomass conversion. From the DFT study, coupled with microkinetic modelling (MKM), we obtained the rate-determining step (RDS), butanol dissociation: $C_4H_9OH^* + {}^* \rightarrow C_4H_9^* + OH^*$, in the HDO mechanism. The RDS is then further studied upon heteroatom doping of the relevant metal (M) site to enhance the activity of β-Mo2C. The electronic structure and geometrical features were studied upon doping, and linear-scaling relationships were obtained. Later, it was established that M (d-band filling) and M(radius) play a key role in governing the activity of the β-Mo2C (101) catalytic surface. These fundamental understandings are expected to provide practical strategies for the rational design of tailor-made TMCs with improved catalytic performances.

Not Antiaromaticity Gain, but Increased Asynchronicity Enhances the Diels-Alder Reactivity of Tropone

Eveline H. Tiekink, Pascal Vermeeren and Trevor A. Hamlin

Vrije Universiteit
e.h.tiekink2@vu.nl

Tropone is an unreactive diene in normal electron demand Diels- Alder reactions, but it can be activated via carbonyl umpolung by using hydrazone ion analogs. Recently, the higher reactivity of hydrazone ion analogs was ascribed to a raised HOMO energy induced by antiaromaticity. This dearomatizing HOMO-raising rationale is frequently used to explain observations in the laboratory. We, however, show that the correlation between a raised HOMO energy and a higher reactivity is not causal. Instead, the real physical mechanism behind the lowering of the activation barrier is the amplified asynchronicity of the reaction mode, resulting in (i) less deformation of the reactants, and (ii) a relief in destabilizing Pauli repulsion between the deformed reactants.

Revisiting Rotational Isomerism of Organic Compounds

Daniela Rodrigues Silva, Lucas de Azevedo Santos, Trevor A. Hamlin, Célia Fonseca Guerra, F. Matthias Bickelhaupt

Department of Theoretical Chemistry, Amsterdam Institute of Molecular and Life Sciences (AIMMS),
Amsterdam Center for Multiscale Modeling (ACMM), Vrije Universiteit Amsterdam
d.rodriguessilva@vu.nl

A firm grasp of the driving forces behind conformational isomerism is crucial for the rational design of molecules with tailor-made properties. Therefore, we have reinvestigated the rotation around the C–C bond in organic compounds within the framework of Kohn-Sham molecular orbital theory. We discuss how geometrical relaxations that occur in response to the internal rotation can hide the original causal factors and need to be taken into account to properly elucidate the physical mechanism at play.[1] Our bonding analyses then reveal that overall rotational energy profiles are always set by steric repulsion between occupied–occupied orbitals. However, the conformational preferences can be shifted if one of the two requirements are met: i) if the relative steric repulsion is too weak and thus easily counteracted by subtle attractive interactions (e.g., hyperconjugation[2,3]), or ii) if stronger intramolecular interactions take place (e.g., hydrogen bonding[4]). Our analyses lead to a novel, fundamentally revisited picture of the physical mechanisms behind well-known conformational effects in organic chemistry.

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Computational design of spiropyran-merocyanine nonlinear optical photoswitches: from isolated molecules to model aggregates

Marilù Grace Maraldi, Angela Dellai, Frédéric Castet

Université Catholique Louvain
Université de Bordeaux
marilu.maraldi@uclouvain.be

For optoelectronic and photonic devices, designing photoresponsive materials that enable remote reversible switching of their electrical or optical properties is a significant challenge. Extensive research has been done on organic photochromic compounds for a variety of applications, including logic gates and optical memories. The majority of these optical devices, however, rely on linear optical properties of the systems both for writing/erasing and reading the information onto the material, which may result in a destructive reading process because the photochromes' state is switched upon light exposure. To solve this problem, it is possible to use second harmonic generation (SHG) as non-destructive readout technique, which exploits the nonlinear (NLO) response of molecules to an optical stimulus. Moreover, functionalization of self-assembled monolayers (SAMs) constitutes the most effective strategy for introducing NLO chromophores into a solid-state device in view of maximizing its macroscopic second-order optical susceptibility. In this context, this work provides a computational workflow for the design of new photonic devices based on 2D-NLO molecular materials. The procedure intends to fill the gap between the in-solution photoswitches and the final material while providing design insights by examining the relationships between the chemistry of each individual photoswitch and its optical properties. The linear and nonlinear optical properties of monosubstituted spiropyran (SP)-merocyanine (MC) systems are characterized using Density Functional Theory. Representative compounds are first investigated in solution; then the effect of aggregation is questioned by investigating interacting dimers, which allows to evaluate, at the quantum mechanical (QM) level, the effect of aggregation in small model systems as well as the optimal intermolecular distance to maximize the first hyperpolarizability. Finally, the problem of simulating larger supramolecular aggregates, more representative of SAMs, using an all-atom QM computation is tackled.

Multiscale modelling of C8S3 dimerization

M.K. Espinoza Cangahuala, T.L.C. Jansen

Zernike Institute for Advanced Materials, Rijksuniversiteit Groningen
m.k.espinoza.cangahuala@rug.nl

The amphiphilic cyanine dye-based chromophore, C8S3, is a promising material that self-assembles in water into double-walled nanotubes with high quantum efficiency and energy transport properties. Yet exactly how this self-assembly process occurs remains shrouded in mystery.

Here, we employ a multiscale approach [1] to determine the absorption and two-dimensional electronic spectra to unravel the first self-assembly step: dimerization. This approach combines molecular dynamics simulations with quantum chemistry calculations to obtain an exciton Hamiltonian that is then used in spectral calculations. We compare results obtained in different solvents and validate our model with experimental data. Our results reveal the spectroscopic signatures of molecular clustering at the initial stage of the self-assembly process: dimerization.

The current approach paves the way for future investigations of the mechanism of self-assembly processes in similar light-harvesting complexes and guides the design of optoelectronic devices.

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Photochemistry, photophysics and spectroscopy using quantum wave packets and ab initio potential energy surfaces

David Picconi

Zernike Institute for Advanced Materials, University of Groningen
d.picconi@rug.nl

Computational protocols are presented to construct realistic molecular Hamiltonian models for photophysical and photochemical processes, starting from electronic structure calculations of energies, forces and force constants. The processes are then simulated quantum mechanically using the hybrid Gaussian/multi-configurational time-dependent Hartree ansatz [1], whereby the motion of a small set of degrees of freedom is treated using flexible single particle functions, and the dynamics of the remaining ”bath” modes are approximated by Gaussian wave packets.

The focus of the simulations is on the prediction and interpretation of spectroscopic observables obtained by ultrafast pump-probe experiments. Two examples will be presented.

The first one is the excited state intramolecular proton transfer of 10-hydroxybenzo[h]quinoline (HBQ) [2]. It is shown that for long excitation wavelengths the reaction proceeds on the single Born-Oppenheimer surface of a ππ* state, in contrast to the interpretation of the most recent experiments, where a nonadiabatic mechanism was proposed. This mechanism is obtained only for an initial excitation to a higher ππ* state, and the proton transfer is mediated by the internal conversion to a dark nπ* state. The long lived quantum beats observed in the transient absorption spectrum of HBQ are reproduced quantitatively by the simulation and assigned to specific vibrational modes.

The second example is the photoinduced charge separation in a symmetric donor–acceptor–donor triad (DAD) [3]. The non-radiative transitions from a locally excited DA*D state to the charge-transfer states D+A−D and DA−D+ are described by a quadratic vibronic coupling model, accounting for the polar solvation dynamics, and including the effect of the temperature using thermo field theory. It is found that temperature strongly affects the rate of the charge separation, that is mediated by low frequency modes, and the intramolecular mechanism of symmetry-breaking charge transfer. The molecular quantum dynamics are connected to theoretical pump-probe spectra, computed on top of the wave packet simulation, which reproduce nicely the spectroscopic bands and the quantum beats of the experimental ones.

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Towards Detection of The Molecular Parity Violation in Helical Ferrocene, Ruthenocene, and Osmocene

Eduardus, Lukáš Félix Pašteka, Shirin Faraji, and Anastasia Borschevsky

University of Groningen
e.eduardus@rug.nl

Naturally, most molecules are observed to have an absolute predominance of one form, called biohomochirality. This phenomenon can be caused by a tiny difference in energy between the two enantiomers which is called parity violating energy difference. Astonishingly, although this symmetry-breaking effect in molecules has a firm theoretical basis, it has never been observed experimentally. Scientists working at the Laboratoire de physique des lasers (LPL) in Paris are trying to measure the energy differences in vibrational spectra using the state-of-the-art laser within the mid-IR range and 100 mHz detection limit. In this work, helical ferrocene, ruthenocene, and osmocene were studied theoretically, with the aim of predicting the size of expected measurable parity violating effect. This work was carried out in 3 main steps;. First, geometry optimization using Q-Chem to get the most stable structures and spin states. Second, relativistic single point energy calculation using DIRAC16 to get vibrational and parity violating energy curve. Last, the parity violating frequency shift was calculated using Numerov-Cooley procedure. The result shows that ruthenocene and osmocene have promising structural stability in the gas phase. The most promising result from this work is the symmetrical ring breathing vibration of helical osmocene predicted to have a 3 Hz frequency shift on symmetrical breathing vibrational motion, which is 30 times larger than the experimental target. Furthermore, extending the analysis to the frequency range of 800 cm-1 to 1.300 cm-1, it is clear that types of vibration is indeed most sensitive to parity violation effects compared to the amount of the connected C atom displacement. However, the reason behind this sensitivity still left to be an open question.

Dielectric constant at metal/water interfaces

Jia-Xin Zhu[1], Marc T.M. Koper[2], Jun Cheng[1],*, Katharina Doblhoff-Dier[2],*

1 State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen
2 Leiden Institue of Chemsitry, Leiden University, Leiden, The Netherlands
*Email: chengjun@xmu.edu.cn, k.doblhoff-dier@lic.leidenuniv.nl

The energetics and kinetics of electrochemical reactions are influenced by the potential and the electric field distribution at the interfacial region. This distribution is directly influenced by the dielectric constant. Unfortunately, relatively little is known about how the dielectric constant changes as we approach the interfaces. In this project, we study the behaviours of two contributions to the dielectric constant, i.e., the electronic dielectric constant and the orientational dielectric constant.

The distribution of the orientational dielectric constant at the interface is obtained from the local dipole fluctuations in molecular dynamics simulations1-2. Aiming at sufficient sampling while retaining ab initio accuracy, these were performed with a newly trained machine-learnt potential (MLP) for Pt/water interfaces. The distribution of the electronic dielectric constant is calculated from DFT calculations under applied potential3, which were performed for a few snapshots extracted from the MLP sampling.

We found that, the electronic dielectric constant is about twice as high on the surface as in bulk, while the orientational dielectric constant is quantitatively similar to that in the force-field-based simulations.

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Floating in Space: How to Treat the Weak Interaction Energy of Interstellar CO Ices

Brian C. Ferrari[1], Germán Molpeceres[2], Jörg Meyer[1], Johannes Kästner[3], Yuri Aikawa[2], Marc C. van Hemert[1], Thanja Lamberts[1,4]

1Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands
2Department of Astronomy, Graduate School of Science, The University of Tokyo, Tokyo, Japan
3Institute for Theoretical Chemistry, University of Stuttgart, 70569 Stuttgart, Germany
4Leiden Observatory, Leiden University, Leiden, The Netherlands

A plethora of molecules have been detected in the interstellar medium, some of which are expected to form through surface reactions on interstellar ices. It is generally thought that interstellar ices are layered, with an amorphous polar water-rich layer and then an amorphous CO-rich layer. However, recent studies have suggested that the CO-rich layer should be crystalline and possibly even segregated as a single crystal atop the water-rich layer. If so, there are far-reaching consequences for the formation of complex organic molecules, such as sugars that use CO as a backbone. To supplement these studies we calculate the binding energies of CO on crystalline α-CO, along with a more atomistic and in depth study of the binding energy of CO on amorphous CO ices. Furthermore, we benchmark the performance of various DFT methods when treating surface processes on CO ices. We find that CO has a large distribution of binding energies (100 - 1200 K with ZPE corrections) on amorphous CO, including a significant amount of weak transient. This is a first step towards understanding the possible crystallization of amorphous CO into α-CO. Lastly, we find that CO binding energies are dominated by dispersion (~ 90%), as such, functionals need dispersion corrections to accurately treat it. In particular, we find the ωB97V-M functional to be a strong candidate for simulation surface processes on CO ices.