Annual Report

[C^4]

Competence Center for Computational Chemistry

July 2009 to July 2010

Impressum

Eidgenössische Technische Hochschule Zürich
Switzerland

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Peter Limacher, ETH Zürich

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C^4 on the Internet:
http://www.c4.ethz.ch

Cover:
Sereina Riniker, winner of the 2009 IBM Research Forschungspreis

Monosubstituted benzene derivatives have two possible binding modes in alpha-cyclodextrin cavities with different binding free energies. The conformation with the substituent residing inside the cavity is generally more stable and stabilization increases for partially charged substituents.

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The Year in Review

The Competence Center for Computational Chemistry (C^4) is a network of computational chemists of the IBM Zürich Research Laboratory, the University of Zürich, and the ETH Zürich. The goal of C^4 is to seek new frontiers and opportunities in molecular modeling and simulation, to cater to the flow of know-how within this community, and to serve as a platform for the interaction with partners from other areas of science or from outside academia. C^4 was launched twenty years ago as a scientific collaboration between the IBM Research Laboratory and ETH Zürich, and has grown considerably since. Today, the C^4 network covers a much broader spectrum of research activities, and its output in terms of scientific results and achievements is still on the increase. With this Annual Report, C^4 reports on its activities between July 2009 and July 2010. We also encourage you to visit our website, *www.c4.ethz.ch*

Change in the Steering Committee

Prof. Alessandro Curioni, head of computational sciences at IBM Zürich Research, joined the C^4 Steering Committee consisting of Profs. Jürg Hutter (University of Zürich), Wilfred F. van Gunsteren, and PD Dr. Hans P. Lüthi (both ETH Zürich).

Alessandro Curioni replaces Prof. Wanda Andreoni, who was appointed director of the Centre Européen de Calcul Atomique et Moléculaire (CECAM), which is based at the EPF Lausanne. Wanda Andreoni was a member of the C^4 Steering Committee since 1993, and made numerous contributions to this network, the most recent one being the introduction of the IBM Research Forschungspreis.

C^4 Seminar

The actual "backbone" of C^4 is its Seminar Program. During the 2009 Fall- and 2010 Spring-Term the C^4 Seminar Program covered 14 lectures, again some of them presented by leaders in the field of computational chemistry. The seminar, which takes place every second Thursday during the semester, enjoys a remarkable popularity bringing together thirty to fifty students and researchers each time. This year, C^4 has extended its collaboration with other seminar programs. For the first time, a C^4 seminar was hosted by the IBM Research Laboratory, and again, two seminars were held jointly with the University of Zürich Physical Chemistry Seminar. The complete seminar program is listed in this report.

Compute Resource

The C^4 compute-cluster Obélix, a 32 node IBM Opteron cluster operated by the ETH Informatikdienste, procured for code development and for the execution of resource-intense computations, again delivered nearly one million CPU hours worth of compute-cycles.

Since 2009, C^4 is also a shareholder of the Brutus cluster, giving the computational chemists of the ETH Department of Chemistry and Applied Biosciences (D-CHAB) guaranteed access to this resource. Many of the members of the C^4 community are also users of the resources of the Centro Svizzero die Calcolo Scientifico (CSCS), *i.e.* were awarded computing time based on proposals they had submitted. These three resources respond to a specific demand, and the results and achievements reported in this report commonly involve "machine cycles" drawn from more than just one of these resources.

C^4 Tutorials

With CECAM being established in Switzerland, the offering for tutorials and workshops has increased considerably, both, in number and in the spectrum of topics covered. CECAM also has a Zurich node lead by our colleague Prof. Matthias Troyer of the Institute of Theoretical Physics. C^4, over the past year, did not offer its own tutorials. However, in order to respond to the specific demand of the local community, C^4 again plans to offer at least one tutorial per semester.

The IBM Research Award

In 2007, the ETH Schulleitung approved the "IBM Research Forschungspreis", an award for outstanding MS and PhD theses sponsored by our partner, the IBM Zürich Research Laboratory. This year, the prize was awarded to Sereina Riniker (Group of W.F. van Gunsteren). For more detail please refer to the corresponding section in this report.

The 2010, the IBM Research Forschungspreis Award Ceremony is to take place for the first time at the ETH Tag! The Rector of ETH Zürich, Prof. Heidi Wunderli-Allenspach, will present the award to the winner. The C^4 Steering Committee is very pleased that future laureates will be honored together with the other winners of major industry and foundation awards.

Outlook

The Zürich computational chemistry community is still growing. Furthermore, the borderlines between disciplines become less and less sharp, also a result of the flow of expertise between the established areas. It is fair to say that C^4 made an important contribution to both of these developments.

In return, it becomes increasingly difficult to present the entire scope of computational chemistry research activities in this report. This Annual Report, which also serves as the "yellow pages" of "computational chemistry made in Zürich", may therefore soon change its appearance. Also in the next year we will make sure that C^4 is a valuable platform for the Zürich computational chemistry community.

Hans P. Lüthi, Leiter C^4
October 27, 2010

2
Areas of Research

This is the 17th Annual Report of the Competence Center for Computational Chemistry [C^4]. It covers the research performed during the period 2009/2010 by the C^4 Community. Only a relatively small fraction of the computations reported in this document were performed on C^4 compute resources; its capacity would be much to small to generate the scientific output listed here. The main idea behind this document is to have a compilation of the research in computational chemistry "made in Zürich", and to offer a listing of competencies and skills available.

Computational Activities at C^4

The C^4 community

Research Group	*Institute*
Prof. K. Baldridge	Organic Chemistry UNI ZH
Prof. P. Chen	Organic Chemistry ETH
Prof. A. Curioni	IBM Zürich Research Laboratory
Prof. W. F. van Gunsteren	Physical Chemistry ETH
Dr. A. Gusev*	Polymers ETH
Dr. P. Hünenberger	Physical Chemistry ETH
Prof. J. Hutter	Physical Chemistry UNI ZH
PD Dr. H.P. Lüthi	Physical Chemistry ETH
Prof. R. Nesper*	Inorganic Chemistry ETH
Prof. M. Parrinello	Physical Chemistry ETH

Research Group	*Institute*
Prof. M. Quack	Physical Chemistry ETH
Prof. M. Reiher	Physical Chemistry ETH
Prof. G. Schneider**	Pharmaceutical Sciences ETH
Prof. F. Schoenebeck**	Organic Chemistry ETH
Prof. M. Troyer	Theoretical Physics ETH
Prof. V. Vogel	Biologically Oriented Materials ETH
Prof. P. Werner**	Theoretical Physics ETH

*) No contributions for this year's report
**) Newly appointed

There are contributions from different participating institutions. The ETH Zürich is represented by the Departments of Chemistry, Physics and Materials Science. Further, there are the Institute of Physical Chemistry and the Institute of Organic Chemistry at the University of Zürich as well as the IBM Zürich Research Laboratory.

This year a total of 103 research projects are being presented in this report. These are contributed from 13 research groups and cover a broad spectrum of research topics and methodologies applied.

Peter Limacher
November 10, 2010

3
C^4 Activities in 2009/2010

C^4 Seminar

The 2009 fall term and 2010 spring term the C^4 Seminar Program covered 14 regular lectures, some of them presented by leaders in the field of computational chemistry and physics. Furthermore there were four extracurricular seminars presented by Profs. H.F. Schaefer III (Georgia), K. Ruedenberg (Iowa), J. Schlitter (Bochum) and J. Pitera (IBM Almaden Research Center). The seminar again enjoyed a remarkable popularity bringing together thirty to fifty (or more) students and researchers each time. One C^4 seminar per term was hosted by the University of Zürich and one seminar took place at the IBM Research Laboratory.

C^4 Tutorials

During the past year, there were no tutorials offered by C^4. Instead there was the opportunity to participate in the CECAM Workshops and Tutorials. A considerable number of workshops and tutorials were held at ETH Zürich since the move of CECAM headquarters to the EPF Lausanne in mid 2008. See also *www.cecam.org*.

C^4 Workshop

The topic of this year's workshop was "High Performance Computing @ C^4" with presentations on parallel computing, Graphical Processing Units and grid computing. All presentations were delivered by students and coworkers of the C^4 community.

COMPETENCE CENTER FOR COMPUTATIONAL CHEMISTRY C4
ETH Zürich / University of Zürich / IBM Research

Seminar Programm Herbstsemester 2009

Auditorium HCI J7, ETH Hönggerberg
13:00-14:00

24. 09. 2009
Ilja Siepmann, University of Minnesota (Minneapolis, MN, USA)
Structure, Solvation, Phase Equilibria and Nucleation in Hydrogen-bonding Systems

08. 10. 2009
Markus Meuwly, Universität Basel, (Basel, Schweiz)
Atomistic Simulations of Chemical and Biological Systems:
Dynamics, Vibrations and Relaxation from Proteins to Doped Ices

22. 10. 2009
Andreas Dreuw, Johann Wolfgang Goethe-Universität Frankfurt,
(Frankfurt, Deutschland)
Excited Electronic States of Large Molecules: a Challenge to Quantum Chemistry

05. 11. 2009
Christel Marian, Heinrich Heine-Universität Düsseldorf, (Düsseldorf, Deutschland)
Singlet-Triplet Coupling in Organic Chromophores

19. 11. 2009
C4 WORKSHOP
High Performance Computing at C4

03. 12. 2009 (at University of Zürich Irchel Campus)
Wolfgang Domcke, TU München, (München, Deutschland)
Photostability of the Building Blocks of Life

17. 12. 2009
Christian Ochsenfeld, Universität Tübingen (Tübingen, Deutschland)
Intermolecular Interactions in Large Molecular Systems:
A Challenge for Quantum Chemistry

COMPETENCE CENTER FOR COMPUTATIONAL CHEMISTRY C4
ETH Zürich / University of Zürich / IBM Research

Seminar Programm Frühjahrssemester 2010

Auditorium HCI J7, ETH Hönggerberg
13:00-14:00

04. 03. 2010
Alessandro Curioni, IBM Research (Zürich, Schweiz)
Multiscale Simulations of (100) Silicon Nanowires

18. 03. 2010
Antonio Rizzo, CNR Pisa (Pisa, Italy)
Linear and Nonlinear Absorption Spectra: Vibrational and Conformational Effects

29. 03. 2010 (at IBM Research Laboratory in Rüschlikon)
Maurizio Persico, University of Pisa (Pisa, Italy)
Extending Time and Size Limits in Simulations of Excited State Dynamics

08. 04. 2010
Celia Schiffer, University of Massachusetts Medical School (Worcester, MA, USA)
Combating Drug Resistance: Lessons from HIV Protease

15. 04. 2010
Giuseppe Milano, University of Salerno (Salerno, Italy)
Soft Matter Simulations: Atoms, Beads, Fields

29. 04. 2010
Daniel Crawford, Virginia Tech (Blacksburg, VA, USA)
On One Hand, But Not the Other:
Ab Initio Computations of the Properties of Chiral Molecules

06. 05. 2010
Per Siegbahn, Stockholm University (Stockholm, Sweden)
Quantum Chemical Studies of Water Oxidation in Photosystem II

20. 05. 2010 (Jointly with University of Zürich Physical Chemistry Seminar)
Maria Andrea Mroginski, Technische Universität Berlin (Berlin, Deutschland)
MM Calculations of Raman Spectra of the Chromophore Site
of Biological Photoreceptors

COMPETENCE CENTER FOR COMPUTATIONAL CHEMISTRY C4
ETH Zürich / University of Zürich / IBM Zürich Research

C4 WORKSHOP 2009
Thursday, November 19, 2009
Auditorium HCI J6, ETH Hönggerberg

HIGH PERFORMANCE COMPUTING @ C4

PROGRAM

13:00 – 13:15 **Hans P. Lüthi** (Leiter C4)
Welcome, C4 Annual Report 2008/2009
Announcement of the winner of the 2009 IBM Research Forschungspreis

13:15 – 13:45 **Olivier Byrde** (Leiter High Performance Computing, ID ETH Zürich)
Brutus, Quo Vadis ?

13:45 – 14:15 **Manuel Guidon** (Gruppe Prof. J. Hutter)
Robust, Massively Parallel Periodic Hartree-Fock Exchange for Large Scale Simulations using Gaussian Basis Sets

14:15 – 14:45 COFFEE BREAK

14:45 – 15:15 **Nathan Schmid** (Gruppe Prof. W.F. van Gunsteren)
GPU Solvent-Solvent Interaction Calculation Accelerator for Biomolecular Simulations using the GROMOS Software

15:15 -15:45 **Sergio Maffioletti** (Gruppe Prof. K. Baldridge)
Grid Computing @ UZH: Providing Seamless Access to a Heterogeneous Distributed Computing Infrastructure for Enabling e-Science

15:45 Closure

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IBM Research Forschungspreis

At the end of the 2007 Summer Term, the ETH Schulleitung approved the “IBM Research Forschungspreis”, an award for outstanding MS and PhD theses sponsored by our partner, the IBM Zurich Research Laboratory. The first winners of the award were Sandra Luber (Group of Prof. M. Reiher) with her MS thesis entitled “Towards the Calculation of Raman Optical Activity Spectra of Large Molecules” and Daan Geerke (Group of Prof. W.F. van Gunsteren) for his PhD thesis entitled “Classical Hamiltonians in Molecular Simulation: Force-Field Development and Explicit Inclusion of Electronic Polarization and Quantum Effects”.

In 2009, the prize in the amount of CHF 2’000 was awarded to Sereina Riniker (Group of Prof. W.F. van Gunsteren) for her MS thesis entitled “Free Energies of Binding of Benzene Derivatives to Alpha-Cyclodextrin: Sensitivity of the Free-Energy Components to Temperature and to the Restraining of Molecular Motion”.

In its Laudatio, the Award Jury, consisting of Profs. Alessandro Curioni, U.W. Suter, J. Hutter and PD Dr. H.P. Lüthi, states:

In her MS thesis, Sereina Riniker probes a simulation framework for the computation of the free energy of binding between host-substrate complexes in solution, using alpha-cyclodextrin (host) and an array of substituted phenols (substrate) as a model system.

Her presentation of the computational strategies, the underlying theory, the analysis of the data, and the conclusions drawn is truly outstanding. This is despite the fact that she had to cope, as it turned out in the course of the four-months project, with a suboptimal choice of substrates. Still, with her studies, she laid the groundwork for a simulation protocols which is being used to probe the entropic contribution to the free energy of binding between ligands and (structurally flexible) DNA fragments.

The Call for Nominations for the 2010 IBM Research Forschungspreis was issued at the end of the Spring Term. It is for PhD theses submitted during the past two years.

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Operation of the C^4 Compute Resources

Overview over the C^4 computing facilities

- IBM Cluster e1350, Type 1410/42X, running RedHat Linux.This cluster consists of 32 e326m clients, each with two dual core AMD Opteron CPUs with either 8 or 16 GB, one e326m login node and a x346 Storage Node DS4100 with about 1.3 TB of cluster-wide disk space
- Ten Sun Fire X4440 with 4 Quad-Core AMD Opteron Processors 8380, 128 GB ECC RAM, and a local scratch space of 2.7 TB per node. The local scratch space is built of attached SAS storage. Five StorageTek 2530 arrays with 12 x 900 GB disks each provide the local scratch space for two attached Sun Fires. There is some additional storage for mid-term data storage.

IBM Cluster e1350 "Obélix"

The cluster is in the fifth year of operation and is now reaching the end of its life cycle. It may soon be decommissioned. Obélix was extremely reliable: some of its nodes had rendered uninterrupted service since July 2006, *i.e.* for about 1'500 days (!)

C^4 Shareholder of "Brutus"

The ETH Department of Chemistry and Applied Biosciences, through C^4, and Profs. Reiher and van Gunsteren, are shareholders of the central ETH-Cluster Brutus. This part of the cluster consists of 480 CPU cores. Ten dedicated computers are installed in Brutus for the exclusive use of these two shareholders to meet the special requirements. All nodes are fully integrated into the Brutus cluster's infrastructure and therefore benefit of the central management, the available work- and lustre- file systems, the high-speed Infiniband interconnect, the software repository of the already installed and maintained packages, the LSF batch system and the support of the CSCS-Cluster Team.

Eric Müller, CSCS, October 2010

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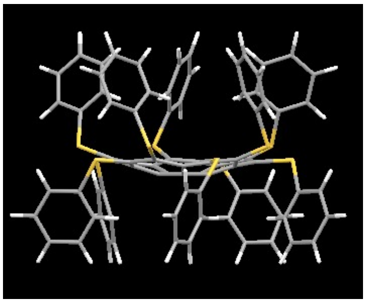
Research Projects

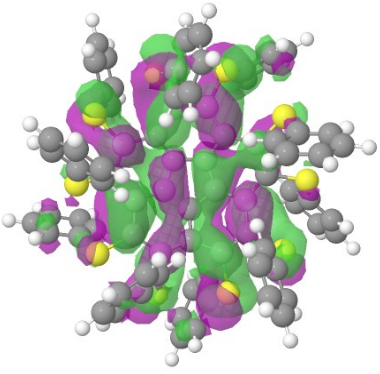
Title: Synthesis, Structure and Properties of Decakis(phenylthio)corannulene

Researchers: Baldridge, K.K.
Hardcastle, K. I.
Seiders, T.J.
Siegel, J.S.

Institute/Group: University of Zürich, OCI, Switzerland
University of California, San Diego, USA

Description:





Bringing several components of functionalized corannulene derivatives together resulted in the experimental and theoretical study of decaphenylthiocorannulene. As previously shown, decasubstitution reduces the depth of the bowl through steric effects around the rim, and tunes the electronic properties of the pi system according to the nature of the substituents. Computational analysis predicts greater distortion of the rim bonds and less compression of the hub compared to corannulene. A D_5 transition state structure revealed a barrier to bowl inversion of 7.38 kcal/mol (C_1 0.0, C_5 2.54, D_5 7.38 kcal/mol). Frontier MO analysis accounts for the longer wavelength absorption spectrum and lower reduction potential of this molecule compared to corannulene. The analysis correlates to lower energy transitions and lower lying radical anion states. The relatively smaller HOMO/LUMO gap is evidenced by the deep red color of the sulfur compound compared to the pale yellow color of corannulene, deca-chloro-corannulene, and deca-methyl-corannulene.

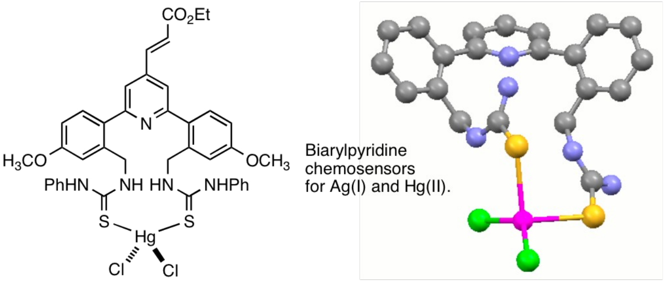
Reference: Baldridge*, K.K. Hardcastle, K.I.; Seiders, T.J.; Siegel*, J.S. Synthesis, Structure and Properties of Decakis(phenylthio)corannulene, *Org. and Biomol. Chem* **2010**, *8*, 53-55.

Title: Efficient Discovery of Fluorescent Chemosensors Based on a Biarylpyridine Scaffold.

Researchers:
Malashikhin, S.A.
Baldridge, K.K.
Finney, N.S.

Institute/Group: University of Zürich, OCI, Switzerland

Description:



Biarylpyridine chemosensors for Ag(I) and Hg(II).

A series of C-shaped, 1,1′-alkyl-bridged 4,4′-diaryl-2,2′-bibenzimidazoles was investigated computationally and also synthesized. Packing diagrams demonstrate that these molecules either form linear intercalated molecular chains or include solvent molecules in the solid state. Crystal structures are compared to computational structures determined using new generation density functional theory. The C-shaped or tweezer-like geometry enables them to act as building blocks for supramolecular architectures.

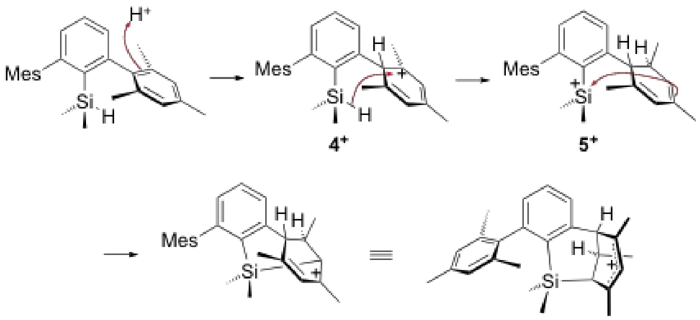
Reference: Malashikhin, S.A.; Baldridge, K.K.; Finney, N.S. Efficient Discovery of Fluorescent Chemosensors Based on a Biarylpyridine Scaffold. *Org. Lett.,* **2010**, *12*, 940.

Title: New class of silicon cation species with novel reactivity.

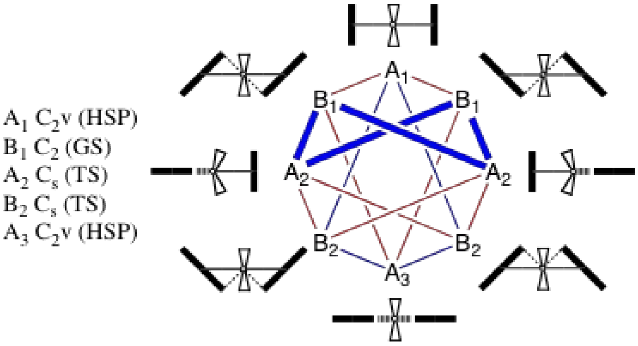
Researchers:
Duttwyler, S.
Linden, A.
Baldridge, K. K.*
Siegel, J.S.*

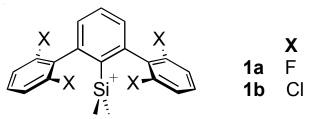
Institute/Group: University of Zürich, OCI, Switzerland

Description:



Related to our earlier findings of a new class of pacified sily cations, a silyl-stabilized allyl cation was investigated, formed by disruption of an arene via a protonation-hydrosilylation sequence. Computation predicts well the experimental structure and provides insight into the bonding via orbital, ^{13}C and ^{1}H NMR shifts, and NBO analysis. The structure suggests an interaction of the Si-C σ bond with the allyl π system. The proposed reaction sequence shown offers an explanation for the observed connectivity and relative stereochemistry in the product. These species are highly reactive Lewis acids, where intramolecular π-coordination in cationic silicon with 2,6-diarylphenyl scaffold distorts the ideal C_{2v} symmetry to a C_1-symmetric Wheland-like complex. Systems with lateral rings of basicity below benzene are likely candidates for cations without internal π coordination. Silyl cations bearing 2,6-dihalophenyl substituents do not reveal free tri-coordinate ions, but rather a trigonal-bipyramidal geometry with bridging halogen atoms as the apical ligands.





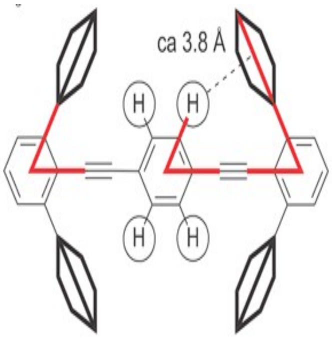
Reference: Duttwyler, S.; Zhang, Y.; Linden, A.; Reed, C.A.; Baldridge, K.K.*; Siegel, J.S.* Synthesis and Crystal Structure of a Silyl-Stabilized Allyl Cation … *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 3787-3790. Romanato, P.; Duttwyler, S.; Linden, A.; Baldridge, K.K.*; Siegel, J.S.* Through-Space Halogen Stabilization of Silylium Ions, *J. Am. Chem. Soc.*, **2010**, **DOI: 10.1021**. Duttwyler, S.; Douvris, C.; Fackler, N.L.; Tham, F.; Reed, C.A.*; Baldridge, K.K.*; Siegel, J.S.* C-F Activation of Fluorobenzene by Silylium Carboranes *Angewante Chem. Int. Engl.* **2010**, *49*, 7519-7522.

Title: Control of Conformation and Dynamics in Aryl-Alkyne Molecular Rotors

Researchers:
Karim, A.R.
Linden, A.;
Baldridge, K.K.*
Siegel, J. S.*

Institute/Group: University of Zürich, OCI, Switzerland

Description:



The central ring of a series of 1,4-bis(arylethynyl)arenes, viewed as molecular rotors with an extremely low barriers to rotation in the gas or solution phase, was investigated. The torsional energy profiles of the central ring are shown to be dependant on the relative conformation of the end capping arenes. When the capping arenes are sterically bulky m-terphenyl units, it is possible to understand the conformational dynamics of the central ring by a factorization analysis, involving perturbation of the basic torsional energy profile by polar-p, and dispersion interactions between the flanking rings of the cap and the central ring of the ditolan. Newly developed dispersion-enabled DFT methods are seen to be essential for accurate assessment of these effects, and comparison between methods that do and methods that do not account for such effects, serve as an illustration of the magnitude of the weak interactions. The basic principles learned apply to the design of materials with oriented free rotors in the solid phase.

Reference: Karim, A.R.; Linden, A.; Baldridge,K.K.*; Siegel, J.S.* Control of Conformation and Dynamics in Aryl-Alkyne Molecular Rotors, *Org. Biomol. Chem.* **2010**, **DOI**: 10.1039/c0sc00117a.

Title: Efficient access to aminomannoside derivatives via formal [2+2] cycloaddition of traizolinediones and tri-O-acetyl-D-glucal.

Researchers: Dahl, R.
Baldridge, K.K.*
Finney, N.S.*

Institute/Group: University of Zürich, OCI, Switzerland

Description:

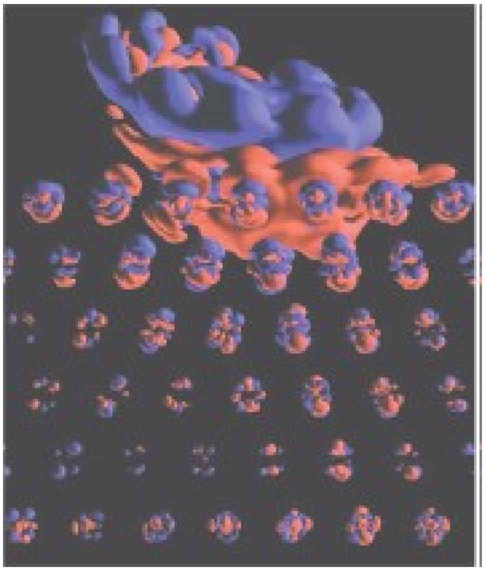
Triazolinediones react with tri-*O*-acetyl-D-glucal to provide the corresponding diazetidines as single stereoisomers possessing the mannosamine configuration at C2. The diazetidines undergo facile ring opening with alcohol and amine nucleophiles. While this methodology is not fully developed, it is the first example of direct intermolecular conversion of a glycal to a mannosamine derivative. Computational analysis provides mechanistic insight that in turn leads to a proposal for the generation of glucosamine derivatives from glycals and triazolinediones.

Reference: Dahl, R.; Baldridge, K.K.; Finney, N.S. Efficient access to aminomannoside derivatives via formal [2+2] cycloaddition of triazolinediones and tri-O-acetyl-D-glucal *J. Syn. Org. Chem.*, **2010**, **DOI**: 10.1055/s-0029-1218803.

Title: Theoretical Investigations of the Binding Process of Corannulene on a Cu(111) Surface.

Researchers: Zoppi, L.
Garcia, A.
Baldridge, K.K.*

Institute/Group: University of Zürich, OCI, Switzerland



Description: DFT-GGA calculations, enhanced to include effects of dispersion, are used to investigate the adsorption process of corannulene on a Cu(111) surface. In accord with experiments, we consider the dynamics of corannulene approaching the surface in a tilted fashion, concave side-up, enabling interactions between one of the six-membered rings and the surface over a 3-fold hollow site. Electronic structure analyses, including projected density of states and detection of work function modification, are used to aid in the understanding of the specific nature of the interaction between the corannulene and the metal surface in the complex system. Results show substantial charge rearrangement at the interface, the net effect being a large interface dipole that, added to the intrinsic molecular dipole, causes a significant decrease of the surface work function. Despite the charge rearrangement, no appreciable charge transfer occurs, and the general orbital structure of the individual components is retained. The analysis suggests that the adsorption of corannulene on Cu(111) is not a chemisorption process. Increased packing of corannulene on the surface leads to progressively smaller adsorption-induced interface dipoles, due to the depolarizing field created by the molecules.

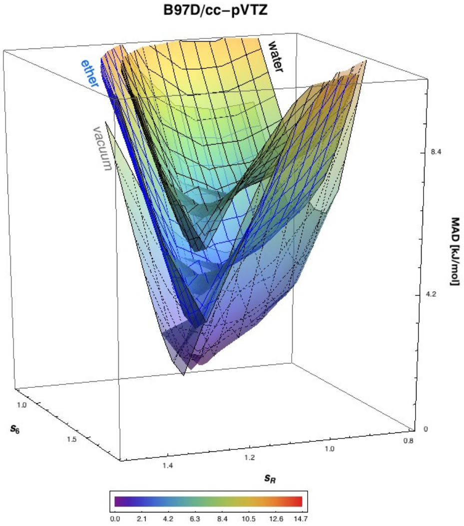
Reference: Zoppi, L.; Garcia, A.; Baldridge, K.K.* Theoretical Investigation of the Binding Process of Corannulene on a Cu(111) Surface, *J. Phys. Chem. A. (Festsschrift Journal dedicated to Klaus Ruedenberg)*, **2010**, *114*, 8864-8872.

Title: Implementation and optimization of DFT-D/COSab with respect to basis set and functional: An approach to study dispersion interactions in solution,

Researchers: Peverati, R.
Baldridge, K.K.*

Institute/Group: University of Zürich, OCI, Switzerland

Description:



This work involved the implementation, optimization, and performance of additional DFT functionals, as well as new DFT-D schemes in GAMESS. A variety of new density functionals were implemented and tested in the GAMESS software. Dispersion correction strategies included semiempirically corrected functionals, hybrid density functionals with conventional MP2 methods, and dispersion enabled functionals, such as offered by Truhlar. For DFT-D schemes involving a semiempirical correction, optimized parameters are proposed for several basis sets, and issues of BSSE are discussed. Performance of the different DFT-D strategies is compared, where functionals include some of the most recently proposed, B97D, B2PLYP, BMK and M06-2X functionals, together with several other well known functionals. Several relevant systems were compared with these strategies, including the benchmark S22 set of molecules, models for polar-p interactions between arenes spaced at van der Waals distances, and a series of functionalized corannulene derivatives and complexes. Results were most promising for the B97D functional. This work was recently extended to include the effects of solvent, using our QM solvation model implementation, COSab.

Reference: Peverati, R.; Baldridge, K.K.; Implementation and optimization of DFT-D/COSab with respect to basis set and functional: An approach to study dispersion interactions in solution, *JCTC* **2010**, ***DOI***: *10.1021/ct900363n*

Title: Assessment of DFT and DFT-D for Potentia Energy Surfaces of Rare Gas Trimers – Implementation and Analysis of Functionals and Extrapolation Procedures.

Researchers:
Peverati, R.
Macrina, M.
Baldridge, K.K.*

Institute/Group: University of Zürich, OCI, Switzerland

Description:

Given the recent developments in methodology associated with the accurate computation of molecular systems with weak interactions, it is of particular interest to revisit systems that are notoriously challenging for determining reliable potential energy surface (PES) descriptions. Additionally, challenges associated with carrying out complete basis set extrapolation procedures and treatment of basis set superposition error (BSSE) are of importance in these descriptions. In this work, investigation into the ability to accurately predict the potential energy surfaces of the main Rg3 molecules (Rg) He, Ne, Ar) is made across a range of wave function types and large basis sets, including the use of several established extrapolation procedures and counterpoise corrections. Wave function types span most classes of density functional types, including the newest DFT-D schemes, and are benchmarked against high accuracy CCSD(T)/CBS methodology. Study of such systems is valuable, as they serve as simple models for many complex properties, most importantly *n*-body weak interaction energies.

Reference: Peverati, R.; Baldridge, K.K.; Implementation and optimization of DFT-D/COSab with respect to basis set and functional: An approach to study dispersion interactions in solution, *JCTC*. **2010***, ASAP* ***DOI****: 10.1021/ct900363n*

Title: A new force field for simulating phosphatidylcholine bilayers

Researchers: D. Poger[1]
Wilfred F. van Gunsteren[2]
A.E. Mark[1, 3]

Institute/ [1]The University of Queensland, School of Chemistry and Molecular Biosciences, Australia
[2]Laboratory of Physical Chemistry, ETH Zurich, Switzerland
[3]The University of Queensland, Institute for Molecular Bioscience, Australia

Group: Computer aided chemistry

Description:

A new force field for the simulation of dipalmitoylphosphatidylcholine (DPPC) in the liquid-crystalline, fluid phase at zero surface tension is presented. The structure of the bilayer with the area per lipid (0.629 nm^2; experiment 0.629–0.64 nm^2), the volume per lipid (1.226 nm^3; experiment 1.229–1.232 nm^3), and the ordering of the palmitoyl chains (order parameters) are all in very good agreement with experiment. Experimental electron density profiles are well reproduced in particular with regard to the penetration of water into the bilayer. The force field was further validated by simulating the spontaneous assembly of DPPC into a bilayer in water. Notably, the timescale on which membrane sealing was observed using this model appears closer to the timescales for membrane resealing suggested by electroporation experiments than previous simulations using existing models.

References: *J. Comput. Chem.* ***31*** *(2010) 1117–1125*

Title: Basic ingredients of free energy calculations: a review

Researchers: C.D. Christ[1]
A.E. Mark[2]
W. F. van Gunsteren[1]

Institute/ [1]Laboratory of Physical Chemistry, ETH-Zurich, Switzerland
[2]School of Molecular and Microbial Sciences, Institute for Molecular Biosciences, University of Queensland

Group: computer aided chemistry

Description:

Methods to compute free energy differences between different states of a molecular system are reviewed with the aim of identifying their basic ingredients and their utility when applied in practice to biomolecular systems. A free energy calculation is comprised of three basic components: (i) a suitable model or Hamiltonian, (ii) a sampling protocol with which one can generate a representative ensemble of molecular configurations, and (iii) an estimator of the free energy difference itself. Alternative sampling protocols can be distinguished according to whether one or more states are to be sampled. In cases where only a single state is considered, six alternative techniques could be distinguished: (i) changing the dynamics, (ii) deforming the energy surface, (iii) extending the dimensionality, (iv) perturbing the forces, (v) reducing the number of degrees of freedom, and (vi) multi-copy approaches. In cases where multiple states are to be sampled, the three primary techniques are staging, importance sampling, and adiabatic decoupling. Estimators of the free energy can be classified as global methods that either count the number of times a given state is sampled or use energy differences. Or, they can be classified as local methods that either make use of the force or are based on transition probabilities. Finally, this overview of the available techniques and how they can be best used in a practical context is aimed at helping the reader choose the most appropriate combination of approaches for the biomolecular system, Hamiltonian and free energy difference of interest.

References: *J. Comput. Chem.* ***31*** *(2010) 1569-1582*

Title: Using one-step perturbation to predict the effect of changing force-field parameters on the simulated folding equilibrium of a β-peptide in solution

Researchers: Z.Lin,[1,2]
H. Liu,[2]
W. F. van Gunsteren[1]

Institute/ [1]Laboratory of Physical Chemistry, ETH Zurich, Switzerland,
[2]School of Life Sciences and Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China (USTC), China

Group: computer aided chemistry

Description:

Computer simulation using molecular dynamics is increasingly used to simulate the folding equilibria of peptides and small proteins. Yet, the quality of the obtained results depends largely on the quality of the force field used. This comprises the solute as well as the solvent model and their energetic and entropic compatibility. It is, however, computational very expensive to perform test simulations for each combination of force-field parameters.
Here, we use the one-step perturbation technique to predict the change of the free enthalpy of folding of a β-peptide in methanol solution due to changing a variety of force-field parameters. The results show that changing the solute backbone partial charges affects the folding equilibrium, whereas this is relatively insensitive to changes in the force constants of the torsional energy terms of the force field. Extending the cut-off distance for nonbonded interactions beyond 1.4 nm does not affect the folding equilibrium. The same result is found for a change of the reaction-field permittivity for methanol from 17.7 to 30. The results are not sensitive to the criterion, e.g., atom-positional RMSD or number of hydrogen bonds, that is used to distinguish folded and unfolded conformations. Control simulations with perturbed Hamiltonians followed by backward one-step perturbation indicated that quite large perturbations still yield reliable results. Yet, perturbing all solvent molecules showed where the limitations of the one-step perturbation technique are met. The evaluated methodology constitutes an efficient tool in force-field development for molecular simulation by reducing the number of required separate simulations by orders of magnitude.

References: *J. Comput. Chem.* ***31*** *(2010) 2419-2427*

Title: Prediction of Folding Equilibria of Differently Substituted Peptides Using One-Step Perturbation

Researchers: Z. Lin[†,‡]
J. Kornfeld[†]
M. Mächler[†]
W. F. van Gunsteren[†]

Institute/ [†]Laboratory of Physical Chemistry, ETH, Zurich, Switzerland
[‡]School of Life Sciences and Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China (USTC), China

Group: computer aided chemistry

Description:

Computer simulation using long molecular dynamics (MD) can be used to simulate the folding equilibria of peptides and small proteins. However, a systematic investigation of the influence of the side-chain composition and position at the backbone on the folding equilibrium is computationally as well as experimentally too expensive because of the exponentially growing number of possible side-chain composition and combinations along the peptide chain. Here, we show that application of the one-step perturbation technique may solve this problem at least computationally, that is, one can predict many folding equilibria of a polypeptide with different side-chain substitutions from just one single MD simulation using an unphysical reference state. The methodology reduces the number of required separate simulations by an order of magnitude.

References: *J. Am. Chem. Soc.* ***132*** *(2010) 7276-7278*

Title: Methods of NMR structure refinement: molecular dynamics
simulations improve the agreement with measured NMR data
of a C-terminal peptide of GCN4-p1

Researchers: Jozia Dolenc[1,2]
John Missimer[3]
Michael O. Steinmetz[3]
W. F. van Gunsteren[1]

Institute/ [1]Laboratory of Physical Chemistry, ETH Zurich, Switzerland
[2]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia
[3]Biomolecular Research, Paul Scherrer Institut, 5232 Villigen, Switzerland

Group: computer aided chemistry

Description:

The C-terminal trigger sequence is essential in the coiled-coil formation of GCN4-p1; its conformational properties are thus of importance for understanding this process at the atomic level. A solution NMR model structure of a peptide, GCN4p16–31, encompassing the GCN4-p1 trigger sequence was proposed a few years ago. Derived using a standard single-structure refinement protocol based on 172 nuclear Overhauser effect (NOE) distance restraints, 14 hydrogen-bond and 11 ø torsional angle restraints, the resulting set of 20 NMR model structures exhibits regular α-helical structure. However, the set slightly violates some measured NOE bounds and does not reproduce all 15 measured $^3J(H_N\text{-}H_{C\alpha})$-coupling constants, indicating that different conformers of GCN4p16–31 might be present in solution. With the aim to resolve structures compatible with all NOE upper distance bounds and ^3J-coupling constants, we executed several structure refinement protocols employing unrestrained and restrained molecular dynamics (MD) simulations with two force fields. We find that only configurational ensembles obtained by applying simultaneously time-averaged NOE distance and ^3J-coupling constant restraining with either force field reproduce all the experimental data. Additionally, analyses of the simulated ensembles show that the conformational variability of GCN4p16–31 in solution admitted by the available set of 187 measured NMR data is larger than represented by the set of the NMR model structures. The conformations of GCN4p16–31 in solution differ in the orientation not only of the side-chains but also of the backbone. The inconsistencies between the NMR model structures and the measured NMR data are due to the neglect of averaging effects and the inclusion of hydrogen-bond and torsional-angle restraints that have little basis in the primary, i.e. measured NMR data.

References: *J. Biomol. NMR* ***47*** *(2010) 221-235*

Title: A one-site polarizable model for liquid chloroform: COS/C

Researchers: Z. Lin[ab]
A. P Kunz[a]
W. F. van Gunsteren[a]

Institute/ [a]Laboratory of Physical Chemistry, ETH Zürich, Switzerland
[b]School of Life Sciences and Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China (USTC), China

Group: computer aided chemistry

Description:

A one-site polarizable liquid chloroform model based on the charge-on-spring method is presented. It consists of five van der Waals sites and point charges, with one polarizable center on the carbon atom. The partial charges were adjusted to fit the gas-phase dipole moment of chloroform, and the Lennard–Jones parameters were varied to reproduce the density and the heat of vapourization of liquid chloroform. In this way, a simple polarizable model for liquid chloroform was obtained that correctly describes a variety of its thermodynamic, dynamic and dielectric properties, while the computational costs are only a factor of 2 higher than for a similar non-polarizable chloroform model. The model is simpler than two previously developed polarizable chloroform models, with four or five polarizable sites. The developed COS/C model is expected to show realistic behaviour of chloroform molecules in response to changes in electric field strength or the dielectric environment and should be applicable in simulations of biomolecules in conjunction with the GROMOS biomolecular force field.

References: *Mol. Phys.* ***108*** *(2010) 1749-1757*

Title: The effect of using a polarizable solvent model upon the folding equilibrium of different β-peptides

Researchers: Z. Lin[†‡]
N. Schmid[†]
Wilfred F. van Gunsteren[†]

Institute/ [†]Laboratory of Physical Chemistry, ETH Zürich, Switzerland.
[‡]School of Life Sciences and Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China (USTC), China

Group: computer aided chemistry

Description:

Folding and unfolding of β-peptides has extensively been studied by molecular dynamics (MD) simulation in the past decade. In these simulations, a non-polarizable model for the solvent (mostly methanol) was used as the solvent of β-peptides. We investigate the effect of using a polarizable methanol solvent model upon the folding equilibrium of β-peptides. Thirteen MD simulations covering a total simulation length of 1.25 μs for three differently folding β-peptides were analyzed. The agreement with the experimental data was slightly improved by applying the polarizable solvent. In polarizable solvent, helical structures, which have a large dipole moment, are stabilized, while no obvious effect was detected in the simulations of peptides that have a hairpin structure as dominant fold. The introduction of electronic polarizability into the solvent model appears of importance to a proper description of folding equilibria if these are determined by competing solute conformations that have different dipole moments.

References: *Molecular Physics, (2010) accepted*

Title: The effect of F-substitution upon the β-hairpin fold of a 4-β-peptide in methanol

Researchers: S. Bachmann[a]
B. Jaun[b]
W. F. van Gunsteren[a]
D. Wang[a]

Institute/ [a]Laboratory of Physical Chemistry, ETH Zürich, Switzerland
[b]Laboratory of Organic Chemistry, ETH Zürich, Switzerland

Group: computer aided chemistry

Description:

The importance of β-peptides lies in their ability to mimic the conformational behavior of α-peptides even with a much shorter chain length, and in their resistance to proteases. To investigate the effect of substitution of β-peptides on their dominant fold, we have carried out a MD simulation study of two tetrapeptides, Ac-(2R,3S)-$\beta^{2;3}$hVal(αMe)-(2S)-β^2hPhe-(R)-β^3hLys-(2R,3S)-$\beta^{2;3}$-Ala(αMe)-NH_2, differing in the substitution at the C_α of Phe2 (pepF with F, and pepH with H). Three simulations, unrestrained (UNRES), using ^{3}J-coupling biasing with local elevation in combination with either instantaneous (INS) or time averaging (AVE) NOE distance restraining, were carried out for each peptide. In the unrestrained simulations, we find 3 (pepF) and 2 (pepH) NOE distance bound violations of maximally 0.22 nm that involve the terminal residues. The restrained simulations match both the NOE distance bounds and ^{3}J-values derived from experiment. The fluorinated peptide shows a slightly larger conformational variability than the non-fluorinated one.

References: *Helv. Chim. Acta (2010) accepted*

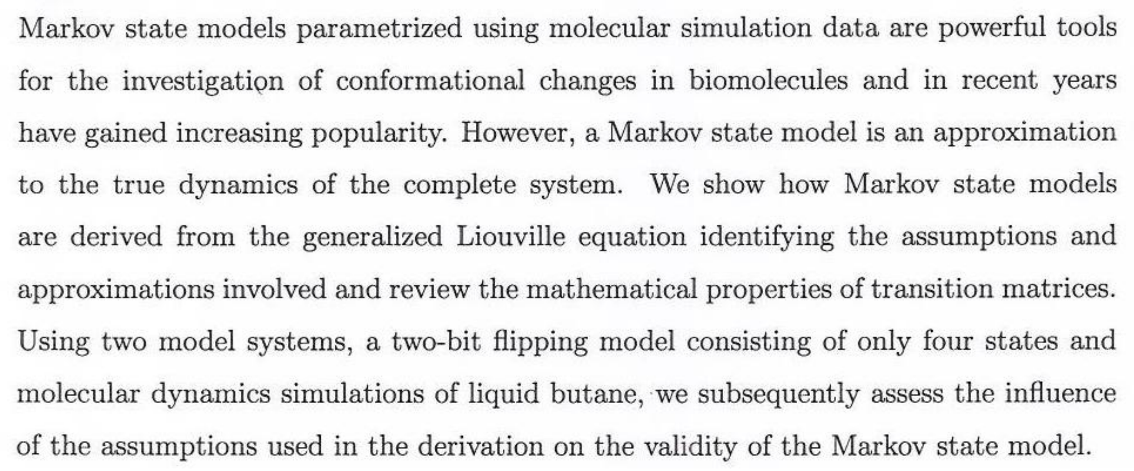
Title: An analysis of the validity of Markov state models for emulating the dynamics of classical molecular systems and ensembles

Researchers: B. Keller
P. H. Hünenberger
W. F. van Gunsteren

Institute/

Group: Laboratory of Physical Chemistry, ETH Zürich, Switzerland
computer aided chemistry

Description:



Markov state models parametrized using molecular simulation data are powerful tools for the investigation of conformational changes in biomolecules and in recent years have gained increasing popularity. However, a Markov state model is an approximation to the true dynamics of the complete system. We show how Markov state models are derived from the generalized Liouville equation identifying the assumptions and approximations involved and review the mathematical properties of transition matrices. Using two model systems, a two-bit flipping model consisting of only four states and molecular dynamics simulations of liquid butane, we subsequently assess the influence of the assumptions used in the derivation on the validity of the Markov state model.

References: *J. Chem. Theory Comput. (2010) submitted*

Title: Exploring the trigger sequence of the GCN4 coiled-coil:
biased molecular dynamics resolves apparent inconsistencies in NMR measurements

Researchers: J. Missimer[1]
J. Dolenc[2,3]
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W. F. van Gunsteren[2]

Institute/ [1]Biomolecular Research, Paul Scherrer Institute, Villigen, Switzerland
[2]Laboratory of Physical Chemistry, ETH Zürich, Switzerland
[3]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

Group: computer aided chemistry

Description:

Trigger sequences are indispensable elements for coiled-coil formation. The monomeric helical trigger sequence of the yeast transcriptional activator GCN4 has been investigated recently using several solution NMR observables including Nuclear Overhauser Enhancement (NOE) intensities and $^3J(HN,HC\alpha)$-coupling constants, and a set of 20 model structures was proposed. Constrained to satisfy the NOE derived distance bounds, the NMR model structures do not appear to reproduce all the measured $^3J(HN,HC\alpha)$-coupling constant values, indicating that the α-helical propensity is not uniform along the GCN4 trigger sequence.

A recent methodological study of unrestrained and restrained molecular dynamics (MD) simulations of the GCN4 trigger sequence in solution showed that only MD simulations incorporating time-averaged NOE distance restraints and instantaneous or local-elevation ^3J-coupling restraints could satisfy the entire set of the experimental data. In this report, we assess by means of cluster analyses the model structures characteristic of the two simulations that are compatible with the measured data and compare them with the proposed 20 NMR model structures. Striking characteristics of the MD model structures are the variability of the simulated configurations and the indication of entropic stability mediated by the aromatic N-terminal residues 17Tyr and 18His, which are absent in the set of NMR model structures.

References: *Proteins, (2010) accepted*

Title: Using one-step perturbation to predict the folding equilibrium of differently stereochemically substituted β-peptides

Researchers: Z. Lin[‡†]
W. F. van Gunsteren[†]

Institute: [‡]School of Life Sciences and Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China (USTC), China
[†]Laboratory of Physical Chemistry, Zürich, Switzerland

Group: computer aided chemistry

Description:

The one-step perturbation technique is used to predict the folding equilibria for 16 peptides with different stereochemical side-chain substitutions through one or two long-time simulations, one of an unphysical reference state and another of one of the 16 peptides for which many folding events can be sampled. The accuracy of the one-step perturbation results was investigated by comparing to results available from long-time MD simulations of particular peptides. Their folding free energies were reproduced within statistical accuracy. The one-step perturbation results show that an axial substitution at either the Cα or the Cβ position destabilizes the 3_{14}-helical conformation of the hepta-β-peptide, which is consistent with data inferred from experimental CD spectra. The methodology reduces the number of required separate simulations by an order of magnitude.

References: *Phys.Chem.Chem.Phys, (2010) accepted*

Title: α-Cyclodextrin Host-Guest Binding: A Computational Study Analyzing the Different Driving Forces

Researchers: S. Riniker[1]
X. Daura[2]
W. F. van Gunsteren[1]

Institute/ [1]Laboratory of Physical Chemistry, ETH Zürich, Switzerland
[2]Catalan Institution for Research and Advanced Studies (ICREA) and Instituteof Biotechnology and Biomedicine (IBB), Universitat Autònoma de, Barcelona, Spain

Group: computer aided chemistry

Description:

Free energy differences govern the equilibrium between bound and unbound states of an enzyme and its substrate. The understanding of the underlying entropic and enthalpic contributions, and their complex interplay are crucial for the design of new drugs and inhibitors. In this study, molecular dynamics simulations were performed with inclusion complexes of α-cyclodextrin (αCD) and three monosubstituted benzene derivatives to investigate host-guest binding. αCD complexes are an ideal model system, which is experimentally and computationally well known. Thermodynamic integration (TI) simulations were carried out under various conditions for the free ligands in solution and bound to αCD. The two possible orientations of the ligand inside the cavity were investigated. Very good agreement with experimental data was only found for the more stable conformation, where the substituent resides inside the cavity. The better stability of this conformation results from stronger van der Waals interactions and a favorable antiparallel dipole-dipole alignment. To estimate the entropic contributions, simulations were performed at three different temperatures (250, 300, and 350 K) and using positional restraints for the host. The system was found to be insensitive to both factors, due to the large and symmetric cavity of αCD, as well as the nondirectional nature of the host-guest interactions.

References: *Helv. Chim. Acta, (2010) accepted*

Title: A comparison of the different helices adopted by α- and β-peptides suggests different reasons for their stability.

Researchers: J. Allison
M. Müller
W. F. van Gunsteren

Institute: Laboratory of Physical Chemistry, ETH Zürich, Switzerland

Group: computer aided chemistry

Description:

The right-handed α-helix is the dominant helical fold of α-peptides, while the left-handed 3_{14}-helix is the dominant helical fold of β-peptides. Using molecular dynamics simulations, the properties of α-helical α-peptides and 3_{14}-helical β-peptides with different C-terminal protonation states and in the solvents water and methanol are compared. The observed energetic and entropic differences can be traced to differences in the polarity of the solvent-accessible surface area and, in particular, the solute dipole moments, suggesting different reasons for their stability.

References: *Prot. Science, (2010) accepted*

Title: A simple, efficient polarisable molecular model for liquid carbon tetrachloride

Researchers: A. P. Kunz
A. Eichenberger
W. F. van Gunsteren

Institute/ Laboratory of Physical Chemistry, ETH Zürich, Switzerland

Group: computer aided chemistry

Description:

A one-site and a five-site polarisable model for liquid carbon tetrachloride (CCl_4) is presented. They are based on a non-polarisable model consisting of five van der Waals sites not carrying any partial charges. In the one-site model, a charge on spring with a polarisability α_{CCl4} of 11.1 $(4\pi\varepsilon_0)$ 10^{-3} nm^3 was attached to the carbon to make the model polarisable, while in the five-site model polarisabilities α_c = 1.848 $(4\pi\varepsilon_0)$ $10^{-3}nm^3$ and α_{Cl} = 2.289 $(4\pi\varepsilon_0)$ $10^{-3}nm^3$ were added to the carbon and chlorine atoms, respectively. Both models exactly reproduce the experimental static dielectric permittivity of 2.238 at 293 K and 1 *atm*. This quantity was calculated by applying a homogeneous external electric field of varying strength. The one-site polarisable model is only about 1.7 times more computationally expensive than the non-polarisable one and is compatible with the GROMOS force field. A selected set of thermodynamic, dynamic and structural quantities was calculated and compared to experiment.

References: *Mol. Phys. (2010) submitted*

Title: Calculation of Binding Free Energies of Inhibitors to Plasmepsin II.

Researchers: D. Steiner[1]
Ch. Oostenbrink[2]
F. Diederich[3]
M. Zürcher[3]
W. F. van Gunsteren[1]

Institute/ [1]Laboratory of Physical Chemistry, ETH Zürich, Switzerland
[2]Institute for Molecular Modeling and Simulation, Department of Material Sciences and Process Engineering, University of Natural Resources and Applied Life Sciences, Vienna, Austria
[3]Laboratory of Organic Chemistry, ETH Zurich, Switzerland

Group: computer aided chemistry

Description:

An understanding at the atomic level of the driving forces of inhibitor binding to the protein plasmepsin (PM) II would be of interest to the development of drugs against malaria. To this end, three state of the art computational techniques were applied to a protein-ligand system of PM II and several *exo*-3-amino-7-azabicyclo[2.2.1]heptanes and the resulting relative free energies were compared to values derived from experimental IC50 values. For this large and flexible protein-ligand system the simulations could not properly sample the relevant parts of the conformational space of the bound ligand, resulting in failure to reproduce the experimental data. Yet, the use of Hamiltonian replica exchange (H-RE) in conjunction with thermodynamic integration (TI) resulted in much enhanced convergence and computational efficiency compared to standard thermodynamic integration calculations. The more approximate method of calculating only energetic and entropic contributions of the ligand in its bound and unbound states from conventionalMolecular Dynamics (MD) simulations reproduced the major trends in the experimental binding free energies, which could be rationalised in terms of energetic and entropic characteristics of the different structural and physico-chemical properties of the protein and ligands.

References: *J. Comput. Chem. (2010) submitted,*

Title: Dynamics May Significantly Influence the Estimation of Interatomic Distances in Biomolecular X-ray Structures

Researchers: A. Kuzmanic[a,b]
D. Kruschel[b]
W. F. van Gunsteren[c]
B. Zagrovic[abd]

Institute/ [a]Department for Structural and Computational Biology Max F. Perutz Laboratories, University of Vienna Campus Vienna Biocenter 5, Austria
[b]Mediterranean Institute for Life Sciences Mestrovicevo setaliste bb, Split, Croatia
[c]Laboratory of Physical Chemistry, ETH Zürich, Switzerland
[d]Department of Physics Faculty of Science, University of Split Teslina 12, Croatia

Group: computer aided chemistry

Description:

Atomic positions obtained by X-ray crystallography are time- and space-averages over many molecules contained in the crystal. Importantly, interatomic distances, calculated between such average positions and frequently used in structural and mechanistic analyses, can be substantially different from the more appropriate time- and ensemble-average interatomic distances. Using crystallographic B-factors, one can deduce corrections to distances between average atomic positions derived from X-ray experiments, to obtain correct average distances as a function of the type of atomic motion. However, these corrections have so far been applied almost exclusively to small molecules. Here, using a set of 4802 known protein X-ray structures, we study the significance of such corrections for different types of atomic motion. Importantly, we show that for distances shorter than 5 Å, corrections of more than 0.5 Å may apply, especially in case of non-correlated or anti-correlated motion. For example, approximately 14% of the studied structures have at least one pair of atoms with a correction that is ≥ 0.5 Å in the case of non-correlated motion. Using molecular dynamics simulations of ubiquitin's unit cell, we demonstrate that the majority of atoms in this protein move in a non-correlated fashion, suggesting that such deviations may truly be relevant. We illustrate the potential mechanistic and biological significance of this in case of the KcsA ion channel, and show that the calculated corrections provide indirect evidence that the atomic motions in its selectivity filter are highly correlated.

References: *Proc. Natl. Acad. Sci. USA (2010) submitted*

Title: Simulating the transition between gel and liquid-crystal phases of lipid bilayers: Dependence of the transition temperature on the hydration level.

Researchers: Bruno A. C. Horta*
Alex H. de Vries**
Philippe H. Hünenberger*

Institute/ Group: * Laboratory of Physical Chemistry
** Groningen Biomolecular Sciences and Biotechnology Institute
University of Groningen (The Netherlands)

Description :

Explicit-solvent molecular dynamics (MD) simulations of the monoglyceride glycerol-1-monopalmitin (GMP; bilayer patch of 2×6×6 lipids) at different hydration levels (full, half or quarter hydration) and at different temperatures (318 to 338 K) are reported. The 40 ns simulations (some extended to 200 ns) are initiated from structures appropriate for the gel (GL) or liquid-crystal (LC) phases, with the goal of investigating whether atomistic MD simulations on this timescale can be used to monitor GL ↔ LC transitions in lipid bilayers, and to evaluate the corresponding transition temperatures T_m (as well as the influence of hydration on T_m) in a reliable fashion. The main conclusions are that : (*i*) the GL → LC transition of GMP can be observed on the 40 ns timescale; (*ii*) the LC → GL transition is comparatively slower, requiring simulations on the 200 ns timescale; (*iii*) a set of simulations initiated from a structure appropriate for the GL phase and carried out at slightly different temperatures permits to determine a reliable value for T_m; (*iv*) the calculated T_m values reproduce the experimentally observed increase in this transition temperature upon decreasing the bilayer hydration; (*v*) the T_m values calculated at the three hydration levels considered are in essentially quantitative agreement with the experimental phase diagram of GMP. To our knowledge, this study represents the first accurate determination of the T_m of a lipid *via* atomistic simulations of the (reversible) GL ↔ LC phase transition, as well as the first direct simulation evidence for the increase in the transition temperature upon dehydration. The possible direct determination of T_m and the characterization of environmental effects on this quantity by simulation opens up promising perspectives in the contexts of force field refinement and of the investigation of dehydration-induced damages in living cells (and bioprotection by cosolutes).

References: B.A.C. Horta, A.H. de Vries and P.H. Hünenberger
J. Chem. Theor. Comput. 6, 2488-2500 (2010).

Title: Computation of methodology-independent single-ion solvation properties from molecular simulations. III. Correction terms for the solvation free energies, enthalpies, entropies, heat capacities, volumes, compressibilities and expansivities of solvated ions.

Researchers: Maria M. Reif*
Philippe H. Hünenberger*

Institute/ Group: * Laboratory of Physical Chemistry

Description :

The raw ionic solvation free energies computed from atomistic (explicit-solvent) simulations are extremely sensitive to the boundary conditions (finite or periodic system, system or box size) and treatment of electrostatic interactions (Coulombic, lattice-sum or cutoff-based) used during these simulations. However, as shown by Kastenholz & Hünenberger [J. Chem. Phys. 124, 224501 (2006)], correction terms can be derived for the effects of : (A) an incorrect solvent polarization around the ion and an incomplete or/and inexact interaction of the ion with the polarized solvent due to the use of an approximate (not strictly Coulombic) electrostatic scheme; (B) the finite size or artificial periodicity of the simulated system; (C) an improper summation scheme to evaluate the potential at the ion site, and the possible presence of a polarized air-liquid interface or of a constraint of vanishing average electrostatic potential in the simulated system; (D) an inaccurate dielectric permittivity of the employed solvent model. Comparison with standard experimental data also requires the inclusion of an appropriate standard-state correction term. In the present study, this correction scheme is extended by: (*i*) providing simple approximate analytical expressions (empirically-fitted) for the correction terms that were evaluated numerically (continuum-electrostatics calculations); (*ii*) providing correction terms for derivative thermodynamic single-ion solvation properties (and corresponding partial molar variables in solution), namely the enthalpy, entropy, isobaric heat capacity, volume, isothermal compressibility and isobaric expansivity (including appropriate standard-state correction terms). The ability of the correction scheme to produce methodology-independent single-ion solvation free energies based on atomistic simulations is tested in the case of Na^+ hydration, and the nature and magnitude of the correction terms for derivative thermodynamic properties is assessed numerically.

References: M.M. Reif and P.H. Hünenberger
J. Chem. Phys., in press (2010).

Title: Computation of methodology-independent single-ion solvation properties from molecular simulations. IV. Optimized Lennard-Jones interaction parameter sets for the alkali and halide ions in water.

Researchers: Maria M. Reif*
Philippe H. Hünenberger*

Institute/ Group: * Laboratory of Physical Chemistry

Description :

The raw ionic solvation free energies computed from atomistic (explicit-solvent) simulations are extremely sensitive to the boundary conditions and treatment of electrostatic interactions used during these simulations. However, as shown recently [Kastenholz & Hünenberger, J. Chem. Phys. 124, 224501 (2006)], the application of appropriate correction terms permits to obtain methodology-independent results. The corrected values are then exclusively characteristic of the underlying molecular model, including in particular the ion-solvent van der Waals interaction parameters, determining the effective ion size and the magnitude of its dispersion interactions. In the present study, the comparison of calculated (corrected) hydration free energies with experimental data (along with the consideration of ionic polarizabilities) is used to calibrate new sets of ion-solvent van der Waals (Lennard-Jones) interaction parameters for the alkali (Li^+, Na^+, K^+, Rb^+, Cs^+) and halide (F^-, Cl^-, Br^-, I^-) ions along with either the SPC or the SPC/E water models. The experimental dataset is defined by conventional single-ion hydration free energies [Tissandier *et al.*, J. Phys. Chem. A 102, 7787 (1998); Fawcett, J. Phys. Chem. B 103, 11181] along with three plausible choices for the (experimentally elusive) value of the absolute (intrinsic) hydration free energy of the proton, namely $\Delta G^{\ominus}_{hyd}[\mathrm{H}^+] = -1100$, -1075 or -1050 kJ·mol^{-1}, resulting in three sets L, M and H for the SPC water model and three sets L_E, M_E and H_E for the SPC/E water model (alternative sets can easily be interpolated to intermediate $\Delta G^{\ominus}_{hyd}[\mathrm{H}^+]$ values). The residual sensitivity of the calculated (corrected) hydration free energies on the volume-pressure boundary conditions and on the effective ionic radius entering into the calculation of the correction terms is also evaluated, and found to be very limited. Ultimately, it is expected that comparison with other experimental ionic properties (*e.g.* derivative single-ion solvation properties, as well as data concerning ionic crystals, melts, solutions at finite concentrations, or non-aqueous s olutions) will permit to validate one specific set and thus, the associated $\Delta G^{\ominus}_{hyd}[\mathrm{H}^+]$ value (atomistic consistency assumption). Preliminary results (first-peak positions in the ion-water radial distribution functions, partial molar volumes of ionic salts in water, and structural properties of ionic crystals) support a value of $\Delta G^{\ominus}_{hyd}[\mathrm{H}^+]$ close to -1100 kJ·mol^{-1}.

References: M.M. Reif and P.H. Hünenberger
J. Chem. Phys., in press (2010).

Title: Enhanced conformational sampling in molecular dynamics simulations of solvated peptides: Fragment-based local elevation umbrella sampling.

Researchers: Halvor S. Hansen*
Xavier Daura**
Philippe H. Hünenberger*

Institute/ Group: * Laboratory of Physical Chemistry
** Institute of Biotechnology and Biomedicine
Universitat Autònoma de Barcelona, Bellatera (Spain)

Description :

A new method, fragment-based local elevation umbrella sampling (FB-LEUS), is proposed to enhance the conformational sampling in explicit-solvent molecular dynamics (MD) simulations of solvated polymers. The method is derived from the local elevation umbrella sampling (LEUS) method [Hansen & Hünenberger, J. Comput. Chem. 31, 1-23, 2010], which combines the local elevation (LE) conformational searching and the umbrella sampling (US) conformational sampling approaches into a single scheme. In LEUS, an initial (relatively short) LE build-up (searching) phase is used to construct an optimized (grid-based) biasing potential within a subspace of conformationally relevant degrees of freedom, that is then frozen and used in a (comparatively longer) US sampling phase. This combination dramatically enhances the sampling power of MD simulations but, due to computational and memory costs, is only applicable to relevant subspaces of low dimensionalities. As an attempt to expand the scope of the LEUS approach to solvated polymers with more than a few relevant degrees of freedom, the FB-LEUS scheme involves an US sampling phase that relies on a superposition of low-dimensionality biasing potentials optimized using LEUS at the fragment level. The feasibility of this approach is tested using polyalanine (poly-Ala) and polyvaline (poly-Val) oligopeptides. Two-dimensional biasing potentials are preoptimized at the monopeptide level, and subsequently applied to all dihedral-angle pairs within oligopeptides of $4, 6, 8$ or 10 residues. Two types of fragment-based biasing potentials are distinguished: (*i*) the basin-filling (BF) potentials act so as to “fill” free-energy basins up to a prescribed free-energy level above the global minimum; (*ii*) the valley-digging (VD) potentials act so as to “dig” valleys between the (four) free-energy minima of the two-dimensional maps, preserving barriers (relative to linearly interpolated free-energy changes) of a prescribed magnitude. The application of these biasing potentials may lead to an impressive enhancement of the searching power (volume of conformational space visited in a given amount of simulation time). However, this increase is largely offset by a deterioration of the statistical efficiency (representativeness of the biased ensemble in terms of the conformational distribution appropriate for the physical ensemble). As a result, it appears difficult to engineer FB-LEUS schemes representing a significant improvement over plain MD, at least for the systems considered here.

References: H.S. Hansen, X. Daura and P.H. Hünenberger
J. Chem. Theor. Comput., in press (2010).

Title: Ball-and-stick local elevation umbrella sampling : Molecular simulations involving enhanced sampling within conformational or alchemical subspaces of low internal dimensionalities, minimal irrelevant volumes and problem-adapted geometries.

Researchers: Halvor S. Hansen*
Philippe H. Hünenberger*

Institute/ Group: * Laboratory of Physical Chemistry

Description :

A new method, ball-and-stick local elevation umbrella sampling (B&S-LEUS) is proposed to enhance the sampling in computer simulations of (bio)molecular systems. It enables the calculation of conformational free-energy differences between states (or alchemical free-energy differences between molecules), even in situations where the definition of these states relies on a conformational subspace involving more than a few degrees of freedom. The B&S-LEUS method consists of the following steps : (*A*) choice of a reduced conformational subspace; (*B*) representation of the relevant states by means of spheres ("balls"), each associated with a biasing potential involving a one-dimensional radial memory-based term and a radial confinement term; (*C*) definition of a set of lines ("sticks") connecting these spheres, each associated with a biasing potential involving a one-dimensional longitudinal memory-based term and a transverse confinement term; (*D*) unification of the biasing potentials corresponding to the union of all the spheres and lines (active subspace) into a single biasing potential according to the enveloping distribution sampling (EDS) scheme; (*E*) build-up of the memory using the local elevation (LE) procedure, leading to a biasing potential enabling a nearly uniform sampling (radially within the spheres, longitudinally within the lines) of the active subspace; (*F*) generation of a biased ensemble of configurations using this preoptimized biasing potential, following an umbrella sampling (US) approach; (*G*) calculation of the relative free energies of the states *via* reweighting and state assignment. The main characteristics of this approach are : (*i*) a low internal dimensionality, *i.e.* the memory only involves one-dimensional grids (acceptable memory requirements); (*ii*) a minimal irrelevant volume, *i.e.* the conformational volume opened to sampling includes a minimal fraction of irrelevant regions in terms of the free energy of the physical system or of user-specified metastable states (acceptable build-up duration requirements, high statistical efficiency); (*iii*) a problem-adapted geometry (*a priori* specification of the conformational regions considered as relevant or irrelevant). As an illustration, the B&S-LEUS method is applied here to three test systems : (*i*) a solvated (blocked) alanine monopeptide (two-dimensional conformational subspace), used as a toy system to illustrate the versatility of the method in promoting the sampling of arbritrary regions of the Ramachandran map; (*ii*) a solvated polyalanine decapeptide (nine-dimensional conformational subspace), to evaluate the relative free energies of three different types of helices (π, α and 3_{10}) based on a single simulation; (*iii*) a solvated artifical hexopyranose, termed the "mother" of all D-hexopyranoses and constructed as a hybrid of all D-hexopyranose stereoisomers, where the method is applied (seven-dimensional mixed alchemical and conformational subspace) to calculate the relative free energies of the corresponding 32 isomers, anomers and chair conformers, based on a single simulation.

References: H.S. Hansen and P.H. Hünenberger
J. Chem. Theor. Comput., in press (2010).

Title: A reoptimized GROMOS force field for hexopyranose-based carbohydrates accounting for the relative free energies of ring conformers, anomers, epimers, hydroxymethyl rotamers and glycosidic linkage conformers.

Researchers: Halvor S. Hansen*
Philippe H. Hünenberger*

Institute/ Group: * Laboratory of Physical Chemistry

Description :

The GROMOS 53A6 force field for hexopyranose-based carbohydrates (nearly equivalent to 45A4 for pure carbohydrate systems) is reoptimized into a new version $56A_{CARBO}$ (nearly equivalent to 53A6 for non-carbohydrate systems). This reoptimization was found necessary in order to repair a number of shortcomings of the 53A6 (45A4) parameter set, and to extend the scope of the force field to properties that had not been included previously into the parameterization procedure. The new $56A_{CARBO}$ force field is characterized by : (*i*) the formulation of systematic build-up rules for the automatic generation of force-field topologies over a large class of compounds including (but not restricted to) unfunctionalized polyhexopyranoses with arbitrary connectivities; (*ii*) the systematic use of enhanced-sampling methods for inclusion of experimental thermodynamic data concerning slow or unphysical processes into the parameterization procedure; (*iii*) an extensive validation against available experimental data in solution and, to a limited extent, theoretical (quantum-mechanical) data in the gas phase. At present, the $56A_{CARBO}$ force field is restricted to compounds of the elements C, O and H presenting single bonds only, no oxygen functions other than alcohol, ether, hemiacetal or acetal, and no cyclic segments other than six-membered rings (separated by at least one intermediate atom). After calibration, this force field is shown to reproduce well the relative free energies of ring conformers, anomers, epimers, hydroxymethyl rotamers and glycosidic linkage conformers. As a result, the $56A_{CARBO}$ force field should be suitable for : (*i*) the characterization of the dynamics of pyranose ring conformational transitions (in simulations on the μs timescale); (*ii*) the investigation of systems where alternative ring conformations become significantly populated; (*iii*) the investigation of anomerization or epimerization in terms of free-energy differences; (*iv*) the design of simulation approaches accelerating the anomerization process along an unphysical pathway.

References: H.S. Hansen and P.H. Hünenberger
J. Chem. Theor. Comput., in press (2010).

Title: Quickstep: A Fast and Accurate Density Functional Program

Researchers: Joost VandeVondele
Marcella Iannuzzi
Valery Weber
Urban Borštnik
Manuel Guidon
Florian Schiffmann
Jürg Hutter

Institute: Institute of Physical Chemistry, University of Zürich

Description:

Our recent work focused on the development of methods to perform Kohn–Sham calculations using accurate basis sets on large systems, including condensed matter systems which require periodic boundary conditions. To device algorithms that exhibit linear scaling, it is essential to exploit the decay properties of the one-particle density matrix. This means that it is necessary to use a basis of localized functions, which optimally describe the locality of the electronic structure. New methods are developed that optimally exploit the structure and properties of Gaussian basis sets.

In order to achieve linear scaling in system size in all parts of the calculation it is necessary to localize the Kohn–Sham orbitals and to represent them using sparse matrices. Efficient optimization algorithms need therefore to be based on sparse matrix-matrix multiplications. We are developing a library of parallelized linear algebra functions for sparse matrix operations for quantum chemical calculations. Since the functions are targeted at distributed-memory parallel computers, the communication latency and data volumes are minimized and the overlapping of communication with calculation is employed. To remain general even for smaller systems, particular attention is paid to retain a performance comparable to operations on full matrices.

References: J. VandeVondele et al., Comp. Phys. Comm. 167, 103 (2005).
M. Iannuzzi et al., Chimia, 59, 499 (2005).
V. Weber et al., J. Chem. Phys. 128 084113 (2008).
V. Weber, J. Hutter, J. Chem. Phys. 128, 064107 (2008).
http://cp2k.berlios.de/

Title: An atomistic picture of the regeneration process in dye sensitized solar cells

Researchers:
Florian Schiffmann
Joost VandeVondele
Jürg Hutter

Institute: Institute of Physical Chemistry, University of Zürich
Description:

A highly efficient mechanism for the regeneration of the cis-bis(isothiocyanato)bis(2,2’-bipyridyl-4,4’-dicarboxylato)-ruthenium(II) sensitizing dye (N3) by I^- in acetonitrile has been identified by molecular dynamics simulations based on density functional theory using the CP2K program package. Barrier-free complex formation of the oxidized dye with both I^- and I_2^-, and facile dissociation of I_2^- and I_3^- from the reduced dye are key steps in this process. In situ vibrational spectroscopy confirms the reversible binding of I_2 to the thiocyanate group. Additionally, simulations of the electrolyte near the interface suggest that acetonitrile is able to cover the (101) surface of anatase with a passivating layer that inhibits direct contact of the redox mediator with the oxide, and that the solvent structure specifically enhances the concentration of I^- at a distance which further favors rapid dye regeneration.

References:
M. Grätzel, Nature 414 (2001) 338.
F. Schiffmann, J.Hutter, J.VandeVondele; J.Phys.:Condesed Matter, 20 (2008)
F. Schiffmann, J. VandeVondele, J. Hutter, A. Urakawa, R. Wirz ,A. Baiker; PNAS 107 4830 (2010)
F. Schiffmann, J. VandeVondele, J. Hutter, R. Wirz, A. Urakawa, A. Baiker J. Phys. Chem. C 114 8398 (2010)

Title: Robust periodic Hartree-Fock Exchange for large scale simulations using Gaussian basis sets

Researchers: Manuel Guidon
Jürg Hutter
Joost VandeVondele

Institute: Institute of Physical Chemistry, University of Zürich

Description:

Hartree-Fock exchange with a truncated Coulomb operator has recently been discussed in the context of periodic plane-waves calculations. In this work, this approach is extended to Gaussian basis sets, leading to a stable and accurate procedure for evaluating Hartree-Fock exchange at the Γ–point. Furthermore, it has been found that standard hybrid functionals can be transformed into short-range functionals without loss of accuracy. The well defined short-range nature of the truncated exchange operator can naturally be exploited in integral screening procedures and makes this approach interesting for both condensed and gas phase systems. The presented Hartree-Fock implementation is massively parallel and scales up to 10'000s of cores. This makes it feasible to perform highly accurate calculations on systems containing 1'000s of atoms or 10'000s of basis functions. The applicability of this scheme is demonstrated by calculating the cohesive energy of a LiH crystal close to the Hartree-Fock basis set limit and by performing an electronic structure calculation of a complete protein (Rubredoxin) in solution with a large and flexible basis set.

References: M. Guidon, F. Schiffmann, J. Hutter and J. VandeVondele, J. Chem. Phys. 128 (2008) 214104.
The CP2K developers group, http://cp2k.berlios.de/
M. Guidon, J. Hutter and J. VandeVondele, J. Chem. Theory and Comp. $\underline{5}$ 3010 (2009)
J. Paier, C. V. Diaconu, G. E. Scuseria, M. Guidon, J. VandeVondele and J. Hutter, Phys. Rv. B $\underline{80}$ 174114 (2009) M. Guidon, J. Hutter and J. VandeVondele, J. Chem. Theory and Comp. $\underline{6}$ 2348 (2010)

Title: Corrugated h-BN and graphene on transition metal support

Researchers: Marcella Iannuzzi
Yun Ding
Ari P. Seitsonen
Jürg Hutter

Institute: Institute of Physical Chemistry, University of Zürich

Description:

Several experimental studies based on STM have shown that h-BN and graphene epitaxially grown on metallic surfaces may display interesting Moire structures, with large periodicity, resulting from the lattice mismatch. In collaboration with an experimental group of the physic department of the university of Zurich, where high resolution STM techniques are developed to study complex nanostructures on surfaces, we investigate the structural and electronic properties of such interfaces. By performing structure optimizations based on DFT, we are able to reproduce the corrugated structures that are observed in experiment. From the analysis of the modification of the electronic structure, as induced by the interaction of BN or C with the metal, the nature of the chemical bonding can be investigated. The goal is to better understand why BN and graphene may display quite different behavior depending on the choice of the supporting metal and to investigate the possibility to employ these structures as templates for the self-assemblying of ordered molecular lattices.

References: M. Corso et al., Science 303, 217 (2004).
T. Brugger et al., Angewandte Chemie 49, 6120 (2010).

Title: DFT investigation of *h*-BN/Rh(111) interaction with water

Researchers: Yun Ding
Marcella Iannuzzi
Jürg Hutter

Institute: Institute of Physical Chemistry, University of Zürich

Description:

The boron nitride nanomesh is a periodic corrugated structure with a periodicity of 3.22 nm. It is formed by decomposition of borazine on a Rh(111) surface at high temperature. This single layer hexagonal boron nitride is regularly corrugated with 2nm diameter pores induced by the lattice mismatch between BN and Rh. In each unit cell, 13×13 BN atoms are on top of a 12×12 rhodium substrate. This structure is stable in gas phase, water and various other liquids. Experiments have shown that molecules can be trapped in the pores, making the nanomesh a perfect template for self-assembly of ordered molecules. Recently STM experiments performed after dosing small amounts of water to the empty nanomesh, indicate that water clusters are trapped in the pores. The distance between the water molecules from the STM image is close to the distance in ice clusters. Moreover, after dosing about 2L water to the surface, all pores are filled with ordered ice clusters, whereas no ordered ice cluster can be seen on the wire, which is less tightly bounded to Rh(111).
We investigate different water clusters on a flat BN layer, 6×6 BN layer with 4 layers of Rh atoms, and the full unit cell of the nanomesh based on density functional theory. Geometry optimization suggested that the three bright spots visible in the STM image with distances around 0.45 nm may not be due to water trimers but water hexamers. Binding energy calculations of water clusters adsorbed on a 6×6 BN layer with a 4-layers Rh slab representing the wire and the pore, respectively, didn't show any preference for the pore rather than the wire. This indicates a crucial role of the corrugation and the resulting modulation in electronic properties. We plan to perform *ab initio* molecular dynamics simulations of the nanomesh in liquid water in order to investigate the effect of the corrugation on water density, diffusivity, ordering of dipoles, and the hydrogen bond network.

References:

M. Corso et al., Science 303 217 (2004).
Haifeng Ma, et al. ChemPhysChem 11 399 (2010).

Title: Time-reversible Born-Oppenheimer Molecular Dynamics with Wannier Functions

Researchers: Valéry Weber [†] [+]
Anders M. N. Niklasson

Institute: [†] Institute of Physical Chemistry, University of Zürich and
[+] Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Description:

A Wannier-function formulation of time-reversible Born-Oppenheimer molecular dynamics is presented. The dynamics is determined by an extended Born-Oppenheimer Lagrangian with auxiliary Wannier functions and their time derivatives occurring as additional dynamical variables that evolve harmonically around the adiabatic propagation of the self-consistent electronic ground state. The auxiliary Wannier functions provide the initial guess to the self-consistent optimization procedure in which the phase of the ground state Wannier functions is determined by minimizing their distance to the auxiliary dynamical variables. The scheme provides a stable and efficient framework for energy conserving Born-Oppenheimer molecular dynamics.

References: A.M.N. Niklasson, C. J. Tymczak, and M. Challacombe, Phys. Rev. Lett., **97**, 123001 (2006).
A.M.N. Niklasson Phys. Rev. Lett. **100** 123004 (2008).
A.M.N. Niklasson et al., J. Chem. Phys. **130** 214109 (2009)
P. Steneteg at al., Phys. Rev. B **82** 075110 (2010)

Title: Photodegradation of a-Si:H-based solar cells: new insights from large scale atomistic simulations

Researchers: Petr A. Khomyakov[†]
Wanda Andreoni[†,+]
Nasser D. Afify[†,*]
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Institute: [†] IBM Zürich Research Laboratory, Säumerstrasse 4,
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Description:

A key problem in photovoltaic technology based on hydrogenated amorphous silicon (a-Si:H) is yield degradation of a-Si:H solar cells under illumination (the Staebler-Wronski effect). Although the photodegradation of the a-Si:H thin films and solar cells has been investigated for many decades since it was observed by Staebler and Wronski in 1977, this phenomenon has not received a well-established explanation that makes difficult a further development of a-Si:H-based solar cells in a systematic way. We approached this problem with large-scale classical and quantum atomistic molecular dynamics simulations to obtain reliable a-Si:H model structures [1]. Using the electronic structure calculations for these structures, we shed light on the nature of gap and band tail states in a-Si:H and proposed a defect model that is based on two types of microscopic defects such as a dangling bond and a region of strained bonds. This model is capable to interpret recent experimental finding of photo-induced volume expansion in a-Si:H thin films. The results of the present study suggest a new mechanism of the Staebler-Wronski effect, and can be helpful in finding ways of preventing this undesirable effect in the a-Si:H-based solar cells.

References:

[1] P. A. Khomyakov, W. Andreoni, N. D. Afify, and A. Curioni *to be published*; *ibid*, a paper at *Psi-K conference* (Berlin, 12-16 September 2010); *ibid*, a paper submitted to *MRS Spring Meeting* (San Francisco, 25-29 April 2011).

Title: Ab initio Molecular Dynamics Study of Li_2O_2, Li_2O and LiO_2 in propylene carbonate.

Researchers: Teodoro Laino[†]
Alessandro Curioni[†]

Institute: [†] IBM Zürich Research Laboratory, Säumerstrasse 4,
CH-8803 Rüschlikon

Description:

Of the various metal-air battery chemical couples, the Li-air battery is the most attractive due to the high voltage of the electrochemical discharge reaction and to the low density of the element involved. Upon discharge Li and O_2 may form, depending on the conditions, lithium peroxide (Li_2O_2), lithium oxide (Li_2O) and lithium superperoxide (LiO_2).
Although the increasing interest, it is a matter of fact that the practical performance of nowadays prototypes is far from being comparable to the theoretical one. Several studies, both experimental and theoretical[1,2] have tried to rationalize the source of such discrepancy, leading to a unanymous consensus of the need of understanding deeper the nature of the possible products of the discharge reaction (Li_2O_2, Li_2O and LiO_2) in aprotic solvents such as propylene carbonate (PC).
We have performed ab initio molecular dynamics simulation of lithium peroxide (Li_2O_2), lithium oxide (Li_2O) and lithium superperoxide (LiO_2) in propylene carbonate, in order to investigate the nature of these species in promising electrolytes (PC with LiPF6, PC with LiTFSI). We demonstrated the instability of PC versus all major discharge products, leading to formation of solid carbonates. This study has provided fundamental insights, pointing the importance of the choice of the solvent in the design of a battery like Li/air and opening the way to other solvents intrinsically more stable than PC.

References:

[1] J. S. Hummelshoj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K. S. Thygesen, A. C. Luntz, K. W. Jacobsen, and J. K. Norskov, *J. Chem Phys.* **2010**, *132*, 071101.

[2] T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, P.G. Bruce, *J. Am. Chem. Soc.* **2006**, *128*, 1390.

Title: Functionalized Tips Leading to Atomic-Resolution Force Microscopy

Researchers:
Nikolaj Moll[1]
Leo Gross[1]
Fabian Mohn[1]
Alessandro Curioni[1]
Gerhard Meyer[1]
Rainer Ebel[2]
Wael M. Abdel-Mageed[2]
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University of Aberdeen, AB24 3UE, UK

Description:

Performing atomic force microscopy (AFM) with a molecule or an atom at the tip, which significantly contributes to the tip-sample interaction, the resolution can be dramatically enhanced. The resolution crucially depends on the chemical nature of the tip termination. Employing a tip functionalized with a COmolecule a pentacene molecule is imaged with atomic resolution. The interactions between the CO tip and the pentacene are studied with first principles calculations The different energy contributions are analyzed, and the Pauli energy is computed. The source of the high resolution is Pauli repulsion, whereas van-der-Waals and electrostatic interactions only add a diffuse attractive background. To validate the usefulness of AFM with functionalized tips as an adjunct to the other tools available for organic structure analysis, the natural product cephalandole A is studied, which had previously been misassigned, and later corrected. The measurements together with first principle calculations demonstrate that the direct imaging of an organic compound with AFM facilitates the accurate determination of its chemical structure. The method may be developed further towards molecular imaging with chemical sensitivity, and could become generally useful in solving certain classes of natural product structures.

References:

[1] Leo Gross, Fabian Mohn, Nikolaj Moll, Peter Liljeroth, and Gerhard Meyer, Science **325**, 1110-1114 (2009).

[2] Leo Gross, Fabian Mohn, Nikolaj Moll, Gerhard Meyer, Rainer Ebel, Wael M. Abdel-Mageed, and Marcel Jaspars, Nat. Chem. **2**, 821-825 (2010).

Title: Molecular motion of amorphous silicone polymers

Researchers: Philip T. Shemella[†]
Teodoro Laino[†]
Oliver Fritz[+]
Alessandro Curioni[†]

Institute: [†] IBM Research – Zurich, Säumerstrasse 4,
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Description:

Silicone polymers based on poly(dimethylsiloxane) (PDMS) molecules have versatile applications in many fields because of their flexible molecular properties. When used for high-voltage insulation, for example, surfaces exposed to weather need to be hydrophobic because a hydrophilic surface could be the cause of electric discharges or leakage currents. Indeed, after damaging bursts of electric field, eventually a self-recovery of the hydrophobic surface occurs, which requires molecular diffusion and surface reconstruction for repair. We use large-scale, all-atom molecular dynamics simulations that enable an atomic-level description of molecular motion in mixed, amorphous, PDMS-based materials. The local properties that contribute to enhanced molecular motion are characterized based on their local structural and electrostatic environment [1]. With this knowledge, molecular components with desirable diffusion properties may be designed for improved material functionality.

References:

[1] P.T. Shemella, O. Fritz, T. Laino, A. Curioni, *to be published*

Title: Computer Simulation of Raman Peak Shifts in Strained Silicon Nanowires

Researchers: Christian Tuma
Alessandro Curioni

Institute: IBM Research – Zürich, Säumerstrasse 4, CH-8803 Rüschlikon

Description:

We perform computational studies of the peak shifts of the Raman active vibrational mode as a function of tensile strain applied to bulk silicon and silicon nanowires using an *ab initio* derived Tersoff interatomic potential. For the bulk, vertical relaxation of the unit cell turned out to be important for quantifying the strain—peak-shift relation. In the case of silicon nanowires the vibrational spectrum is dominated by thousands of acoustic-like phonons making it hard to identify Raman active modes. We introduce criteria for filtering Raman active modes based on the atomic displacements of the Raman active eigenmode in the bulk. Our test case is a [111] silicon nanowire with dimensions of 2.2 nm in diameter and a length of 55 nm (10'678 atoms).

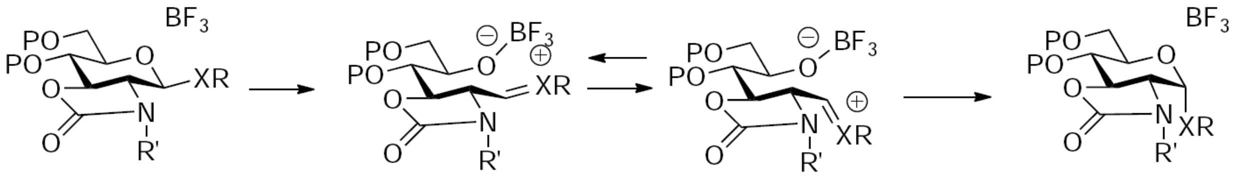
Title: Investigating the Mechanism of the *Endo*-cleavage Induced Anomerization of Pyranosides

Researchers:
Hiroko Satoh[1,2]
Shino Manabe[3]
Jürg Hutter[4]
Teodoro Laino[4]
Hans Peter Lüthi[1]

Institute/Group:
[1]Laboratory of Physical Chemistry, ETH Zurich, Switzerland
[2]National Institute of Informatics, Tokyo, Japan
[3]Advanced Science Institute, RIKEN, Saitama, Japan
[4]Institute of Physical Chemistry, University of Zürich, Switzerland

Description:

In carbohydrate chemistry, the mechanism of glycoside cleavage is a fundamental issue. Glycosides with an *N*-benzyl-2,3-*trans*-oxazolidinone group, a glycosyl donor for 1,2-*cis* stereoselective glycosylation, easily anomerize under mild acidic conditions.[1] Experimental evidence that the anomerization is caused by *endo*-cleavage rather than by *exo*-cleavage was obtained (Scheme below). *Endo*-cleavage in glycosides is rather uncommon, however.



P = Protecting group
X = O or S

Based on quantum chemical calculations, we found pronounced differences in the transition state energies between pyranosides with and without oxazolidinone groups attached.[2] This observation was confirmed by experiment. It was also shown that there is a strong correlation between the strain in the oxazolidinone group and the energy of the transition state.[3] Based on these studies, we are now exploring the reaction mechanism at greater detail performing *ab initio* molecular dynamics studies

References:

[1] Manabe, S.; Ishii, K.; Ito, Y. *J. Am. Chem. Soc.* **2006**, *128*, 10666
[2] Satoh, H.; Hutter J.; Lüthi H.P.; Manabe S.; Ishii K.; Ito Y. Eur. J. Org. Chem., **2009**, 1127
[3] Satoh, H.; Manabe, S.; Ito, Y.; Lüthi, H.P.; Laino, T.; Hutter, J. submitted for publication

Title: Electron Delocalization and Conjugation Efficiency in Linearly π-Conjugated Compounds: A Donor-Acceptor Based Scheme

Researchers:
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Maurizio Bruschi[2]
Hans Peter Lüthi[1]

Institute/Group:
[1]Laboratory of Physical Chemistry, ETH Zurich, Switzerland
[2]Università degli Studi Milano-Bicocca, Milan, Italy

Description:

For the design of donor/acceptor functionalized π-conjugated compounds, electron delocalization is a widely used concept to make structure-property predictions. We deveoloped a various schemes based on the Natural Bond Orbital (NBO) analysis to "measure" electron delocalization in π-conjugated compounds.[1] The method maps rather complex information obtained from quantum chemical calculations onto simple concepts used by the general chemist, and has been proven useful in a number of applications. For example, we were able to address the issues of efficiency of cross (*geminal*) versus through (*cis/trans*) conjugation.[2]

More recently, the method was extended towards the study of the conjugation efficiency, i.e. the ability of a conjugation path to support the interaction of donors and acceptors.[3] Different protocols were suggested and aplied towards the study of the conjugation efficiency in various polyactylenes. The study shows that the incorporation of triple bonds in a polyacetylene (PA) chain, to give polydiacetylene (PDA) or polytriacetylene (PTA), increases the total amount of π-delocalization, but, on the other hand, reduces the efficiency with which π-delocalization extends along the chain. This observation can be explained by means of the (donor-acceptor-)orbital-interaction patterns along the polymer chain. Whereas the interactions between like orbitals (double with double, triple with triple bonds) leads to smooth energy profiles, the interaction between unlike orbitals is usually smaller. The relatively weaker interaction between double and triple bonds results in a more limited flow of charge, i.e. a lesser degree of charge delocalization.[3]

References:

[1] M.G. Giuffreda, M. Bruschi, and H.P. Lüthi, *Chemistry Eur. J.*, **2004**, *10*, 5671-5680.
[2] M. Bruschi, M.G. Giuffreda, and H.P. Lüthi, *Chimia*, **2005**, *59,* 1-6.
[3] M. Bruschi, P.A. Limacher, J. Hutter, and H.P. Lüthi,
J. Chem. Theory Comput., **2009**, *5*, 506–514.

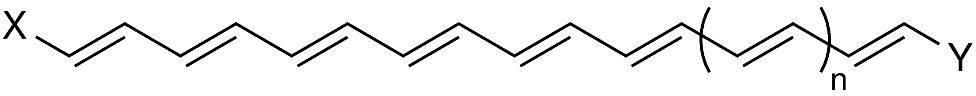
Title: Analyzing Bond Length Alternation and (Hyper)polarizability Properties of Polyacetylene Oligomer Chains using the Coulomb-Attenuating CAM-B3LYP Density Functional

Researchers:
Peter A. Limacher
Hans Peter Lüthi

Institute/Group: Laboratory of Physical Chemistry, ETH Zürich

Description:

Although electron delocalization is a concept rather than a physical observable, it is used to explain a plethora of properties in π conjugated systems such as the polyacetylenes. Its presence and strength can be estimated by inspection of the carbon-carbon bond distances, especially the difference in length of a single and a double bond. Electronic properties such as the dipole polarizability and hyperpolarizabilities are also expected to depend strongly on the amount of π conjugation present in the system.[1]



However, it is known that standard density functional theory fails in predicting accurate geometries and, more importantly, severely overestimates hyperpolarizabilities for polymers of extended size due to an incorrect electric field dependence modeled by the the commonly used exchange functionals. This led to the development of long-range corrected density functionals containing range dependent contributions of DFT and HF exchange. We could show that the CAM-B3LYP functional delivers accurate geometries for polyacetylenic systems and removes the overestimation of hyperpolarizabilities to large parts.[2] Recent CCSD investigations on elongated oligomer chains show that the second hyperpolarizability might be calculated accurately even at the HF level of theory.[3]

References:

[1] M. Bruschi, P.A. Limacher, J. Hutter, and H.P. Lüthi, *J. Chem. Theory Comput.*, **2009***, 5*, 506–514.
[2] P.A. Limacher, K.V. Mikkelsen, and H.P. Lüthi, *J. Chem. Phys.*, **2009**, *130*, 194114.
[3] P.A. Limacher, H.P. Lüthi, *J. Chem. Phys.*, *submitted*.

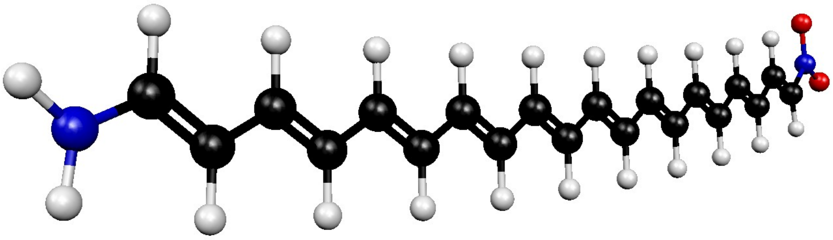
Title: A Systematic Analysis of the Structure and (Hyper-) polarizability of Donor-Acceptor Substituted Polyacetylenes Using a Coulomb-attenuating Density Functional

Researchers:
Stefano Borini
Peter A. Limacher
Hans Peter Lüthi

Institute/Group: Laboratory of Physical Chemistry, ETH Zurich

Description:

We performed a systematic investigation on all-*trans* polyacetylene chains of different lengths, end-capped with moieties of different donor or acceptor natures and different strengths, to infer useful structure/property relationship rules and behavioral patterns. The values for bond length alternation (BLA), longitudinal polarizability, and first and second hyperpolarizabilities have been computed by means of density functional theory with the Coulomb-attenuating B3LYP functional, using response theory. A comparison of the relative effect that each end-capping combination contributes to BLA, linear, and nonlinear optical coefficients has been performed. This results in useful insights and general rules to *ad hoc* tailoring the molecular response for a specific characteristic.[1]



The inspection of the optimized structures revealed that the donor-acceptor substituted polyacetylene chains are not perfectly linear, but take a slight bow- or S-shape, depending on the chosen substitution (bow shape for heteropolar- and S-shape for homopolar substitution).[2]

References:

[1] S. Borini, P.A. Limacher and H.P. Lüthi, *J. Chem. Phys.*, **2009**, *131*, 124105.
[2] S. Borini, P.A. Limacher and H.P. Lüthi, *J. Phys. Chem. A*, **2010**, *114*, 2221.

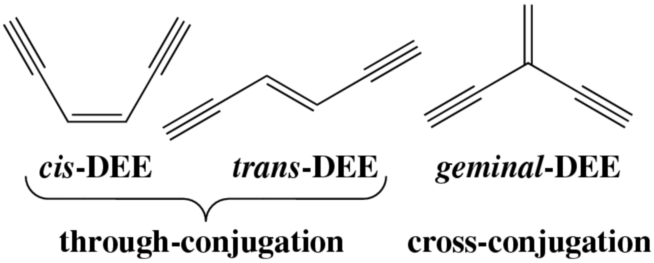
Title: Cross Conjugation: A Lost Case?

Researchers: Peter A. Limacher
Hans Peter Lüthi

Institute/Group: Laboratory of Physical Chemistry, ETH Zurich

Description:

Cross conjugation, even though very common in chemistry, has only sparsely been visited by experiment or by theory. Until very recently, this form of conjugation, where two separate conjugated branches are linked to the same carbon atom which is part of a (shared) double bond, was considered to be much less able to promote electron delocalization than through conjugation. Therefore, exploiting cross conjugation to design new materials was considered difficult and not very promising.



We showed recently that view, at least for neutral molecules in their electronic ground state, is essentially correct.[1] For cross conjugated radical ions the situation is different: there is appreciable charge delocalization across the bifurcation point, i.e. the point where the two conjugated branches meet. Simple Hückel molecular orbital considerations show that the connectivity pattern encountered in cross conjugation will lead to enhanced electron delocalization effects. This observation, confirmed by density functional calculations, also applies for electronically excited species. Therefore, cross conjugation may be exploited to build molecular switches or may be used to design devices such as molecular transistors.

References:

[1] P.A. Limacher and H.P. Lüthi, *WIREs Comput. Mol. Sci.*, *in press*.

Title: Superionic Conduction in Substoichiometric LiAl Alloy: An *Ab Initio* Study

Researchers:
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G. Miceli**
P. Raiteri***
M. Krack****
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**** Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

Description:

Based on the new *ab initio* molecular dynamics method by Kühne *et al.* [Phys. Rev. Lett. **98**, 066401 (2007)], we studied the mechanism of superionic conduction in substoichiometric Li-poor $Li_{1+x}Al$ alloys by performing simulations at different temperatures for an overall simulation time of about 1 ns. The dynamical simulations revealed the microscopic path for the diffusion of Li vacancies. The calculated activation energy (0.11 eV) and the prefactor (D_0=6.9×10^{-4} cm^2/s) for Li diffusivity via a vacancy-mediated mechanism are in good agreement with experimental NMR data. The calculation of the formation energies of different defects—Li and Al Frenkel pair and Li antisites—revealed that only Li^+ vacancies and Li_{Al} antisites are present in the stability range of the Zintl phase $-0.1<x<0.2$.

References: *Phys. Rev. Lett.* 103, 125901 (2009)

Title: Ensemble of Transition State Structures for the Cis−Trans Isomerization of *N*-Methylacetamide

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Description:

The cis−trans isomerization of *N*-methylacetamide (NMA), a model peptidic fragment, is studied theoretically in vacuo and in explicit water solvent at 300 K using the metadynamics technique. The computed cis−trans free energy difference is very similar for NMA(g) and NMA(aq), in agreement with experimental measurements of population ratios and theoretical studies at 0 K. By exploiting the flexibility in the definition of a pair of recently introduced collective variables (Branduardi, D.; Gervasio, F. L.; Parrinello, M. *J. Chem. Phys.* 2007, *126*, 054103), an ensemble of transition state structures is generated at finite temperature for both NMA(g) and NMA(aq), as verified by computing committor distribution functions. Ensemble members of NMA(g) are shown to have correlated values of the backbone dihedral angle and a second dihedral angle involving the amide hydrogen atom. The dynamical character of these structures is preserved in the presence of solvent, whose influence on the committor functions can be modeled using effective friction/noise terms.

References: *J. Phys. Chem. B,* 113 (37), pp 12521–12529 (2009)

Title: PLUMED: A portable plugin for free-energy calculations with molecular dynamics

Researchers:
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C. Camilloni**
D. Provasi***
P. Raiteri****
D. Donadio*****
F. Marinelli******,F. Pietrucci******
R.A. Broglia**
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Description:

Here we present a program aimed at free-energy calculations in molecular systems. It consists of a series of routines that can be interfaced with the most popular classical molecular dynamics (MD) codes through a simple patching procedure. This leaves the possibility for the user to exploit many different MD engines depending on the system simulated and on the computational resources available. Free-energy calculations can be performed as a function of many collective variables, with a particular focus on biological problems, and using state-of-the-art methods such as metadynamics, umbrella sampling and Jarzynski-equation based steered MD. The present software, written in ANSI-C language, can be easily interfaced with both Fortran and C/C++ codes.

References: *Computer Physics Communications*, 180 (10), 1961-1972 (2009)

Title: Phase Selection and Energetics in Chiral Alkaline Earth Tartrates and Their Racemic and *Meso* Analogues: Synthetic, Structural, Computational, and Calorimetric Studies

Researchers:
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A. V. Radha**, Petra Simoncic**, Alexandra Navrotsky **
Michele Parrinello
Anthony K. Cheetham***

Institute/Group:
ETH Zurich, Department of Chemistry and Applied Biosciences
*University of California, Santa Barbara
**University of California, Davis, ***University of Cambridge

Description:

The hydrothermal reactions of calcium, strontium, and barium with l-, *meso*-, and d,l-tartaric acid were examined from room temperature to 220 °C. We report the synthesis of 13 new phases and crystal structures of 11 alkaline earth tartrates, including an unusual I^3O^0 framework, [Ba(d,l-Tar)] (Tar = $C_4H_4O_6^{2-}$), with 3-D inorganic connectivity. Each alkaline earth exhibits different phase behavior in the reactions with the three forms of tartaric acid. Calcium forms unique l-, *meso*-, and d,l-tartrate phases which persist to 220 °C. Strontium forms three unique phases at lower temperatures, but above 180 °C reactions with l- and d,l-tartaric acid yield the *meso* phase. Likewise, Ba forms three unique low-temperature phases, but above 200 °C reactions with l- and *meso*-tartaric acid yield the d,l phase. Computational and calorimetric studies of the anhydrous calcium phases, [Ca(l-Tar)] and [Ca(*meso*-Tar)], strontium phases, [Sr(l-Tar)] and [Sr(*meso*-Tar)], and barium phases, [Ba(l-Tar)] and [Ba(d,l-Tar)], were performed to determine relative phase stabilities and elucidate the role of thermodynamic and kinetic factors in controlling phase behavior. The computational and calorimetric results were in excellent agreement. The [Ca(*meso*-Tar)] phase was found to be 9.1 kJ/mol more stable than the [Ca(l-Tar)] phase by computation (total electronic energies) and 2.9 ± 1.6 kJ/mol more stable by calorimetry (enthalpies of solution). The [Sr(*meso*-Tar)] phase was found to be 13.4 and 8.1 ± 1.4 kJ/mol more stable than [Sr(l-Tar)] by computation and calorimetry, respectively. Finally, the [Ba(l-Tar)] phase was found to be 6.4 and 7.0 ± 1.0 kJ/mol more stable than the [Ba(d,l-Tar)] phase. Our results suggest that the calcium and strontium *meso* phases are the most thermodynamically stable phases in their systems over the temperature range studied. The phase transitions are controlled by relative thermodynamic stabilities but also by a kinetic factor, likely the barrier to isomerization/racemization of the tartaric acid, which is hypothesized to preclude phase transformations at lower temperatures. In the barium system we find the [Ba(l-Tar)] phase to be the most thermodynamically stable phase at low temperatures, while the [Ba(d,l-Tar)] phase becomes the thermodynamic product at high temperatures, due to a larger entropic contribution.

References: *J. Am. Chem. Soc.*, 131 (42), pp 15375–15386 (2009)

Title: Signature of Tetrahedral Ge in the Raman Spectrum of Amorphous Phase-Change Materials

Researchers:
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*Dipartimento di Scienza dei Materiali and CNISM, Università di Milano-Bicocca, Via R. Cozzi 53, I-20125 Milano, Italy

Description:

We computed the Raman spectrum of amorphous GeTe by *ab initio* simulations and empirical bond polarizability models. The calculated spectrum is in very good agreement with experimental data and contains the signatures of all the peculiar local structures of the amorphous phase revealed by recent *ab initio* simulations, namely, tetrahedral Ge and defective octahedral sites for a fraction of Ge (mostly 4-coordinated) and for all Te (mostly 3-coordinated) atoms. In particular, the spectrum above 190 cm^{-1} is dominated by tetrahedral structures, while the most prominent peaks around 120 and 165 cm^{-1} are mainly due to vibrations of atoms in defective octahedral sites. Finally, the peak around 75 cm^{-1}, which dominates the spectrum in *HV* scattering geometry, is mostly due to vibrational modes involving threefold coordinated Te atoms.

References: *Phys. Rev. Lett.*, 104 (8), 085503 (2010)

Title: First-principles study of liquid and amorphous Sb_2Te_3

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Description:

Based on *ab initio* molecular-dynamics simulations, we generated models of liquid and amorphous Sb_2Te_3 of interest for applications as phase change material in optical and electronic data storage. The local geometries of Sb and Te atoms in *a*-Sb_2Te_3 are similar to that found in the extensively studied $Ge_2Sb_2Te_5$ and GeTe phase change materials already exploited for nonvolatile memory applications. Analysis of the vibrational properties and electronic structure of *a*-Sb_2Te_3 is presented and compared to the crystalline counterparts.

References: *Phys. Rev. B*, 81 (1), 014201 (2010)

Title: Molecular basis of cyclooxygenase enzymes (COXs) selective inhibition

Researchers:
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M. Bonomi
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F.L. Gervasio**
A. Cavalli***/****
E. Novellino*
M. Parrinello

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*Dipartimento di Chimica Farmaceutica e Tossicologica, Università degli Studi di Napoli "Federico II", Via D. Montesano, 49, I-80131 Naples, Italy;
**Computational Biophysics Group, Spanish National Cancer Research Center (CNIO), calle Melchor Fernández Almagro, 3, E-28029 Madrid, Spain;
***Department of Pharmaceutical Science, University of Bologna, Via Belmerolo 6, I-40126, Bologna, Italy; and
****Department of Drug Discovery and Development, Italian Institute of Technology, Via Morego 30, I-16163, Genoa, Italy

Description:

The widely used nonsteroidal anti-inflammatory drugs block the cyclooxygenase enzymes (COXs) and are clinically used for the treatment of inflammation, pain, and cancers. A selective inhibition of the different isoforms, particularly COX-2, is desirable, and consequently a deeper understanding of the molecular basis of selective inhibition is of great demand. Using an advanced computational technique we have simulated the full dissociation process of a highly potent and selective inhibitor, SC-558, in both COX-1 and COX-2. We have found a previously unreported alternative binding mode in COX-2 explaining the time-dependent inhibition exhibited by this class of inhibitors and consequently their long residence time inside this isoform. Our metadynamics-based approach allows us to illuminate the highly dynamical character of the ligand/protein recognition process, thus explaining a wealth of experimental data and paving the way to an innovative strategy for designing new COX inhibitors with tuned selectivity.

References: *PNAS*, 107 (12), 5411-5416 (2010)

Title: Graphite-diamond phase coexistence study employing a neural-network mapping of the *ab initio* potential energy surface

Researchers:
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H. Eshet
T.D. Kühne*
J. Behler**
M. Parrinello

Institute/Group:
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*Department of Physics and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA
**Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Description:

An interatomic potential for the diamond and graphite phases of carbon has been created using a neural-network (NN) representation of the *ab initio* potential energy surface. The NN potential combines the accuracy of a first-principles description of both phases with the efficiency of empirical force fields and allows one to perform a molecular-dynamics study, of *ab initio* quality, of the thermodynamics of graphite-diamond coexistence. Good agreement between the experimental and calculated coexistence curves is achieved if nuclear quantum effects are included in the simulation.

References: *Phys. Rev. B,* 81 (10), 100103(R) (2010)

Title: Colored-Noise Thermostats à la Carte

Researchers:
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G. Bussi*
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Institute/Group:
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*Università di Modena e Reggio Emilia and INFM-CNR-S3, via Campi 213/A, 41100 Modena, Italy

Description:

Recently, we have shown how a colored-noise Langevin equation can be used in the context of molecular dynamics as a tool to obtain dynamical trajectories whose properties are tailored to display desired sampling features. In the present paper, after having reviewed some analytical results for the stochastic differential equations forming the basis of our approach, we describe in detail the implementation of the generalized Langevin equation thermostat and the fitting procedure used to obtain optimal parameters. We also discuss the simulation of nuclear quantum effects and demonstrate that by carefully choosing parameters one can successfully model strongly anharmonic solids such as neon. For the reader's convenience, a library of thermostat parameters and some demonstrative code can be downloaded from an online repository.

References: *J. Chem. Theory Comput.*, 6 (4), pp 1170–1180 (2010)

Title: *Ab initio* quality neural-network potential for sodium

Researchers:
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R.Z. Khaliullin
T.D. Kühne*
J. Behler**
M. Parrinello

Institute/Group:
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**Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Description:

An interatomic potential for high-pressure high-temperature (HPHT) crystalline and liquid phases of sodium is created using a neural-network (NN) representation of the *ab initio* potential-energy surface. It is demonstrated that the NN potential provides an *ab initio* quality description of multiple properties of liquid sodium and bcc, fcc, and cI16 crystal phases in the *P-T* region up to 120 GPa and 1200 K. The unique combination of computational efficiency of the NN potential and its ability to reproduce quantitatively experimental properties of sodium in the wide *P-T* range enables molecular-dynamics simulations of physicochemical processes in HPHT sodium of unprecedented quality.

References: *Phys. Rev. B,* 81 (18), 184107 [8 pages] (2010)

Title: Enhanced Sampling in the Well-Tempered Ensemble

Researchers:
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M. Parrinello

Institute/Group: ETH Zurich, Computational Science, Department of Chemistry and Applied Biosciences, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

Description:

We introduce the well-tempered ensemble (WTE) which is the biased ensemble sampled by well-tempered metadynamics when the energy is used as collective variable. WTE can be designed so as to have approximately the same average energy as the canonical ensemble but much larger fluctuations. These two properties lead to an extremely fast exploration of phase space. An even greater efficiency is obtained when WTE is combined with parallel tempering. Unbiased Boltzmann averages are computed on the fly by a recently developed reweighting method. We apply WTE and its parallel tempering variant to the 2*d* Ising model and to a Gō model of HIV protease, demonstrating in these two representative cases that convergence is accelerated by orders of magnitude.

References:
J. Comput. Chem., 30, 1615 (2009) M. Bonomi et al.,
Phys. Rev. Lett., 104 (19), 190601 [4 pages] (2010)

Title: Linking well-Tempered Metadynamics Simulations with Experiments

Researchers: A. Barducci
M. Bonomi
M. Parrinello

Institute/Group: ETH Zurich, Computational Science, Department of Chemistry and Applied Biosciences, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

Description:

Linking experiments with the atomistic resolution provided by molecular dynamics simulations can shed light on the structure and dynamics of protein-disordered states. The sampling limitations of classical molecular dynamics can be overcome using metadynamics, which is based on the introduction of a history-dependent bias on a small number of suitably chosen collective variables. Even if such bias distorts the probability distribution of the other degrees of freedom, the equilibrium Boltzmann distribution can be reconstructed using a recently developed reweighting algorithm. Quantitative comparison with experimental data is thus possible. Here we show the potential of this combined approach by characterizing the conformational ensemble explored by a 13-residue helix-forming peptide by means of a well-tempered metadynamics/parallel tempering approach and comparing the reconstructed nuclear magnetic resonance scalar couplings with experimental data.

References: *Biophysical Journal*, 10 L44-L46 (2010)

Title: Targeting biomolecular flexibility with metadynamics

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***Theoretical Molecular Biophysics Group, Max-Planck Institute of Biophysics, Frankfurt am Main, Germany
****German Research School for Simulation Science, FZ-Juelich and RWTH, Germany

Description:

Metadynamics calculations allow investigating structure, plasticity, and energetics in a variety of biological processes spanning from molecular docking to protein folding. Recent theoretical developments have led to applications to increasingly complex systems and processes stepping up the biological relevance of the problem solved. Here, after summarizing recent technical advances and applications, we give a perspective of the method as a tool for enzymology and for the prediction of NMR and other spectroscopic data.

References: *Structure Biology,* 18 (2) 148-154 (2010)

Title: Probing the Mechanism of pH-Induced Large-Scale Conformational Changes in Dengue Virus Envelope Protein Using Atomistic Simulations

Researchers:
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A. Barducci
M. Parrinello

Institute/Group: ETH Zurich, Computational Science, Department of Chemistry and Applied Biosciences, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

Description:

One of the key steps in the infection of the cell by dengue virus is a pH-induced conformational change of the viral envelope proteins. These envelope proteins undergo a rearrangement from a dimer to a trimer, with large conformational changes in the monomeric unit. In this article, metadynamics simulations were used to enable us to understand the mechanism of these large-scale changes in the monomer. By using all-atom, explicit solvent simulations of the monomers, the stability of the protein structure is studied under low and high pH conditions. Free energy profiles obtained along appropriate collective coordinates demonstrate that pH affects the domain interface in both the conformations of E monomer, stabilizing one and destabilizing the other. These simulations suggest a mechanism with an intermediate detached state between the two monomeric structures. Using further analysis, we comment on the key residue interactions responsible for the instability and the pH-sensing role of a histidine that could not otherwise be studied experimentally. The insights gained from this study and methodology can be extended for studying similar mechanisms in the E proteins of the other members of class II flavivirus family.

References: *Biophysical Journal*, 99 (2), 588-594 (2010)

Title: First principles study of the optical contrast in phase change materials

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*Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via R. Cozzi 53, 20125 Milano, Italy

Description:

We study from first principles the optical properties of the phase change materials $Ge_2Sb_2Te_5$ (GST), GeTe and Sb_2Te_3 in the crystalline phase and in realistic models of the amorphous phase generated by quenching from the melt in *ab initio* molecular dynamics simulations. The calculations reproduce the strong optical contrast between the crystalline and amorphous phases measured experimentally and exploited in optical data storage. It is demonstrated that the optical contrast is due to a change in the optical matrix elements across the phase change in all the compounds. It is concluded that the reduction of the optical matrix elements in the amorphous phases is due to angular disorder in p-bonding which dominates the amorphous network in agreement with previous proposals (Huang and Robertson 2010 *Phys. Rev.* B 81 081204) based on calculations on crystalline models.

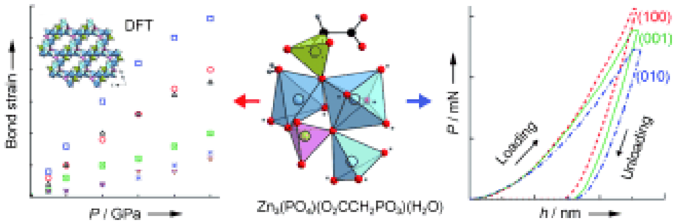
References:
Phys. Rev. B, 81, 081204 (2010) Huang and Robertson
Journal of Physics, Condenses Matter, 22 (31), 315801 (2010)

Titel: Probing the Mechanical Properties of Hybrid Inorganic–Organic Frameworks: A Computational and Experimental Study

Researchers:
M. Kosa
J.-C. Tan*
C.A. Merrill*
M. Krack**
A.K. Cheetham*
M. Parrinello

Institute/Group:
Computational Science, Department of Chemistry and Applied Biosciences, ETH Zürich c/o USI Campus, Via Giuseppe Buffi 13, 6900 Lugano (Switzerland)
*Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ (UK)
**Paul Scherrer Institut, 5232 Villigen PSI (Switzerland)

Description:



Elastic anisotropy in hybrids: First-principles DFT calculations and single-crystal nanoindentation experiments reveal the anisotropic mechanical behavior of a novel hybrid framework material that is akin to ZnO (see picture). Possible causes of discrepancies between the existing theories and experiments are discussed.

References: *ChemPhysChem*, 11 (11), 2332-2336 (2010)

Title: Protein motion and solvent effect in the Adenosine Deaminase ligand binding

Researchers:
V. Limongelli
L. Marinelli*
S. Cosconati*
C. La Motta**
S. Sartini**
F. Da Settimo**
E. Novellino*
M. Parrinello

Institute/Group:
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** Dipartimento di Scienze Farmaceutiche, Università di Pisa, Via Bonanno 6, 56126 Pisa, Italy

Description:

We have developed a new series of potent Adenosine Deaminase inhibitors containing the pyrazolo[1,5-a]pyrimidin-7-one ring and revealed their mechanism of binding both experimentally and theoretically. We have first performed a large number of docking calculations which are the most economical way of obtaining molecular information on ligand/protein interaction. Unfortunately these calculations failed to yield reliable results due to the dynamical character of the enzyme and the complex role of the solvent. Thus, we have used an extensive computational protocol based on the recently developed well-tempered metadynamics, which allows dealing with protein flexibility and solvation during ligand binding in an affordable computational time. This approach overcomes the major hurdles of the classic docking methods representing a valuable methodology which complements the experiments. This has allowed identifying with confidence the lowest energy binding modes of the most promising compound, 4-decyl-pyrazolo[1,5-a]pyrimidin-7-one, an important first step towards lead optimization and structure-based drug design.

References: Submitted to *Nature Chemistry*, August 2010

Title: First principle study of the LiNH2 / Li2NH transformation

Researchers: G. Miceli*
C.S. Cucinotta
M. Bernasconi*
M. Parrinello

Institute/Group: ETH Zurich, Computational Science, Department of Chemistry and Applied Biosciences, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland
*Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via R. Cozzi 53, 20125 Milano, Italy

Description:

Based on ab-initio simulations, we propose a scenario for the decomposition pathway of Li amide into Li imide and ammonia (2 LiNH2 -> Li2NH + NH3) which represents the first step of the dehydrogenation reaction of the LiNH2 / LiH mixture. Activation energies for formation of NH3 in LiNH2, for diffusion of charged species (H+, Li+) in LiNH2 and Li2NH, for H+/Li+ transfer across the LiNH2 / Li2NH interface and for NH3 desorption at the surface of LiNH2 and Li2NH have been computed from first principles. The results actually suggest that the transformation path depends on the surface-to-volume ratio of the LiNH2 crystallites.

References: Submitted 2010

Title: Static disorder and structural correlations in the low temperature phase of lithium imide

Researchers:
G. Miceli*
M. Ceriotti
M. Bernasconi*
M. Parrinello

Institute/Group:
ETH Zurich, Computational Science, Department of Chemistry and Applied Biosciences, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland
*Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via R. Cozzi 53, 20125 Milano, Italy

Description:

Based on ab-initio molecular dynamics simulations, we investigate the low temperature crystal structure of Li2NH which in spite of its great interest as H-storage material is still matter of debate. The dynamical simulations reveal a precise correlation in the fractional occupation of Li sites which leads average atomic positions in excellent agreement with diffraction data and solves inconsistencies of previous proposals.

References: Submitted 2010

Title: Multiple routes and milestones in the folding of HIV-1 protease monomer

Researchers:
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ETH Zurich, Computational Science, Department of Chemistry and Applied Biosciences, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland
*Computational Bipphysics Group, Structural Biology and Biocomputing Programme, Spanisch National Research Centre, C/Melchor Fdez. Almagro 3, 28029 Madrid, Spain

Description:

Proteins fold on a time scale incompatible with a mechanism of random search in conformational space thus indicating that somehow they are guided to the native state through a funneled energetic landscape. At the same time the heterogeneous kinetics suggests the existence of several different folding routes. Here we propose a scenario for the folding mechanism of the monomer of HIV–1 protease in which multiple pathways and milestone events coexist. A variety of computational approaches supports this picture.

These include very long all-atom molecular dynamics simulations in explicit solvent, an analysis of the network of clusters found in multiple high-temperature unfolding simulations and a complete characterization of free-energy surfaces carried out using a structure-based potential at atomistic resolution and a combination of metadynamics and parallel tempering.

Our results confirm that the monomer in solution is stable toward unfolding and show that at least two unfolding pathways exist. In our scenario, the formation of a hydrophobic core is a milestone in the folding process which must occur along all the routes that lead this protein towards its native state. Furthermore, the ensemble of folding pathways proposed here substantiates a rational drug design strategy based on inhibiting the folding of HIV–1 protease.

References: Submitted 2010

Title: A chirality-based metrics for free-energy calculations in biomolecular systems

Researchers:
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D. Branduardi*
M. Bonomi
M. Parrinello

Institute/Group:
ETH Zurich, Computational Science, Department of Chemistry and Applied Biosciences, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland
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Description:

In this work we exploit the chirality index introduced in [A. Pietropaolo et al. Proteins (2008) 70, 667-677] as an effective descriptor of the secondary structure to explore the complex free-energy landscape of proteins. We introduce the chirality index as an alternative metrics in the path collective variables (PCVs) framework and we show in the prototypical case of the C- terminal domain of immunoglobulin binding protein GB1 that relevant configurations can be efficiently sampled in combination with well-tempered metadynamics.
While the projections of the configurations found onto a variety of different descriptors show full consistency with previously reported calculations, this approach provides a unifying perspective of the folding mechanism which was not possible with the previous formulation of PCVs.

References: Submitted 2010

Title: A self-learning algorithm for biased molecular dynamics

Researchers:
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M. Ceriotti
M. Parrinello

Institute/Group: ETH Zurich, Computational Science, Department of Chemistry and Applied Biosciences, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

Description:

A new self-learning algorithm for accelerated dynamics, reconnaissance metadynamics, is proposed that is able to work with a very large number of collective coordinates. Acceleration of the dynamics is achieved by constructing a bias potential in terms of a patchwork of one-dimensional, locally valid collective coordinates. These collective coordinates are obtained from trajectory analyses so that they adapt to any new features encountered during the simulation. We show how this methodology can be used to enhance sampling in real chemical systems citing examples both from the physics of clusters and from the biological sciences.

References: In press PNAS 2010

Title: High Resolution Infrared Spectroscopy and Global Vibrational Analysis for the CH_3D and CHD_3 Isotopomers of Methane.

Researchers:
O. N. Ulenikov*
E. S. Bekhtereva*
S. Albert**
S. Bauerecker***
H. Hollenstein**
M. Quack**

Institute/Group:
* Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, RU-634050 Tomsk,
** Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich
*** Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D-38106 Braunschweig

Description:

We report infrared spectra of CH_3D and CHD_3 in the range 2900 to 9000 cm^{-1} measured with the Zürich high resolution Fourier transform infrared (FTIR) interferometer Bruker IFS 125 prototype (ZP 2001) at 80K in a collisional-cooling cell with optical paths ranging from 5 to 10 m. In all, 57 new ro-vibrational bands of CH_3D and 40 for CHD_3 were assigned and analysed. Using a strategy of the direct assignment of the $J = 0$ states of excited vibrational levels, precise experimental values of the band centres with uncertainties in the range of about 0.0001 to 0.0003 cm^{-1} were obtained. Including 15 previously known band centres of CH_3D and 12 previously known band centres of CHD_3, these data were used as the initial information for the determination of the harmonic frequencies, anharmonic coefficients, and vibrational resonance interaction parameters in an effective hamiltonian. A joint set of 64 parameters reproduces the 124 experimental vibrational energies of both molecules up to 6500 cm^{-1} with a root mean deviation of $d_{rms} = 0.73$ cm^{-1}. The results are discussed in relation to intramolecular dynamics on a global potential hypersurface of methane, intramolecular vibrational redistribution, and the spectroscopy of the atmospheres of the earth and planetary systems. Computations are used to analyse the spectra.

References:

O. N. Ulenikov, E. S. Bekhtereva, S. Albert, S. Bauerecker, H. Hollenstein, M. Quack, *Mol. Phys.* **108**, 1209-1240 (2010).

Title: High resolution spectrum and rovibrational analysis of the ν_1 CH-stretching fundamental in CHD_2I

Researchers: S. Albert
C. Manca Tanner
M. Quack

Institute/Group: Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

With the long-term aim of understanding the detailed mechanism of intramolecular vibrational redistribution (IVR) from the CH-stretching mode to the low-frequency modes of the heavy atom framework, we have studied the infrared spectrum of CHD_2I below 3100 cm^{-1} and around 6000 cm^{-1} using high-resolution Fourier transform infrared spectroscopy. A detailed analysis of the ν_1 fundamental based on 1349 assigned transitions results in an accurate band centre $\tilde{\nu}_1^0 = 3029.67904(5)$ cm^{-1} and further spectroscopic parameters are summarised in Table 3. Numerous local perturbations are observed in the analysis. The results are discussed in relation to previous spectroscopic work on this molecule and to IVR processes observed previously by fs pump-probe spectroscopy in our group. Computations are used to analyse the spectra.

References:

S. Albert, C. Manca Tanner, M. Quack, Mol. Phys. **108**, 2403 – 2426 (2010)

Title: Synchrotron Based High Resolution Infrared Spectroscopy of Naphthalene ($C_{10}H_8$): Rovibrational Analysis of the ν_{46} Band.

Researchers:
S. Albert*
K. K. Albert*
Ph. Lerch**
M. Quack*

Institute/Group:
* Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich
** Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen

Description:

We report a rotationally resolved analysis of the high resolution FTIR spectrum of the simplest Polycyclic Aromatic Hydrocarbon (PAH), naphthalene. The spectrum has been measured with a new high resolution FTIR spectrometer connected to the Swiss Light Source (SLS) at the Paul-Scherrer-Institute (PSI). Due to the high brightness of the synchrotron radiation in the spectral region of interest and the high resolution of the new interferometer, it was possible to record the rotationally resolved infrared spectrum of naphthalene and to analyse the ν_{46} band (ν_0 = 782.330753 cm^{-1}). The results are discussed in relation to the Unidentified Infrared Band (UIB) found in interstellar spectra at 11.25 µm. Computations are used to simulate and analyse the complex spectra.

References:

S. Albert, K. K. Albert, P. Lerch, M. Quack, in *Proceedings of the 17th Symposium on Atomic, Cluster and Surface Physics 2010 (SASP 2010), Obergurgl Austria, 24 to 29 January 2010* (Eds.: I. Milewski, A. Kendl, P. Scheier), Innsbruck University Press (IUP), Innsbruck (2010), 134-137 and manuscript in preparation.

Title: Cavity enhanced saturation spectroscopy of NH_3 in the near infrared.

Researchers:
P. Dietiker,
M. Quack
A. Schneider
G. Seyfang
F. Ünlü

Institute/Group: Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

Quite often a line by line analysis of measured infrared (IR)-spectra is complicated due to the congestion of overlapping lines and resolution being limited by the Doppler widths. If only a few lines are overlapped, a line shape analysis for overlapping lines can result in reliable line positions. But the method will fail if the lines are too close or if too many lines are overlapped. Then sub-Doppler methods have to be applied in order to reveal the exact line positions. We applied cavity enhanced saturation spectroscopy to determine the line positions of congested parts of the near-IR spectrum of NH_3 around 6600 cm^{-1}. The measured dip positions are compared to line positions obtained from a multiline fit of measured Fourier transform infrared (FTIR) spectra recorded with an instrumental bandwidth significantly smaller than the Doppler width. Computations are used to analyse the spectra.

References:

P. Dietiker, M. Quack, A. Schneider, G. Seyfang, F. Ünlü, in *Proc. of the 17th SASP 2010* (Eds.: I. Milewski, A. Kendl, P. Scheier), Innsbruck University Press (IUP), Innsbruck (2010), 161-164, and manuscript in preparation.

Title: Supersonic Jet Isotope Selective Infrared Spectroscopy of the Second Overtone Polyad of the NH-Stretching Vibration in $C_6H_5NH_2$, $C_6D_5NH_2$ and C_6H_5NDH.

Researchers:
E. Miloglyadov
A. Kulik
M. Quack
G. Seyfang

Institute/Group: Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

We report the spectra of the second NH-stretching overtone (polyad with N=3) of rotationally cold $C_6H_5NH_2$, $C_6D_5NH_2$ and C_5H_5NHD isotopomers of aniline measured by mass and isotope selective overtone spectroscopy (ISOS) in a molecular beam. Comparison of the assignments for $C_6D_5NH_2$ and normal aniline $C_6H_5NH_2$ confirmed the applicability of the normal mode model to the NH_2-infrared-chromophore in aniline. To extract the tunnelling splitting the second NH-stretching overtone spectrum in the C_5H_5NHD has been measured at different rovibrational temperatures. The further decrease of the tunneling splitting in C_6H_5NHD with higher NH-stretching excitation demonstrates the inhibiting nature of the NH-stretching mode. Computations are used to analyse the spectra.

References:

E. Miloglyadov, A. Kulik, M. Quack, G. Seyfang, in *Proceedings of the 17th Symposium on Atomic, Cluster and Surface Physics 2010 (SASP 2010), Obergurgl Austria, 24 to 29 January 2010* (Eds.: I. Milewski, A. Kendl, P. Scheier), Innsbruck University Press (IUP), Innsbruck (2010), 216-219.

Title: CH Stretching Overtone Spectra of $^{12}CH_3I$ and $^{12}CHD_2I$ Measured by NIR-Pump UV -Probe Experiments.

Researchers:
E. Miloglyadov
V. Krylov
A. Kushnarenko
M. Quack
G. Seyfang

Institute/Group: Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

We report the vibrational spectra of the first CH-stretching overtone of rotationally cold $^{12}CH_3I$ and CHD_2I, measured by isotope selective overtone spectroscopy (ISOS) in a molecular beam. The action spectra of $^{12}CH_3I$ measured at a rotational temperature of 5 K differ significantly from the room temperature FTIR spectrum, which may be indicative of incomplete redistribution of vibrational energy (IVR) at a delay time of about 100 ns. The observed vibrational structure is attributed to the combination bands of sets of the CI-stretching vibrations with levels strongly coupled to the overtone of the CH-stretching vibration. Computations are used to analyse the experimental results.

References:

E. Miloglyadov, V. Krylov, A. Kushnarenko, M. Quack, G. Seyfang, in *Proceedings of the 17th Symposium on Atomic, Cluster and Surface Physics 2010 (SASP 2010), Obergurgl Austria, 24 to 29 January 2010* (Eds.: I. Milewski, A. Kendl, P. Scheier), Innsbruck University Press (IUP), Innsbruck (2010), 220-223, and manuscript in preparation.

Title: Rotational Line Shifts due to Parity Violation in Chiral Molecules

Researchers: J. Stohner*
M. Quack**

Institute/Group: * Zürich University of Applied Sciences (ZHW), ICBC Institute of Chemistry & Biological Chemistry, 8820 Wädenswil
** Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

We extend our earlier theoretical studies on spectroscopic signatures of molecular parity violation [1] by investigating the influence on rotational spectra. Therefore, we determine vibrationally averaged moment of inertia tensors with anharmonic vibrational wavefunctions including effects from parity violating potentials. This approach goes beyond the calculation of the influence on rotational constants via changes in the geometry and therefore also in the moment of inertia tensor [2]. It turns out that the rotational constants are very strongly influenced by parity violation when including excitation in bending modes. These investigations help our understanding of fundamental symmetry violation in nature.

References:

1 J. Stohner, M. Quack, in *Proceedings of the 17th Symposium on Atomic, Cluster and Surface Physics 2010 (SASP 2010), Obergurgl Austria, 24 to 29 January 2010* (Eds.: I. Milewski, A. Kendl, P. Scheier), Innsbruck University Press (IUP), Innsbruck (2010), 249-253.
2 M. Quack, J. Stohner, Phys. Rev. Lett. **84**, 3807 (2000)

Title: Cavity Ring-Down (CRD) Spectrum of the $\nu_2 + 2\nu_3$ Subband of CH_4 in a Supersonic Expansion Below 40 K

Researchers:
M. Suter
C. Manca Tanner
M. Quack

Institute/Group: Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

We have studied the $N = v_1 + v_3 + 0.5(v_2 + v_4) = 2.5$ polyad of $^{12}CH_4$ [1], composed of 20 overtone and combination bands. The CRD measurements performed in our group some years ago [2] were the first using supersonic expansions; they provided first high resolution analyses and an accurate location of the vibrational level $v_2 + 2v_3$ at 7510.3378 cm^{-1}. Since these measurements, we have devoted a large effort to improve the supersonic expansion itself. We reinvestigate this spectral region at lower temperatures. In a first approach, we use the assignment of the $v_2 + 2v_3$ band already known in our group to better estimate the rotational temperature of the expansion. As we obtain spectra at very low temperatures, these measurements can also be considered as a further investigation of nuclear spin symmetry conservation in CH_4 in a supersonic expansion at temperatures below 40 K. Computations are used to analyze the spectra.

References:

1. M. Suter, C. Manca Tanner, M. Quack, in *Proceedings of the 17th Symposium on Atomic, Cluster and Surface Physics 2010 (SASP 2010), Obergurgl Austria, 24 to 29 January 2010* (Eds.: I. Milewski, A. Kendl, P. Scheier), Innsbruck University Press (IUP), Innsbruck (2010), 254-257.
2. M. Hippler and M. Quack, *J. Chem. Phys.* **116**, 6045 (2002).

Title: Handbook of High-Resolution Spectroscopy

Researchers: M. Quack
F. Merkt

Institute/Group: Physical Chemistry, ETH Zürich

Description:

This three volume handbook [1] describes the state of the art of current theory and experiment for high-resolution spectroscopy in numerous articles by experts in the field.
It is the first comprehensive survey of the field since the famous 3 volume textbook series by G. Herzberg, of which the last volume appeared in 1966.

References:

1. M. Quack, F. Merkt (eds.), *Handbook of High-Resolution Spectroscopy*, Wiley Chichester, 2010, in press.

Title: Molecular Quantum Mechanics and Molecular Spectra, Molecular Symmetry, and Interaction of Matter with Radiation

Researchers: F. Merkt
M. Quack

Institute/Group: Physical Chemistry, ETH Zürich

Description:

The basic experimental and theoretical concepts underlying molecular spectroscopy are presented. The equations and relations needed in practical applications of high-resolution spectroscopy are provided. Group theoretical tools and their use in high-resolution spectroscopy are introduced and illustrated by simple examples. Time-dependent processes and quantum dynamics are presented and discussed in relation to spectroscopic observations. Coherent and incoherent radiative excitation and radiationless transitions are treated in relation to applications in molecular spectroscopy.

References:

F. Merkt, M. Quack, in *Handbook of High-Resolution Spectroscopy* (Eds.: M. Quack, F. Merkt), Wiley, Chichester, Vol. 1, 2010, in press.

Title: Fundamentals of Rotation-Vibration Spectra

Researchers: S. Albert
K. K. Albert
H. Hollenstein
C. Manca Tanner
M. Quack
G. Seyfang

Institute/Group: Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

We provide a survey of fundamental aspects of vibration–rotation spectra. A basic understanding of the concepts is obtained from a detailed discussion of vibration–rotation spectra of diatomic molecules with only one vibrational degree of freedom. This includes approximate and exact separation of rotation and vibration, effective spectroscopic constants, the effects of nuclear spin and statistics, and transition probabilities derived from the form of the electric dipole moment function. The underlying assumptions and accuracy of the determination of molecular structure from spectra are discussed. Polyatomic molecules show many interacting vibrational degrees of freedom. Energy levels and spectra are discussed on the basis of normal coordinates and effective Hamiltonians of interacting levels in Fermi resonance, and in more complex resonance polyads arising from anharmonic potential functions. The resulting time-dependent dynamics of intramolecular energy flow is introduced as well. Effective Hamiltonians for interacting rotation–vibration levels are derived and applied to the practical treatment of complex spectra. Currently available computer programs aiding assignment and analysis are outlined.

References:

S. Albert, K. K. Albert, H. Hollenstein, C. Manca Tanner, M. Quack, in *Handbook of High-Resolution Spectroscopy* (Eds.: M. Quack, F. Merkt), Wiley, Chichester, Vol. 1, 2010, in press.

Title: Conventions, Symbols, Quantities, Units and Constants for High Resolution Molecular Spectroscopy

Researchers: J. Stohner
M. Quack

Institute/Group: * Zürich University of Applied Sciences (ZHW), ICBC Institute of Chemistry & Biological Chemistry, 8820 Wädenswil
** Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

A summary of conventions, symbols, quantities, units, and constants which are important for high-resolution molecular spectroscopy is provided. In particular, great care is taken to provide definitions which are consistent with the recommendations of the IUPAC "Green Book", from which large parts of this article are drawn. While the recommendations in general refer to the SI (Système International), the relation to other systems and recommendations, which are frequently used in spectroscopy, for instance atomic units, is also provided. A brief discussion of quantity calculus is provided as well as an up-to-date set of fundamental constants and conversion factors together with a discussion of conventions used in reporting uncertainty of experimentally derived quantities. The article thus should provide an ideal compendium of many quantities of practical importance in high-resolution spectroscopy.

References:

J. Stohner, M. Quack, in *Handbook of High-Resolution Spectroscopy* (Eds.: M. Quack, F. Merkt), Wiley, Chichester, Vol. 1, 2010, in press.

Title: Global Analytical Potential Energy Surfaces for High Resolution Molecular Spectroscopy and Reaction Dynamics

Researchers: R. Marquardt*
M. Quack**

Institute/Group: * Laboratoire de Chimie Quantique, Institut de Chimie, Université de Strasbourg, 4, F-67081 Strasbourg
** Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

Analytical representations of potential energy hypersurfaces for the nuclear motion in polyatomic molecules from ab initio theory and experiment are discussed in a general way. The qualification of potential hypersurface representations from ab initio theory regarding the description of experimental data from rovibrational high-resolution spectroscopy and chemical reaction kinetics is analyzed in more detail for a restricted group of molecules including methane, CH4, ammonia, NH_3, H_2O_2, and $(HF)_2$. Current methods for the derivation of analytical representations of potential energy surfaces as well as some applications are reviewed.

References:
R. Marquardt, M. Quack, in *Handbook of High-Resolution Spectroscopy* (Eds.: M. Quack, F. Merkt), Wiley, Chichester, Vol. 1, 2010, in press.

Title:	Fundamental Symmetries and Symmetry Violations from High Resolution Spectroscopy
Researchers:	M. Quack
Institute/Group:	Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

Parity (P), together with time reversal symmetry (T) and charge conjugation (C) constitute a fundamental set of discrete symmetries in physics. We review the current status of molecular parity violation in the framework of the fundamental symmetries of physics in general and in relation to intramolecular quantum dynamics. Work of the last decade in electroweak quantum chemistry, including the weak force of the standard model of particle physics in quantum calculations on chiral molecules, has resulted in an increase of the predicted parity violating energies by one to two orders of magnitude. This results in a new outlook on possible experiments which are discussed. We discuss furthermore the conceptual foundations of molecular symmetry breaking (spontaneous, de facto, de lege) in relation to molecular chirality, the evolution of biomolecular homochirality and irreversibility and the origin of the second law of thermodynamics. It is shown that there arise closely parallel situations in the lack of our current understanding of the true physical origins of all three phenomena. For molecular chirality some of the fundamental questions have been answered quantitatively by recent theory. The new theoretical approaches are summarized briefly, as well as some current results. Recent results on a new molecular isotope effect arising from parity violation are reviewed as well.

References:

M. Quack, in *Handbook of High-Resolution Spectroscopy* (Eds.: M. Quack, F. Merkt), Wiley, Chichester, Vol. 1, 2010, in press.

Title: High Resolution Fourier Transform Infrared Spectroscopy

Researchers:
S. Albert
K. K. Albert
M. Quack

Institute/Group: Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

Recent developments and applications of high-resolution Fourier transform spectroscopy are reviewed. A short historical summary of the development of high-resolution interferometric Fourier transform infrared (FTIR) spectrometers is given and the possibilities of the currently most highly resolving FTIR spectrometers, including a current prototype built for the Zürich group at the Swiss Light Source SLS as a synchrotron light source, are discussed. A short description of the principles of FTIR spectroscopy is given and the resolution of current spectrometers is illustrated by FTIR spectra of CO, CO_2 OCS, N_2O, CS_2, and CH_4 and its isotopomers. The computational tools necessary to analyze FTIR spectra are described briefly. As examples of rovibrational analysis of more complex spectra, selected molecules $CHCl_2F$, CDBrClF, pyridine (C_6H_5N) and pyrimidine ($C_4H_4N_2$), and naphthalene ($C_{10}H_8$) are discussed. The spectrum of $CHCl_2F$, a fluorochlorocarbon, is of interest for a better understanding of the chemistry of the Earth's atmosphere. It also possesses an isotopically chiral isotopomer $CH_{35}Cl_{37}ClF$ analyzed in natural abundance. CDBrClF is a chiral molecule and therefore the analysis of its rovibrational spectra provides the basis for carrying out further experiments toward the detection of molecular parity violation. The analyses of the pyridine, pyrimidine, and naphthalene FTIR spectra illustrate the potential of the new generation of FTIR spectrometers in the study of spectra and rovibrational dynamics of aromatic systems and molecules of potential biological interest. In particular, naphthalene is a prototype molecule useful in gaining an understanding of the unidentified infrared bands (UIBs) detected in several interstellar objects. Computations support the analysis of spectra.

References:

S. Albert, K. K. Albert, M. Quack, in *Handbook of High-Resolution Spectroscopy* (Eds.: M. Quack, F. Merkt), Wiley, Chichester, Vol. 2, 2010, in press.

Title: High Resolution FTIR and Diode Laser Spectroscopy of Supersonic Jets

Researchers: M. Snels*
V. Horká-Zelenková**
H. Hollenstein**
M. Quack**

Institute/Group: * Istituto di Scienze dell' Atmosfera e del Clima (ISAC), Sezione di Roma, Consiglio Nazionale delle Ricerche (CNR), I-00133 Roma
** Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

Fourier transform infrared (FTIR) spectrometers and tunable diode lasers in combination with a supersonic molecular beam expansion are a perfect tool for the investigation of molecules, ions, and radicals at low temperatures. The internal degrees of freedom of the molecules are adiabatically cooled to very low temperatures and thus only low-lying energy levels are populated. The reduction of the number of populated levels at low temperatures makes the assignment of the spectra much easier as compared to the congested room-temperature spectra. Under certain conditions, the Doppler linewidths are greatly reduced, corresponding to very low effective translational temperatures. Supersonic expansion also provides a suitable method for producing and investigating van der Waals clusters and hydrogen-bonded complexes. Unstable species such as radicals and ions can be efficiently produced and studied in a molecular beam. The low rotational temperature allows for the study of nuclear spin symmetry conservation or conversion between nuclear spin isomers. A molecular beam expansion can be obtained by expanding gas through a slit or a circular nozzle. Both expansion geometries can be used in combination with a multipass optical setup and with cavity ring down spectroscopy, which enhances the effective absorption path length. Cooling of the molecules can be promoted by seeding in noble gases. This article summarizes the general aspects of the experimental technique as well as current developments. To demonstrate how powerful the combination of a molecular beam expansion with tunable diode laser and FTIR spectroscopy can be, we report results on some important current examples. Computations aid the analysis of spectra.

References:

M. Snels, V. Horká-Zelenková, H. Hollenstein, M. Quack, in *Handbook of High-Resolution Spectroscopy* (Eds.: M. Quack, F. Merkt), Wiley, Chichester, Vol. 2, 2010, in press.

Title: Mass and Isotope Selective Infrared Spectroscopy

Researchers:
M. Hippler*
E. Miloglyadov**
M. Quack**
G. Seyfang**

Institute/Group:
* Dept of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom
** Group for Molecular Kinetics and Spectroscopy, Physical Chemistry, ETH Zürich

Description:

Recent advances in laser spectroscopic techniques make it possible to obtain mass- and isotope-selective infrared spectra of gas-phase species at high resolution and reduced hot-band spectral congestion. In these techniques, infrared excitation is coupled with ultraviolet multiphoton ionization and detection of the resulting ions in a mass spectrometer, which allows the separation of contributions of different isotopomers and, more generally, species of different mass in a mixture. In combination with jet cooling techniques, spectra are obtained for very cold molecules. These spectra can then be analyzed to extract information on dynamical processes such as intramolecular vibrational redistribution or tunneling and rearrangement processes, and on how intramolecular dynamics is influenced by vibrational excitation and isotope effects. In this review, we introduce isotope-selective infrared spectroscopic techniques and present some selected applications on isotope effects and intramolecular dynamics of vibrationally excited chloroform, aniline, and benzene obtained by isotope-selective infrared spectroscopy. Computations aid the analyses of spectra.

References:

M. Hippler, E. Miloglyadov, M. Quack, G. Seyfang, in *Handbook of High-Resolution Spectroscopy* (Eds.: M. Quack, F. Merkt), Wiley, Chichester, Vol. 2, 2010, in press.

Title: Theoretical Raman Optical Activity Study of the β Domain of Rat Metallothionein

Researchers: Sandra Luber
Markus Reiher

Institute/Group: Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

We presented the calculated vibrational Raman optical activity (ROA) spectrum of the β domain of rat metallothionein, which is the by far largest molecule for which full ab initio ROA calculations were performed up to date with more than 400 atoms. While ROA signatures of regular secondary structure elements like β-sheets and α-helices can be conveniently studied in terms of small model structures, this is no longer possible for more irregular proteins like metallothionein. The only secondary structure elements occurring in the molecule are turns, in particular β turns. Our calculations revealed that especially bands in the wavenumber range from about 1100 to 1400 cm^{-1} may be employed as signatures of such β turns. This was also found in comparison to experimental data. In addition, good agreement between calculated and experimental spectra was found.

References: S. Luber, M. Reiher, *J. Phys. Chem. B*, **2010**, *114*, 1057.

Title: Subvalent Organometallic Compounds of the Alkaline Earth Metals in Low Oxidation States

Researchers:
Sven Krieck[1]
Lian Yu[2]
Markus Reiher[2]
Matthias Westerhausen[1]

Institute/Group:
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[2]Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

Alkaline earth metals (Ae) are regarded as redox-inactive, and their chemistry is dominated by the oxidation state +2. Nevertheless, in recent years several compound classes with alkaline earth metals in low oxidation states were investigated. Various concepts proved to be valid for the stabilization of such compounds and are discussed in this review. In the solid state, subvalency can be achieved by offering a matrix that takes over the excess electrons as, for example, in subnitrides. This fact leads to normal-valent alkaline earth metals with electrons free to move between alkaline-earth-metal-containing cages with or without a metal matrix. Another concept focuses on the synthesis of $[Ae_2]^{2+}$ cations with adequate substituents. The homodinuclear Ae–Ae bonds exhibit binding energies that should allow the synthesis of molecules such as R–Ae–Ae–R. The synthesis of magnesium derivatives succeeded by use of extremely bulky bidentate ligands with a delocalized anionic charge. The heavier alkaline earth metal derivatives are investigated by quantum chemical methods. Another possibility takes advantage of the fact that the first and second ionization potentials of the alkaline earth metals are clearly separated. Therefore, an arene with an extended π-system having an energy level between the two ionization potentials should be able to overtake only one electron, which leads to Ae^+ cations. Sophisticated procedures allowed the synthesis of a calcium(I) derivative, $[(thf)_3Ca(\eta^6\text{-}\eta^6,\eta^6\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3)Ca(thf)_3]$, and such structures are investigated by quantum chemical methods also for the other alkaline earth metals.

References: S. Krieck, L. Yu, M. Reiher, M. Westerhausen, *Eur. J. Inorg.Chem.*, **2010**, *2010*, 197.

Title: Enhancement and de-enhancement effects in vibrational resonance Raman optical activity

Researchers:
Sandra Luber[1]
Johannes Neugebauer[2]
Markus Reiher[1]

Institute/Group:
[1]Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich
[2]Leiden Institute of Chemistry, Leiden University, 2300 RA Leiden

Description:

In this study, we investigated interference between several excited electronic states in resonance enhanced vibrational Raman optical activity (RROA) spectra. A gradient Franck-Condon model for the excited-state potential energy surface was applied in order to include vibronic effects in the description of the RROA intensities. Both sum-over-states and time-dependent expressions for the RROA intensities in case of close-lying excited states were given. As an example, we compared the calculated RROA and resonance Raman spectra of (S)-(+)-naproxen-OCD3 to the experimental ones. Subsequently, we examined the excitation profiles of (S)-(+)-naproxen and studied the vibration at 1611 cm^{-1} in more detail in order to demonstrate how the consideration of a second excited electronic state can lead to significant changes in the RROA intensities.

References: S. Luber, J. Neugebauer, M. Reiher, *J. Chem. Phys.*, **2010**, *132*, 044113.

Title: Relativistic effects on the Fukui function

Researchers:
Nick Sablon[1]
Remigius Mastalerz[2]
Frank De Proft[1]
Paul Geerlings[1]
Markus Reiher[1]

Institute/Group:
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[2]Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

The extent of relativistic effects on the Fukui function, which describes local reactivity trends within conceptual density functional theory (DFT), and frontier orbital densities was analysed on the basis of three benchmark molecules containing the heavy elements: Au, Pb, and Bi. Various approximate relativistic approaches were tested and compared with the four-component fully relativistic reference. Scalar relativistic effects, as described by the scalar zeroth-order regular approximation methodology and effective core potential calculations, already provided a large part of the relativistic corrections. Inclusion of spin-orbit coupling effects improved the results, especially for the heavy p-block compounds. We thus expected that future conceptual DFT-based reactivity studies on heavy-element molecules could rely on one of the approximate relativistic methodologies.

References: N. Sablon, R. Mastalerz, F. De Proft, M. Reiher, *Theor. Chem. Acc.*, **2010**, *127*, 195.

Title: Prediction of Raman Optical Activity Spectra of Chiral 3-Acetylcamphorato-Cobalt Complexes

Researchers: Sandra Luber
Markus Reiher

Institute/Group: Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

We examined calculated vibrational Raman optical activity (ROA) spectra of octahedral cobalt complexes containing different combinations of acetylacetonato and 3-acetylcamphorato ligands. Starting from the Δ-tris(acetylacetonato)cobalt(III) complex, the ROA spectra of isomers generated by successive replacement of acetylacetonato ligands by chiral (+)- or (−)-3-acetylcamphorato ligands were investigated. In this way, it was possible to assess the influence of the degree of ligand substitution, ligand chirality, and geometrical isomerism on the ROA spectra. In addition, the effect of the Λ-configuration was studied. It was found that the ROA spectra contain features that make it possible to identify each of the isomers, demonstrating the great sensitivity of ROA spectroscopy to the chiral nature of the various complexes.

References: S. Luber, M. Reiher, *ChemPhysChem*, **2010**, *11*, 1876.

Title: Analysis of Vibrational Raman Optical Activity Signatures of the $(TG)_N$ and $(GG)_N$ Conformations of Isotactic Polypropylene Chains in Terms of Localized Modes

Researchers:
Vincent Liégeois[1,3]
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Benoît Champagne[1]
Markus Reiher[3]

Institute/Group:
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[2]Center for Functional Nanostructures, Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe
[3]Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

In a previous study [Lamparska, E.; Liégeois, V.; Quinet, O.; Champagne, B. *ChemPhysChem*, **2006**, *7*, 2366], signatures associated to the helical structure of a small oligomer of a polypropylene chain were highlighted in the vibrational Raman optical activity (VROA) spectra. Nevertheless, it was difficult to pursue the analysis of longer chains. Indeed, the number of normal modes is becoming large and they are delocalized over the whole chain, increasing the complexity of their analysis. With a new tool developed to analyze the vibrational spectra [Jacob, Ch. R.; Reiher, M. *J. Chem. Phys.*, **2009**, *130*, 084106], one can understand the normal modes, the VROA intensity of the bands, and the band shapes of long polymer chains by investigating the vibrational coupling matrices and the intensity coupling matrices. The VROA couplet at around 1100 cm^{-1} (previously evidenced as a signature of the $(TG)_N$ helical pitch) could now be thoroughly analyzed and compared to the corresponding signature in the $(GG)_N$ conformer. The mode localization approach showed that for both conformations this couplet arised from a phase difference within the localized modes of both peaks, leading to the inversion of the sign of the total VROA intensity. Comparing the $(TG)_N$ and $(GG)_N$ conformers, the vibrational and intensity coupling matrices completely changed with the modification of the structure. This led for the $(TG)_{19}$ conformer to a negative-positive couplet, whereas for the $(GG)_{19}$ conformation, a characteristic positive-negative-positive pattern was found.

References: V. Liégeois, C.R. Jacob, B. Champagne, M. Reiher, *J. Phys. Chem. A*, **2010**, *114*, 7198.

Title: Accurate frozen-density embedding potentials as a first step towards a subsystem description of covalent bonds

Researchers:
Samuel Fux[a]
Christoph R. Jacob[b]
Johannes Neugebauer[c]
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[d] Amsterdam Center for Multiscale Modeling, Vrije Universiteit Amsterdam, 1081 HV Amsterdam

Description:

The frozen-density embedding (FDE) scheme [Wesolowski and Warshel, J. Phys. Chem. 97, 8050 (1993)] relies on the use of approximations for the kinetic-energy component $v_T[\rho_1, \rho_2]$ of the embedding potential. While with approximations derived from generalized-gradient approximation kinetic-energy density functional weak interactions between subsystems such as hydrogen bonds can be described rather accurately, these approximations break down for bonds with a covalent character. Thus, to be able to directly apply the FDE scheme to subsystems connected by covalent bonds, improved approximations to v_T are needed. As a first step toward this goal, we have implemented a method for the numerical calculation of accurate references for v_T. We present accurate embedding potentials for a selected set of model systems, in which the subsystems are connected by hydrogen bonds of various strength (water dimer and F-H-F-), a coordination bond (ammonia borane), and a prototypical covalent bond (ethane). These accurate potentials are analyzed and compared to those obtained from popular kinetic-energy density functionals.

References: S. Fux, C. R. Jacob, J. Neugebauer, L. Visscher, M. Reiher, *J. Chem. Phys.*, **2010**, *132*, 164101.

Title: Complete-Graph Tensor Network States:
A New Fermionic Wave Function Ansatz for Molecules

Researchers: Konrad H. Marti[1]
Bela Bauer[2]
Markus Reiher[1]
Matthias Troyer[2]
Frank Verstraete[3]

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[2]Institut für Theoretische Physik, ETH Zürich, 8093 Zürich
[3]Fakultät der Physik, Universität Wien, A-1090 Wien

Description:

We present a class of tensor network states specifically designed to capture the electron correlation within a molecule of arbitrary structure. In this ansatz, the electronic wave function is represented by a Complete-Graph Tensor Network (CGTN) ansatz which implements an efficient reduction of the number of variational parameters by breaking down the complexity of the high-dimensional coefficient tensor of a full-configuration-interaction (FCI) wave function. This ansatz applied to molecules is new and based on a tensor network wave function recently studied in lattice problems. We demonstrate that CGTN states approximate ground states of molecules accurately by comparison of the CGTN and FCI expansion coefficients. The CGTN parametrization is not biased towards any reference configuration in contrast to many standard quantum chemical methods. This feature allows one to obtain accurate relative energies between CGTN states which is central to molecular physics and chemistry. We discuss the implications for quantum chemistry and focus on the spin-state problem. Our CGTN approach is applied to the energy splitting of states of different spin for methylene and the strongly correlated ozone molecule at a transition state structure. The parameters of the tensor network ansatz are variationally optimized by means of a parallel-tempering Monte Carlo algorithm.

References: K. H. Marti, B. Bauer, M. Reiher, M. Troyer, F. Verstraete, *New J. Phys.*, **2010**, 12, 103008, arXiv:1004.5303v1 [physics.chem-ph].

Title: DMRG control using an automated Richardson-type error protocol

Researchers: Konrad H. Marti
Markus Reiher

Institute/Group: Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

The density matrix renormalization group (DMRG) algorithm solves the many-particle electronic Schrödinger equation as accurately as possible in a full-configuration-interaction (FCI) sense for a given one-electron basis. The FCI limit is approached by increasing the number of many-particle DMRG states which span the Hilbert space of interest. In this work we investigate an automated DMRG error protocol which extrapolates the electronic energy using Richardson's deferred approach to the limit. The key idea is to consider the result of a DMRG algorithm as an analytical function of an adjustable parameter like the number of DMRG states. We can then probe this analytical function by performing calculations for different set sizes of renormalized DMRG basis states. None of these calculations has to actually provide the desired accuracy but after we have collected enough information about the function's behaviour, we can represent it by an analytic rational function that may then be used to extrapolate to the converged energy. The advantage of this approach is that it delivers an error estimate for the electronic energy which can be used for accuracy control and as a convergence criterion. In addition, one may detect convergence to local energy minima by automatically increasing the analytic parameter (i.e., the number of renormalized DMRG states). The error estimates also allows us to aim at relative energies from extrapolated total energies of similar accuracy that is then independent of the number of renormalized DMRG states or of the truncation error of the reduced density matrix.

References: K. H. Marti and M. Reiher, *Mol. Phys.*, **2010**, *108*, 3, 501–512.

Title: The Density Matrix Renormalization Group Algorithm in Quantum Chemistry

Researchers: Konrad H. Marti
Markus Reiher

Institute/Group: Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

In this work, we derive the density matrix renormalization group (DMRG) algorithm in the language of configuration interaction. Furthermore, the development of DMRG in quantum chemistry is reviewed and DMRG-specific peculiarities are discussed. Finally, we present new results for a dinuclear μ-oxo bridged copper cluster, which is an important active-site structure in transition-metal chemistry, an area in which we pioneered the application of DMRG.

References: K. H. Marti and M. Reiher, *Z. Phys. Chem.*, **2010**, *224*, 583–599.

Title: Nitrogen Fixation to Produce Ammonia: Finding the Ideal Catalyst System via Computational Screening Methods

Researchers: Steven M. A. Donald
Markus Reiher

Institute/Group: Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

Whereas nature successfully fixes dinitrogen, converting one dinitrogen molecule into to two of ammonia, via the nitrogenase enzymes, attempts to mimic nature, creating a synthetic nitrogen fixation cycle, have proven highly challenging. The current industrial method involves both high pressures and temperatures in the Haber-Bosch process. Schrock et al. reported in 2003 a catalyst system which converts dinitrogen to ammonia in the presence of reducing agent and a proton source at ambient temperature and pressure. However, this catalyst system is destroyed under reaction conditions after approximately six cycles, rendering the process unfit for industrial application.
Theoretical studies within this group have provided fundamental insight into the Schrock catalyst, and we now report further work in the search for new catalyst systems that can fix dinitrogen just as the Schrock catalyst, but show improved catalyst stability.
Promising experimental systems by the Peters group, specifically the $[\mathrm{Si}(o\text{-}\mathrm{C}_6\mathrm{H}_4\text{-}\mathrm{P}^i\mathrm{Pr}_3)_3]^-$ (SiP_3) ligand system, are described with the BP86 functional and mixed TZVP/SVP basis set. We study the performance of the $[\mathrm{Fe}(\mathrm{SiP}_3)]$ and $[\mathrm{Mo}(\mathrm{SiP}_3)]$ catalysts in key steps of the Schrock-cycle such as the first protonation/reduction step and $\mathrm{NH}_3/\mathrm{N}_2$ ligand exchange, comparing them to the Schrock catalyst itself. We also look in greater detail at the $\mathrm{NH}_3/\mathrm{N}_2$ ligand exchange process and perform a full analysis of the possible pathways and determine the barrier to this process.

References: S. M. A. Donald, M. Reiher, *in preparation.*

Title: A unifying structural and electronic concept for Hmd and [FeFe] hydrogenase active sites.

Researchers: Martin T. Stiebritz
Markus Reiher

Institute/Group: Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

The hydrogenases [FeFe] and Hmd feature at first sight rather different active sites. A closer inspection reveals striking similarities, which allow us to define swapped ligand spheres in such a way that the single active iron center of Hmd functions in a first-shell ligand environment resembling the reacting iron atom in [FeFe] hydrogenase and vice versa. These redesigned ligand environments can be conveniently studied with quantum chemical methods and point to general reactivity principles for iron centers with hydrogenase activity.

References: M. T. Stiebritz, M. Reiher, *Inorg. Chem.*, **2010**, *49*, 5818.

Title: A Local-Mode Model for Understanding the Dependence of the Extended Amide III Vibrations on Protein Secondary Structure

Researchers:
Thomas Weymuth[1]
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Institute/Group:
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Description:

The extended amide III region in vibrational spectra of polypeptides and proteins is particularly sensitive to changes in secondary structure. To investigate this structural sensitivity, we have performed density-functional calculations on the small model compound N-acetyl-L-alanine-N-methylamide, which are analyzed using the recently developed analysis in terms of localized modes [J. Chem. Phys. 2009, 130, 084106]. We find that the local modes obtained for different backbone conformations are actually rather similar. To probe the secondary structure sensitivity, we investigate the dependence of the local-mode frequencies and coupling constants on the torsional angles ϕ and ψ. This enables us to set up a local-mode model of the extended amide III region for better understanding its structural sensitivity.

References: T. Weymuth, C. R. Jacob, M. Reiher, *J. Phys. Chem. B*, **2010**, *114*, 10649.

Title: An enquiry into Theoretical Bioinorganic Chemistry: How heuristic is the character of present-day quantum chemical methods?

Researchers:
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Martin T. Stiebritz
Markus Reiher

Institute/Group: Laboratorium für Physikalische Chemie, ETH Zürich, 8093 Zürich

Description:

Bioinorganic Chemistry is a very complex and diverse field. Structures with different types of ligands, varying number of interacting (transition) metals provide the stage for the most complex chemical transformations and for intricate reaction mechanisms. examples are the dioxygen evolution at the water-oxidizing complex of Photosystem II or reductions at the active centers of Hydrogenases.

The optimum way to understand the function of such systems is to accomplish a perfect structural and time resolution of their catalytic chemical reactions to obtain results that explain experimental studies but also to provide complementary information not accessible in experiment. Exactly this is at least in principle possible by a quantum mechanical description. However, the mono- and polynuclear transition-metal active sites demand highly accurate electronic structure methods.

Reliability and predictability of calculations on such systems depend crucially on the accuracy of these necessarily approximate electronic structure methods. Unfortunately, up to date there still does not exist a universal and well-established methodology for the study of bioinorganic reaction mechanisms in proteins and enzymes. Because of the method-inherent errors and the large set of parameters to cope within an electronic structure method—for example in Density Functional Theory: structural model, spin state, charge, solvation, choice of the density functional etc.—that could hardly be investigated systematically for every system only different protocols of various schools exist that feature a somewhat heuristic character.

One challenge has to be to develop universally valid concepts that allow us to assess the chemical significance of calculated results despite the method-inherent errors. These concepts must be transferable to different systems beyond the consideration of individual case studies.

In this study we elaborate on how new concepts of this type may be developed. We discuss new concepts to address structure and reactivity of an active site in metalloenzymes and demonstrate this at the example at the dioxygen activation reaction at model clusters as well as for oxygen inhibition processes in [FeFe]- and [Fe]-Hydrogenases. We will focus on structure–reactivity correlations and investigate the flexibility of the active sites, which should be designed such that the chemical conclusions do not suffer from method-inherent errors and are persistent.

Reference: M. Podewitz, M. T. Stiebritz, M. Reiher, *Faraday Discuss.*, **2010**, *148*, *DOI: 10.1039/c004195e.*

Title: Quantum chemical studies of the magnetic properties of M_6-wheel-like transition-metal clusters

Researchers:
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Astrid Malassa[2]
Christine Agthe[2]
Helmar Görls[2]
Lian Yu[1]
Carmen Herrmann[1]
Matthias Westerhausen[2]
Markus Reiher[1]

Institute/Group:
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[2] Institut für Anorganische Chemie und Analytische Chemie, Friedrich-Schiller Universität Jena, D-07743 Jena

Description:

The transamination of 8-(tert-butyldimethylsilylamino)quinoline with $(thf)_2Cr[N(SiMe_3)_2]_2$ yields monomeric bis[8-(tert-butyldimethylsilylamido)quinoline] chromium(II)(**1**). Similar reactions of $M[N(SiMe_3)_2]_2$ (M=Mn,Fe,Co) with 8-(trialkylsilylamino)quinoline lead to the formation of monomeric bis[8-(trialkylsilylamido)quinoline] metal(II) [M=Mn, SiR_3=$SiMe_2$*t*Bu(**2a**), Si*i*Pr_3(**2b**); M=Fe, SiR_3=$SiMe_2$tBu(**3a**), Si*i*Pr_3(**3b**); M=Co, SiR_3=$SiMe_2$*t*Bu(**4a**), Si*i*Pr_3(**4b**)]. The transamination of 8-aminoquinoline with $M[N(SiMe_3)_2]_2$ (M=Mn,Fe,Co) allows the isolation of the heteroleptic 1:1 and homoleptic 2:1 products. The 1:1 complexes bis[8-amidoquinoline metal(II) bis(trimethylsilyl)amide] [M=Mn(**5**),Fe(**6**),Co(**7**)] are dimeric with bridging 8-amidoquinoline moieties. The 2:1 complexes of Mn and Fe, bis(8-amidoquinoline) manganese(II)(**8**) and bis(8-amidoquinoline) iron(II)(**9**), form hexamers with wheel-like molecular structures consisting of metal-centered nitrogen octahedra interconnected by common N$\cdots$N edges. The cobalt complex, bis(8-amidoquinoline) cobalt(II)(**10**), precipitates as a microcrystalline powder. Investigations of the magnetic properties by DFT corroborate the experimental data for the Mn derivative **8**, where an antiferomagnetic coupling is observed. By contrast, calculations on the Fe_6-wheel **9** yield very close lying ferromagnetically and antiferromagnetically coupled states.

Reference: A. Malassa, C. Agthe, H. Görls, M. Podewitz, L. Yu, C. Herrmann, M. Reiher, M. Westerhausen , *Eur. J. Inorg. Chem.*, **2010**, 1777-1790.

Title: Ion Dynamics in Confined Spaces: Sodium Ion Mobility in Icosahedral Container Molecules

Researchers:
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Jacco D. van Beek[1]
Michael Wörle[2]
Timo Ott[2]
Daniel Stein[2]
Heinz Rüegger[2]
Beat H. Meier[1]
Markus Reiher[1]
Hansjörg Grützmacher[2]

Institute/Group:
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[2] Laboratorium für Anorganische Chemie, ETH Zürich, 8093 Zürich

Description:

Cage it: A central PH_2^- ion is encapsulated within a container of twelve tert-butoxides in an icosahedral arrangement. The twelve or thirteen sodium countercations are dynamically disordered over the twenty corners of a regular dodecahedron. X-ray diffraction, solid-state NMR, and DFT calculations demonstrate that the crystalline forms of $[Na_{13}(PH_2)(OtBu)_{12}]$ and $[Na(DME)_3]+[Na_{12}(PH_2)(OtBu)_{12}]^-$ contain interlocked ionic cages of near-icosahedral symmetry with PH_2^- in the center of an inner sodium cage. At room temperature the sodium ions show fast dynamics with a correlation time of up to 7.5×10^{-10}s for $[Na_{13}(PH_2)(OtBu)_{12}]$ within the alkoxide cage. One sodium cation may be reversibly removed or added from the aggregates. Quantum-chemical calculations highlight that such onion-like arrangements of ions of opposite charge are energetically stable regardless of whether the PH_2^- is present inside the cage or not. A purely electrostatic model is able to account for all structural features of the complexes.

Reference: M. Podewitz, J. D. van Beek, M. Wörle, T. Ott, D. Stein, H. Rüegger, B .H Meier, M. Reiher, H. Grützmacher , *Angew. Chem. Int. Ed.*, **2010**, *49*, 7465-7469.

Title: Stretching fibronectin fibers disrupts binding of bacterial adhesins by physically destroying an epitope

Researchers:
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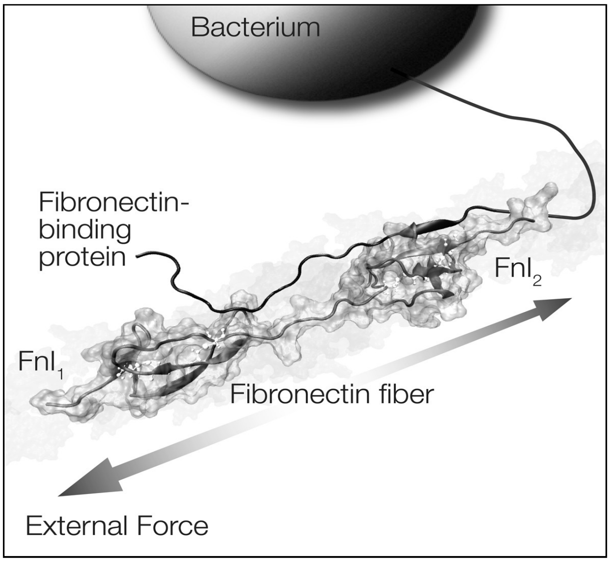
Samuel Hertig *
Michael Smith **
Viola Vogel *

Institute/Group:
* Laboratory for Biologically Oriented Materials,
ETH Zurich, Zürich, Switzerland
** Department of Biomedical Engineering, Boston University,
Boston, Massachusetts 02215

Description:



While soluble inhibitors are frequently used to block cell binding to extracellular matrix (ECM), mechanical stretching of a protein fiber alone can physically destroy a cell binding site. Using experiments and steered molecular dynamics (SMD), we show that mechanical tension along fibronectin (Fn) fibers causes a structural mismatch between Fn binding proteins (FnBP) from the bacteria *S. dysgalactiae* and *S. aureus*. Both adhesins target a multi-modular site on Fn that is switched to low affinity by stretching the inter-modular distances on Fn. The structural details of the unbinding mechanism were obtained using all-atom, explicit water SMD simulations. The mechanical force externally applied *in silico* to the two Fn modules mimics the stress that the molecule would encounter *in vivo* when exposed to cell-generated tension.

These results obtained in SMD simulations were confirmed experimentally by performing binding studies using an assay with Fn fibers that can be mechanically tuned and fluorescently labeled bacterial peptides. This demonstration of the existence of a mechano-sensitive cell binding site provides a never considered perspective of how the mechano-biology of ECM might regulate bacterial and cell binding events, virulence and the course of bacterial infection.

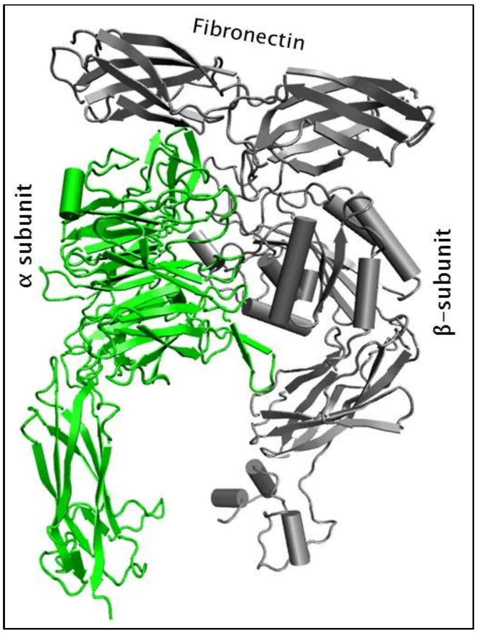
References: Chabria, Hertig, Smith, Vogel, *Nature Communications*, accepted

Title: The role of the integrin α_V domain in regulating integrin activation

Researchers: Garif Yalak
Viola Vogel

Institute/Group: Laboratory for Biologically Oriented Materials,
ETH Zurich, Zürich, Switzerland

Description:



Integrins can exist in an inactivated state where they show low ligand affinity, and an activated state. Integrin activation occurs via allosteric conformational changes, either resulting from cytoplasmic or extracellular interactions. So far, the complete sequential details of these conformational changes leading to integrin activation are not fully understood, and are the subject of controversy. Today the allosteric pathway leading to integrin activation is regarded to be a process occurring only in the β subunit [1]. While the dimerization of the transmembrane domains was highly investigated, the dimerization of the extracellular domains is barely analyzed. Understanding the dimerization of the extracellular domains, in addition to the transmembrane domains, would allow to decipher the role of another important factor in the complex activation mechanism. Moreover it might help to understand why the 18 α and 8 β integrin subunits specifically dimerize to the 24 known integrins. To address these questions in order to get high-resolution information, computational methods are necessary, since experiments fall short to provide this high-resolution information. With large-scale computational resources, molecular dynamics (MD) and steered molecular dynamics (SMD) simulations are two powerful methods to reveal structural details at atomic-level resolution.

References:

[1] Eileen Puklin-Faucher, Viola Vogel, Integrin activation dynamics between the RGD-binding site and the headpiece hinge, J Biol Chem 284 (2009) 36557-68

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Publications* in 2009/2010

* only computation-related articles
in refereed journals

Group of K. K. Baldridge

Duttwyler, S.; Zhang, Y.; Linden, A.; Reed, C.A.; Baldridge, K.K.*; Siegel, J.S.*
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