



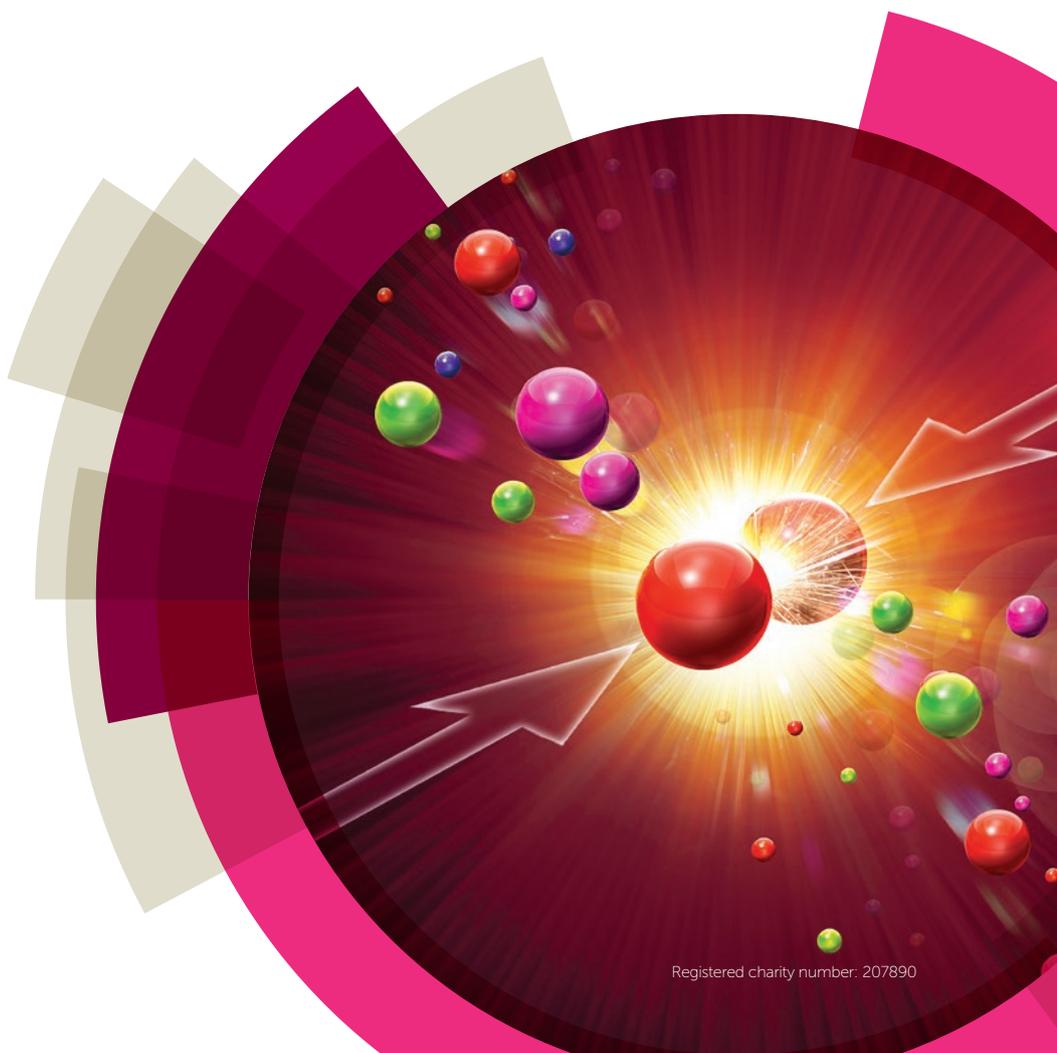
19 - 21 September 2016, Cambridge, UK

Reaction Rate Theory

Faraday Discussion

 #ratetheory

Book of
Abstracts



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Introduction

Reaction Rate Theory: Faraday Discussion is organised by the Faraday Division of the Royal Society of Chemistry.

This book contains abstracts of the 46 posters presented at this Faraday Discussion. All abstracts are produced directly from typescripts supplied by authors. Copyright reserved.

Oral presentations and discussions

All delegates at the meeting, not just speakers, have the opportunity to make comments, ask questions, or present complementary or contradictory measurements and calculations during the discussion. If it is relevant to the topic, you may give a 5 minute presentation of your own work during the discussion. These remarks are published alongside the papers in the final volume and are fully citable. If you would like to present slides during the discussion please let the session chair know and load them onto the computer in the break before the start of the session.

Posters

Posters have been numbered consecutively: **P01-P46**

The formal poster viewing sessions have been scheduled to take place on Monday 19 September and Tuesday 20 September.

Poster prize

The Faraday Discussions Poster Prize, will be awarded to the best student poster as judged by the committee.

Faraday discussion volume

Copies of the Discussion Volume will be distributed approximately 6 months after the meeting. To expedite this, it is essential that summaries of contributions to the discussion are received no later than Wednesday 28 September for questions and comments and Wednesday 12 October for responses. In order to keep the students fees low the Discussion Volume is NOT included in the student conference fees. A copy of the publication may be purchased at a reduced price, only for orders placed at the meeting; an application form is available from the information desk at the meeting.

Scientific committee and speaker list

Scientific committee

Stuart Althorpe
University of Cambridge, UK

Peter Bolhuis
University of Amsterdam, the Netherlands

Cecilia Clementi
Rice University, USA

Scott Habershon
University of Warwick, UK

Angelos Michaelides
University College London, UK

Adrian Mulholland
University of Bristol, UK

Invited speakers

William H. Miller
University of California, Berkeley, USA

David Chandler
University of California, Berkeley, USA

Nancy Makri
University of Illinois at Urbana-Champaign, USA

Tom Miller
California Institute of Technology, USA

Nandini Ananth
Cornell University, USA

Sharon Hammes-Schiffer
University of Illinois at Urbana-Champaign, USA

Michele Parrinello
ETH Zurich, Switzerland

Eric Vanden-Eijnden
New York University, USA

Christoph Dellago
University of Vienna, Austria

Christof Schütte
Freie Universität Berlin, Germany

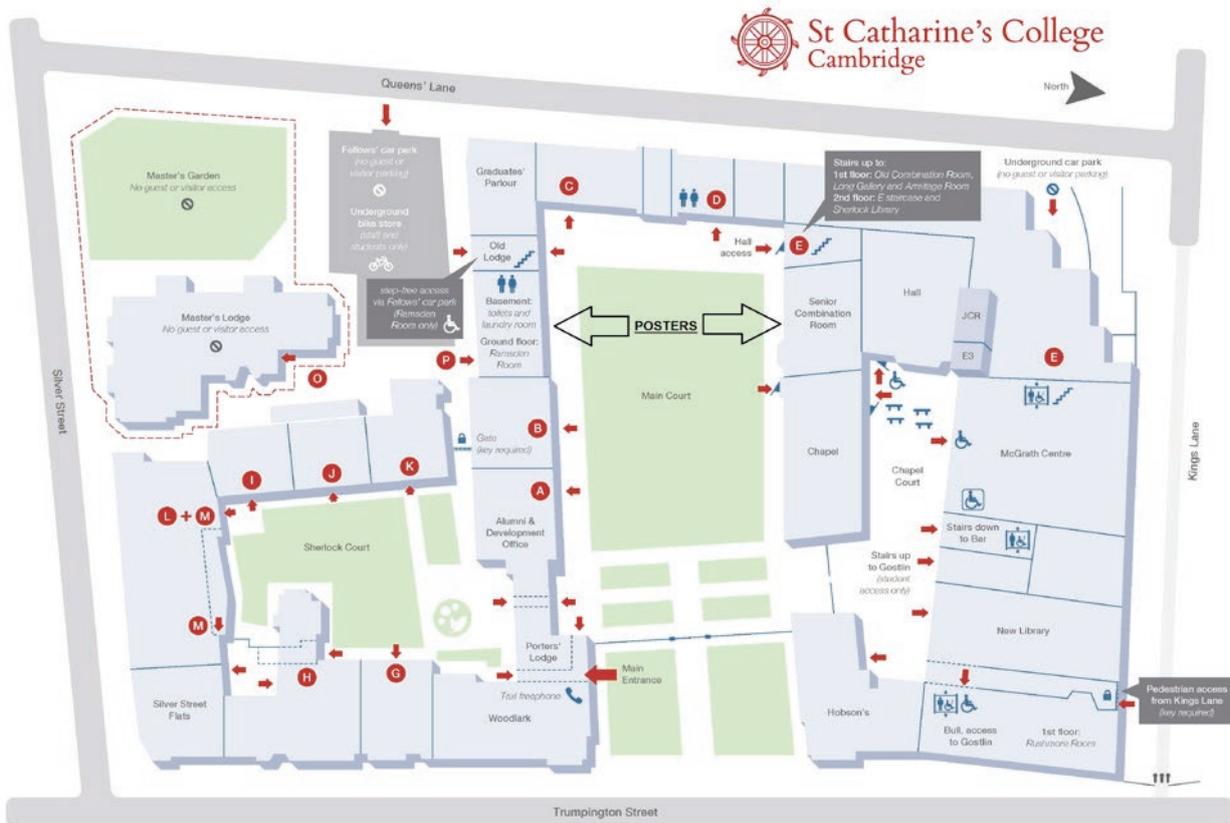
Meeting information

Lectures

All lectures will take place in McGrath Centre lecture theatre.

Poster session

The poster sessions will take place on Monday 19 September and Tuesday 20 September after the main lectures and will be in the SCR and Ramsden Room.



Catering

Catering during the daytime will take place in the McGrath Centre.

	Morning	Lunch	Afternoon	Dinner
Monday 19 September	11:00	12:00	15:30	No dinner – free evening
Tuesday 20 September	11:00	13:00	16:00	Pre-dinner drinks: 18:00 Dinner: 19:00
Wednesday 21 September	10:30	13:15		

There is no dinner on the evening of Monday 19 September, this is a free evening.

Conference dinner

The Conference Banquet on the evening of Tuesday 20 September will take place in the main hall from 19:00. Dinner is available for all registered delegates.

Reaction Rate Theory: Faraday Discussion

Using the Web Forum www.rscweb.org/forums/fd/

The unique aspect of *Faraday Discussions* is that most of the meeting is devoted to discussion of the papers presented. Therefore an important feature of *Faraday Discussions* is that a record of the remarks made at the meeting is published in the printed volume.

If you ask any questions or make any comments during the Discussion meeting, you will receive a **question number** by email along with a brief record of your question or comment. Delegates are then required to use our **web forum** to submit the text of all their questions or comments in full.

The deadline for receipt of questions and comments is **28 September 2016**.

If you wish to make a communicated comment *after* the meeting, please contact the Faraday Editorial Office with the text of your question or comment at faraday@rsc.org.

If any of the questions or comments are directed to you, as well as responding in person at the meeting, you will need to access the web forum to submit your responses in full. You will be notified by email when a question or comment that requires a response from you has been uploaded.

The deadline for receipt of responses is **12 October 2016**.

The web forum can be accessed at www.rscweb.org/forums/fd/ where you can log in using the username and password which will be sent to you one week prior to the meeting. If you forget what your username and password are, please ask a member of RSC staff at the meeting or email faraday@rsc.org.

As an alternative to using the forum, any questions/comments made at the meeting can be emailed to us at faraday@rsc.org.

The forum will be activated at the start of the Discussion meeting on **19 September 2016**.

If you have any problems using the forum please do not hesitate to contact the editorial team at faraday@rsc.org.

The screenshot shows a web browser window displaying the RSC Forums page. The page title is "RSC Publishing" and "RSC Forums Online Faraday Discussions". Below the title is a section for "Faraday Discussion comment collection". There are links for "FAQ" and "Log out". A message states "Not in multiple discussions." Below this is a "Question or comment" form. The form includes fields for "YOU ARE:", "QUESTION NO:", "Q/C:", "WHICH DELEGATE ARE YOU ADDRESSING?", and "DURING DISCUSSION OF PAPER:". There is a large text area for "YOUR QUESTION OR COMMENT:" and a rich text editor toolbar with options for italic, bold, super, and sub. A note on the right side of the form says "You must log in to post material." and "To submit a question/comment that was not asked at the discussion meeting and does not have a question number, please e-mail the Editorial Office at faraday@rsc.org".

Programme

Monday 19 September

Time	Event	
11:00	Registration, tea and coffee	
12:00	Lunch	
12:45	Welcome and introductions Stuart C. Althorpe, <i>Chair of Scientific Committee</i>	
12:55	Outline of discussion format Ruth Zadik and Nicola Convine, <i>Royal Society of Chemistry Publishing Editors</i>	
13:00	Introductory lecture Session chair: David Clary, <i>University of Oxford</i> William H. Miller <i>University of California, Berkeley</i>	
Session 1 Fundamentals Session chair: David Clary, <i>University of Oxford</i>		
14:00	Low temperature chemistry using the R-matrix method <u>Jonathan Tennyson</u> , Laura K McKemmish and Tom Rivlin <i>University College London</i>	Paper 11347
14:05	Microcanonical and thermal instanton rate theory for chemical reactions at all temperatures <u>Jeremy O. Richardson</u> <i>Durham University</i>	Paper 11378
14:10	Atom tunnelling in the reaction $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$ and its astrochemical relevance Sonia Álvarez-Barcia, Marie-Sophie Russ, Jan Meisner and <u>Johannes Kästner</u> <i>University of Stuttgart</i>	Paper 11245
14:15	Discussion	
15:30	Afternoon tea	
16:00	Blip-summed quantum-classical path integral with cumulative quantum memory <u>Nancy Makri</u> <i>University of Illinois at Urbana-Champaign</i>	Paper 10868
16:05	Classical to quantum mechanical tunneling mechanism crossover in thermal transitions between magnetic states Sergei Vlasov, Pavel F. Bessarab, Valery M. Uzdin and <u>Hannes Jónsson</u> <i>University of Iceland</i>	Paper 11393
16:10	Kramers' theory for diffusion on a periodic potential Reuven Ianconescu and <u>Eli Pollak</u> <i>Weizmann Institute of Science</i>	Paper 11326
16:15	Discussion	
17:30	Lightning presentations, SCR and Ramsden rooms (by invitation of the scientific committee)	
18:00	Poster session and wine reception	
19:30	Close & free evening	

Tuesday 20 September

Time	Event	
Session 2 Non-adiabatic reactions Session chair: Scott Habershon		
09:00	Proton-coupled electron transfer reactions: Analytical rate constants and case study of kinetic isotope effects in lipoxygenase Alexander V. Soudackov and Sharon Hammes-Schiffer <i>University of Illinois at Urbana-Champaign</i>	Paper 10871
09:05	Kinetically-constrained ring-polymer molecular dynamics for non-adiabatic chemistries involving solvent and donor-acceptor dynamical effects Joshua S. Kretchmer and Thomas F. Miller III <i>California Institute of Technology</i>	Paper 10869
09:10	Confronting surface hopping molecular dynamics with Marcus theory for a molecular donor-acceptor system Jacob Spencer, Laura Scalfi, Antoine Carof and Jochen Blumberger <i>University College London</i>	Paper 11355
09:15	Photorelaxation of imidazole and adenine via electron-driven proton transfer along H₂O wires Rafał Szabla , Robert W. Góra, Mikołaj Janicki and Jiří Šponer <i>Institute of Biophysics, Academy of Sciences of the Czech Republic</i>	Paper 11392
09:20	Discussion	
11:00	Morning tea	
11:30	State space path integrals for electronically nonadiabatic reaction rates Jessica Ryan Duke and Nandini Ananth <i>Cornell University</i>	Paper 10870
11:35	Deriving the exact nonadiabatic quantum propagator in the mapping variable representation Timothy J. H. Hele and Nandini Ananth <i>Cornell University</i>	Paper 11314
11:40	Reactive trajectories of the Ru^{2+/3+} self-exchange reaction and the connection to Marcus' theory Ambuj Tiwari and Bernd Ensing <i>Van't Hoff Institute for Molecular Sciences</i>	Paper 11310
11:45	Discussion	
13:00	Lunch	

Tuesday 20 September continued

Time	Event	
Session 3 Structural dynamics Session chairs: Nina Rohringer and Dwayne Miller		
14:00	S-shooting: A Bennett–Chandler-like method for the computation of rate constants from committor trajectories Georg Menzl, Andreas Singraber and Christoph Dellago <i>University of Vienna</i>	Paper 10874
14:05	Direct generation of loop-erased transition paths in non-equilibrium reactions Ralf Banisch and Eric Vanden-Eijnden <i>New York University</i>	Paper 10873
14:10	Adaptive free energy sampling in multidimensional collective variable space using boxed molecular dynamics Mike O'Connor, Emanuele Paci, Simon McIntosh-Smith and David R. Glowacki <i>University of Bristol</i>	Paper 11390
14:15	The intrinsic rate constants in diffusion-influenced reactions Adithya Vijaykumar , Peter G. Bolhuis and Pieter Rein ten Wolde <i>University of Amsterdam</i>	Paper 11356
14:20	Discussion	
16:00	Afternoon tea	
16:30	Effective dynamics along given reaction coordinates, and reaction rate theory Wei Zhang, Carsten Hartmann and Christof Schütte <i>Freie Universität Berlin</i>	Paper 10875
16:35	Jump Markov models and transition state theory: the quasi-stationary distribution approach Giacomo Di Gesù, Tony Lelièvre , Dorian Le Peutrec, Boris Nectoux <i>Ecole des Ponts ParisTech, CERMICS</i>	Paper 11308
16:40	Uncertainty quantification for quantum chemical models of complex reaction networks Jonny Proppe, Tamara Husch, Gregor N. Simm and Markus Reiher <i>ETH Zürich</i>	Paper 11126
16:45	Discussion	
18:00	Close	
18:00	Poster Session and Pre-Dinner Drinks, SCR and Ramsden rooms	
19:00	Conference Dinner	

Wednesday 21 September

Time	Event	
Session 4: Application to large systems Session chair: Angelos Michaelides		
09:00	A variational approach to nucleation simulation Pablo M. Piaggi, Omar Valsson and Michele Parrinello <i>ETH Zurich</i>	Paper 10872
09:05	Lattice mold technique for the calculation of crystal nucleation rates Jorge R. Espinosa, Pablo Sampedro, Chantal Valeriani, Carlos Vega and Eduardo Sanz <i>Universidad Complutense de Madrid</i>	Paper 11381
09:10	Optical vs. chemical driving for molecular machines R. Dean Astumian <i>University of Maine</i>	Paper 11224
09:15	Discussion	
10:30	Morning tea	
11:00	Unimolecular dissociation of peptides: statistical vs. non-statistical fragmentation mechanisms and time scales Riccardo Spezia , Ana Martin-Somer, Veronica Macaluso, Zahra Homayoon, Subha Pratihari and William L. Hase <i>Université Paris Saclay, CEA CNRS</i>	Paper 11331
11:05	Faraday efficiency and mechanism of electrochemical surface reactions: CO₂ reduction and H₂ formation on Pt(111) Javed Hussain, Hannes Jónsson and Egill Skúlason <i>University of Iceland</i>	Paper 11384
11:10	Pressure-dependent rate constants for PAH growth: Formation of indene and its conversion to naphthalene Alexander M. Mebel , Yuri Georgievskii, Ahren W. Jasper and Stephen J. Klippenstein <i>Florida International University</i>	Paper 11354
11:15	Discussion	
12:30	Concluding Remarks Lecture Session chair: Angelos Michaelides David Chandler <i>University of California, Berkeley</i>	
13:10	Acknowledgements	
13:15	Close of meeting and lunch	

Poster presentations

- P01 A DFT study on electron transfer in oligothiophene-based organic solar cells**
Shaohui Zheng, Mengyue Xiao
Southwest University, China
- P02 A matsubara analysis of CMD, RPMD and the planetary model of Poulsen et al**
Michael Willatt, Stuart Althorpe
University of Cambridge, UK
- P03 - F A quantum approximate method for the calculation of thermal reaction rate constants**
Chiara Donatella Aieta, Michele Ceotto
Università degli Studi di Milano, Italy
- P04 A tribute to James Keck and his reactive flux algorithm for treating rare events in molecular dynamics**
James Anderson
Pennsylvania State University, USA
- P05 - F A virtual reality environment for interactively exploring dynamical pathways in chemical systems**
Michael O'Connor, David Glowacki, Rebecca Sage, Philip Tew
University Of Bristol, UK
- P06 - F Analogue mechanism but different activation barriers**
Florian Gisdon, Matthias Ullmann
University of Bayreuth, Germany
- P07 Approximating quantum diffusion in liquid para-hydrogen with classical rigid-body dynamics**
George Trenins, Michael Willatt, Stuart Althorpe
University of Cambridge, UK
- P08 Quantitative estimation of dynamic effects in condensed phase reactions. Application to enzymatic hydride transfer**
Kirill Zinovjev, Iñaki Tuñón
Universitat de València, Spain
- P09 Dependence of double layer on Warburg impedance**
Jingyuan Chen, Koichi Aoki,
University of Fukui, Japan
- P10 - F Efficient path integral dynamics on modern many-core hardware**
Martin Richter, Benjamin P Fingerhut
Max Born Institute, Germany
- P11 Electron transfer in organic and biological materials**
Antoine Carof, Laura Scalfi, Jacob Spencer, Jochen Blumberger
University College London, UK
- P12 Experimental and theoretical challenges in the study of the mechanism of heterocyclization reaction between mixed phosphonium-iodonium ylides and acetylenes**
Tatiana Nekipelova, Tatyana Podrugina, Olga Klimovich, Alexander Kovarskii, Valerii Kasprov, Irina Levina, Lidiya Kurkovskaya, Vladimir Kuzmin, Nikolay Zefirov
Emanuel Institute of Biophysical Chemistry RAS, Russia
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- P13 Full- and one-dimensional semiclassical calculations of reaction rate constants**
Xiao Shan, Samuel M Greene, David C Clary
University of Oxford, UK
- P14 - F Influence of the excitation light intensity on the rate of bimolecular electron transfer reactions**
Jadwiga Milkiewicz, Gonzalo Angulo, Cezław Radzewicz, Paweł Wnuk, Günter Grampp
Polish Academy of Sciences, Poland
- P15 Interpretation of electron transport with experimental and Markov Chain Monte Carlo simulations across Fe/Ti layered double hydroxide for efficient photocatalytic applications**
Priyadarshi Roy Chowdhury, Krishna G Bhattacharyya
Gauhati University, India
- P16 - F Investigating the dynamics of the disk- to slab- geometry phase transition**
Clemens Moritz, Andreas Tröster, Christoph Dellago
University of Vienna, Austria
- P17 - F Kinetics and thermodynamics of heteromolecular filament and cluster assembly**
Alexander Dear, Thomas Michaels, Gonzalo Garcia, Andela Saric, Tuomas Knowles
University of Cambridge, UK
- P18 Lindblad approach to quantum transition rate theory**
Chiara Liverani, Michael W. Finnis, Eva-Maria Graefe
Imperial College London, UK
- P19 Locating instantons in calculations of tunneling splittings**
Marko Tomislav Cvitaš
Institute Rudjer Boskovic, Croatia
- P20 Mechanism of tungsten-containing benzoyl-CoA reductase**
Martin Culka, G. Matthias Ullmann
University of Bayreuth, Germany
- P21 - F Molecular dynamics simulations for the detection of unfolding pathways and stable conformations of DNA oligonucleotide in the presence of urea**
Ewa Anna Oprzeska-Zingrebe, Jens Smiatek
University of Stuttgart, Germany
- P22 Molecular dynamics study of reaction kinetics in Li-O₂ systems**
Artem Sergeev, Alexander Chertovich, Daniil Itkis
Lomonosov Moscow State University, Russia
- P23 - F Non-equilibrium quantum correlation functions from ring-polymer molecular dynamics**
Ralph Welsch, Stuart C Althorpe, Thomas F Miller III
California Institute of Technology, USA
- P24 Nonadiabatic rate coefficients and dynamics of atmospheric oxidation intermediates: Photolysis of isoprene oxidation intermediates**
Basile Curchod, David Glowacki
University of Bristol, UK
- P25 Potential energy surfaces in quantum dynamics using gaussian process regression**
Gareth Richings, Scott Habershon
University of Warwick, UK
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- P26** **Boxed molecular dynamics: Cheap *in silico* screening of medicinal cyclic peptides by estimating rates of cyclization and Kinetics of AFM protein unfolding**
Jonathan Booth, Dmitry Shalashilin
University of Leeds, UK
- P27** **Quantum path integral and correlation functions in coherent state representation with the help of classical dynamics in extended phase space**
Dmitry Shalashilin
University of Leeds, UK
- P28 - F** **Reaction coordinate, free energy and rate for the key proton transfer reaction in human carbonic anhydrase II**
Srabani Taraphder, Tanmoy Kumar Paul
Indian Institute of Technology Kharagpur, India
- P29 - F** **Reactive trajectories of the Ru^{2+/3+} self-exchange re- action and the connection to Marcus' theory**
Ambuj Tiwari, Bernd Ensing
University of Amsterdam, The Netherlands
- P30** **Slow and low yield N-alkylation of 3-(2-phenylhydrazono)indolin-2-one, compared to that of 1H-indole-2,3-dione; reasons by theoretical investigation**
A-Reza Nekoei
Shiraz University of Technology, Iran
- P31 - F** **State space path integrals and mean field dynamics for nonadiabatic reaction rates**
Jessica Duke, Nandini Ananth
Cornell University, USA
- P32** **Stochastic model of multistage non-equilibrium electron transfer reaction in polar solvents with several relaxation timescales**
Sergey Feskov
Volgograd State University, Russia
- P33** **Studying complex reactive systems with accurate Potential Energy Surfaces**
João Brandão, César Mogo, Wenli Wang, Carolina Rio, Daniela Coelho
Universidade do Algarve, Portugal
- P34** **Studying the pressure dependence of the termolecular reaction $H + O_2 + M \rightarrow HO_2 + M$**
João Brandão, César Mogo, Wenli Wang, Carolina Rio, Daniela Coelho
Universidade do Algarve, Portugal
- P35** **The dynamical coupling of electrons and nuclei within the nuclear velocity perturbation theory**
Sascha Jähnigen, Arne Scherrer, Rodolphe Vuilleumier, Daniel Sebastiani
Martin-Luther-Universität Halle-Wittenberg, Germany
- P36 - F** **Unexpected behavior of hydrogen tunneling on transition metal surfaces**
Fang, Wei, Jeremy O Richardson, Chen, Ji, Li, Xin-Zheng and Michaelides, Angelos
University College London, UK
- P37** **Towards a microcanonical tunnelling theory**
Andreas Loehle, Johannes Kaestner
University of Stuttgart, Germany
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- P38 Tracking solvent controlled photoinduced electron transfer using broadband fluorescence up-conversion**
Pakorn Pasitsuparoad, Gonzalo Angulo, Cezław Radzewicz, Paweł Wnuk, Eric Vauthey, Arnulf Rosspeintner, Anna Ochab-Marcinek, Jakub Jedrak
Polish Academy of Sciences, Poland
- P39 Tunnelling rates in reduced instanton theory**
Sean McConnell, Johannes Kaestner
University of Stuttgart, Germany
- P40 - F Variational free energy flooding for nucleation rates calculation**
Pablo Piaggi, Omar Valsson, Michele Parrinello
Ecole Polytechnique Fédérale de Lausanne, Switzerland
- P41 Reduction mechanism of a coordinated superoxide by benzyl alcohol and 2-propanol**
Ritu Mukherjee (Mishra), Rupendranath Banerjee
Heritage Institute of Technology, India
- P42 On the temperature dependence of the rate coefficient of formation of C_2^+ from $C + CH^+$ on a new bond-order based potential energy surface**
Sergio Rampino, Leonardo Pacifici, Antonio Laganà, Ernesto Garcia
Scuola Normale Superiore, Italy
- P43 Effect of oxide promoters on the total oxidation functionality of *nanocomposite* MnO_x catalysts: Mechanism and kinetics of the CO oxidation reaction**
Roberto Di Chio, Layla Filiciotto, Claudia Espro, Giuseppe Trunfio, Lorenzo Spadaro, Francesco Arena
University of Messina, Italy
- P44 Spectacular rate enhancements of the Diels-Alder reaction at the ionic liquid/*n*-hexane interface**
Vijay Beniwal, Arpan Manna, Anil Kumar
CSIR-National Chemical Laboratory, Pune, India
- P45 On the short-time behavior of mapping variable ring polymer molecular dynamics**
Austin Green, Nandini Ananth
Cornell University, USA
- P46 Quantum dynamics on time-independent and time-dependent PES's**
Diptesh Dey, Ashwani Tiwari
Indian Institute of Science Education and Research Kolkata, India

Underline denotes presenting author to whom affiliation applies

A DFT study on electron transfer in oligothiophene-based organic solar cells

Dr. Shaohui Zheng, Mengyue Xiao

Faculty of Materials and Energy, Southwest University, China

Organic photovoltaic (OPV) material is one of the most important solar devices because of its low cost, easy large-scale production, and flexibility. However, the power conversion efficiency (PCE) of OPV is still too low for commercial application. Here, we select oligothiophene-based molecules (DRCNnT, donor) and PC71BM (acceptor) to explore the characters of electron transfer in these systems. We utilize DFT (density functional theory) and TD-DFT calculations to show how we can obtain the different electron transfer rates by engineering orientations of these donors and acceptors.

A matsubara analysis of CMD, RPMD and the planetary model of poulsen et al

Michael J Willatt* and Stuart C Althorpe

Department of Chemistry, University of Cambridge, United Kingdom

It is well-known that the Linearized Semiclassical Initial Value Representation (LSC-IVR) results in a classical dynamics that does not conserve the quantum Boltzmann distribution. We have shown that a single change in the derivation of LSC-IVR results in a classical dynamics that does: 'Matsubara dynamics'.¹ Matsubara dynamics is derived from an exact quantum expression and explains how quantum statistics and classical dynamics should be combined in quantum time-correlation functions.² Here we present an analysis of Centroid Molecular Dynamics (CMD)³, Ring Polymer Molecular Dynamics (RPMD)⁴ and the planetary model of Poulsen et al⁵ from the perspective of Matsubara dynamics.

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A quantum approximate method for the calculation of thermal reaction rate constants

Chiara D. Aieta* and Michele Ceotto

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The calculation of thermal reaction rate constants is a central problem in theoretical chemistry, and exact classical and quantum expressions have been formulated¹. However, approximate approaches are necessary when dealing with complex reactions, and several techniques have been developed in recent years. They include taking quantum corrections into consideration in classical transition state theory (TST)², semiclassical theories³, ring polymer molecular dynamics (RPMD)⁴, and quantum approaches⁵. In this work, we have developed a new quantum mechanical method to compute reaction rate constants, which is related to Miller's quantum instanton (QI)⁶. Starting from the exact definition of the thermal rate constant as the time integral of the quantum flux-flux correlation function, upon introduction of a steepest descent approximation, we have derived an expression which has the same structure of the original quantum instanton but includes a contribution from real-time dynamics. This new method has been tested on the one-dimensional Eckart barrier (both symmetric and asymmetric), and on the two-dimensional H + H₂ and D + H₂ collinear reactions. Results over a wide range of temperatures have been found to be in agreement within 10% of the exact quantum mechanical estimates.

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A tribute to James Keck and his reactive flux algorithm for treating rare events in molecular dynamics

James B. Anderson

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For all but the simplest systems James Keck's reactive flux approach provides the only method for treating rare events in molecular dynamics without a prohibitive computational effort. The combination of transition state theory and molecular dynamics proposed by Keck in 1962¹ makes such simulations possible. Keck was the first to test trajectories crossing a dividing surface by following them forward and backward in time to determine which are 'reactive' trajectories. In 1983 Miller, Schwartz and Tromp² listed the features desired in a method for computing rate constants and stated "Within the realm of classical mechanics there is actually a procedure with all the features being sought." They cited Keck's "variational theory of reaction rate" and followed with a short description which used a much more descriptive term "reactive flux". Thus we now have "Keck's reactive flux algorithm".

The method has been found to enable many types of rare events in molecular dynamics to be treated. A list of the first one hundred (1962 to 1995) is given in Ref.³. In the case of the reaction $\text{H}_2 + \text{I}_2$ (or 2I) \rightarrow $\text{HI} + \text{HI}$ the method reduced the calculation effort by six orders magnitude⁴. The list contains everything from dissociation and recombination, to diffusion of vacancies in solids, to activated processes in proteins, to reactions on surfaces, to membrane transport, to protein reactions in solution, to enzyme catalyzed reactions, to ligand escape from the heme pocket of myoglobin. Now there are thousands of examples. For many of these systems Keck's reactive flux approach is at least as important in calculations of molecular dynamics as the development of fast computers.

See also: James C. Keck Collected Works and Biography, www.jameskeckcollectedworks.org

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A virtual reality environment for interactively exploring dynamical pathways in chemical systems

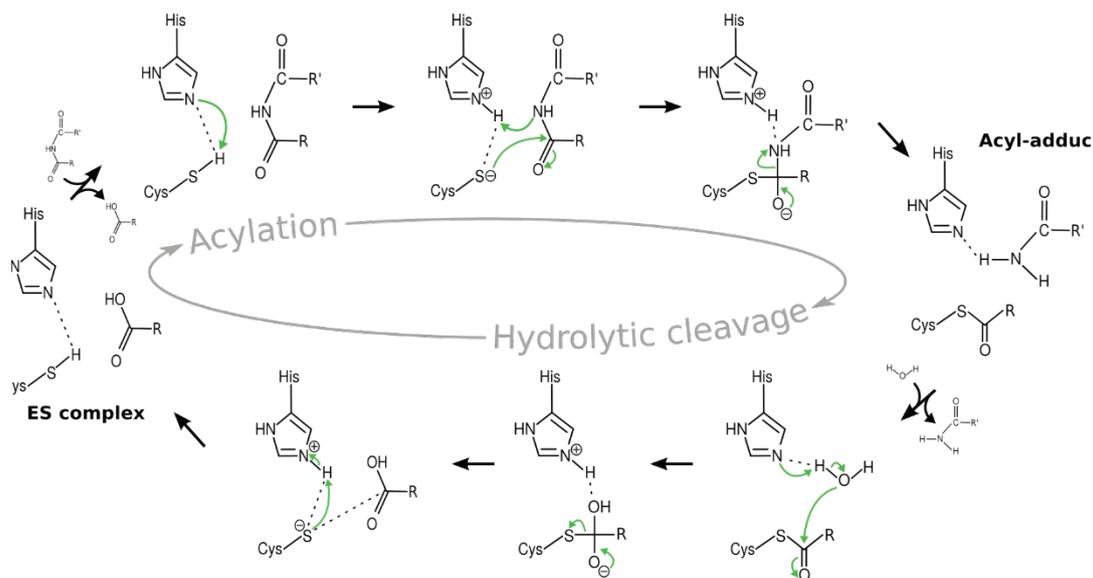
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This poster, along with accompanying technical demonstration, will present a new framework for performing interactive molecular dynamics in a virtual reality (VR) environment. The recent proliferation of VR technologies has opened new avenues for exploring 3-dimensional environments, with molecular systems being a clear candidate. Our initial implementation of a prototype framework, running on consumer grade hardware, allows for real-time interaction with a molecular dynamics simulation, in which the user manipulates the system through tuneable force-fields. This interaction, achieved using the HTC Vive VR headset and accompanying wireless controllers, enables full manipulation of the system in three dimensions. Initial applications have been to accelerate a simple chemical reaction ($\text{CH}_4 + \text{OH}$), simulated using the Empirical Valence Bond (EVB) method, as well as exploring the unwinding and re-winding of the helical structure of deca-alanine. The eventual aim is to couple the intuitive exploration that comes from the virtual environment with rigorous analysis, to allow scientists to bring their intuition to the exploration of dynamical pathways.

Analogue mechanism but different activation barriers

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Peptidases are key players in many essential biological pathways, e.g. trigger in the cell cycle or apoptosis or in defence against pathogens or pollutants. One well studied group is the C1A subfamily of papain-like cysteine peptidases. They cover a wide variety of activities. While some C1A members catalyse specific reactions, others have a broad substrate range and even can participate simultaneously in different physiological processes. The mechanism of C1A peptidases is based on the highly conserved catalytic dyad consisting of the active site cysteine and histidine. The general mechanism can be described in two parts: (1) The acylation, which describes the cleavage of a substrate's peptide bond and the formation of an enzyme-substrate (ES) ester, the acyl-adduct. (2) The hydrolytic cleavage of the acyl-adduct by attack of an activated water molecule at the enzyme-substrate ester bond. For the first part of the reaction the imidazole ring is accepting the proton of the catalytic cysteine. This proton transfer promotes the attack of the substrate by the nucleophilic cysteine anion. The resulting tetrahedral state further reacts to the acyl-adduct. The second part of the reaction is similar to the first part. A water molecule enters the active site and gets activated by the imidazole ring of the catalytic dyad. Again this promotes a nucleophilic attack where the acyl-adduct ester is attacked by the oxygen of the water. Also in this second part the reaction goes via a tetrahedral state, which is followed by the hydrolytic cleavage of the acyl-adduct. The release of the cleavage product and the protonation of the catalytic cysteine restores the active site. Also two other active site residues can be mentioned: Asp/Asn following the catalytic histidine to complete the charge relay system and orientate the imidazole ring. The second residue is a glutamine which contributes to a so called 'oxyanion hole', which stabilises the characteristic tetrahedral state in both parts of the mechanism.



Despite this mechanism of the C1A family is highly conserved it is not well understood, why the rates of these enzymes can differ significantly. Our QM/MM studies showed an analogue mechanism for two members of this family. Since the activation barrier for both enzymes are significantly different, we analyse possible reasons for that. Our goal is to understand the key reasons for the different energy profiles and to characterise them for several proteolytic enzyme families.

Approximating quantum diffusion in liquid para-hydrogen with classical rigid-body dynamics

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Self-diffusion in low-temperature, low-pressure liquid para-hydrogen has been studied extensively using a variety of quasi-classical approaches.¹ In this work we consider an approach in which replicas of quantum particles are connected into “necklaces” (ring polymers) that are propagated according to classical rigid body equations of motion. Also considered is “frozen-fluctuation dynamics”, in which the rotations of such rigid bodies are restricted. Comparing the results yielded by the two methods with previously known treatments reveals the importance of ring-polymer orientational degrees of freedom in calculations of quantum diffusion coefficients and gives support to rigid-body dynamics as an accurate and efficient method for carrying out such calculations.

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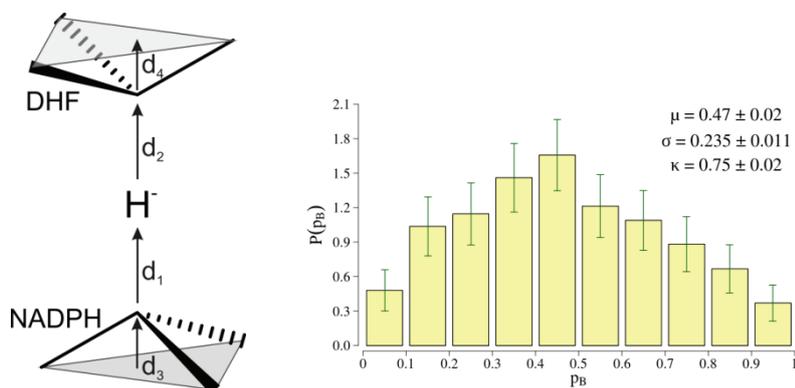
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Quantitative estimation of dynamic effects in condensed phase reactions. Application to enzymatic hydride transfer

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The nature of the reaction coordinate (RC) in enzymatic processes is the subject of a hot debate in the field. Transmission coefficients obtained with RCs based in valence geometrical coordinates (like the length of a dissociating bond) in some cases are low and, therefore, such coordinates do not describe the process well. This is considered as an indicator that a good enzymatic RC might be impossible to obtain without including protein degrees of freedom or even atomic velocities. The latter would mean that no rate theory based on configurational RC, including TST, would be able to provide an adequate reaction rate for an enzymatic process. This is the motivation for the “promoting vibrations” hypothesis.



To address this issue we have applied the hyperplanar transition state optimization technique¹ to human dihydrofolate reductase (hsDHFR). It was proposed² that in hsDHFR promoting vibrations are important for the reactive event to occur. Therefore, it is a proper system to look for dynamic effects. The transmission coefficient obtained for the optimized RC based on solely substrate atomic coordinates is 0.75. Since no protein degrees of freedom at all were included in the RC, the protein does not seem to participate significantly in the RC during barrier crossing. Moreover, using ensemble reweighting we have calculated the transmission coefficient directly on the 0.5 isocommittor surface. The resulting value (0.93) indicates that dynamic effects have negligible impact on the reaction rate. This approach can be easily applied to check the validity of TST and the magnitude of dynamic effects for other processes in condensed phases.

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Dependence of double layer on Warburg impedance

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This basic work was inspired by the frequency-dependence of the double layer (DL) capacitance, which is caused by the long-range interaction of solvent molecules¹.

The relevance of the electrode reactions to the DL structure has been discussed in the context of acceleration or deceleration of heterogeneous rate constants of the charge transfer reactions², called the Frumkin correction³. Since heterogeneous kinetics can be observed as the second effect of mass transport, it is reasonable to discuss the effect of the DL capacitance on diffusion rather than the heterogeneous kinetics.

A simple redox reaction is often controlled by both a charge transfer step and a diffusional step. The former is complicated directly with the DL impedance because of involvement of a surface process, whereas the latter may be distinguished from the DL effect in that it occurs in solution phase. We should at the first stage examine the latter, i.e. the effects of the Warburg impedance on the double layer impedance. If both impedances are independent each other, they can be represented as a parallel equivalent circuit. A real part of the Warburg impedance for infinite diffusion has the same value as that of the imaginary one, according to the solution of the diffusion equation^{4, 5}, although complications occur at several geometries with combinations of reactions⁶. As a result, values of the observed real admittance subtracted from the imaginary one should agree with those of the DL impedance without involving redox species. This is a point to examine a detailed relation between the Warburg impedance and the DL impedance here.

We use here (ferrocenylmethyl) trimethylammonium (FcTMA) as a redox species without any effect of heterogeneous rates. Observed ac-currents necessarily include harmonic components on the assumption of a small value of the amplitude of the applied ac-voltage. The relation between the harmonics and the amplitude will be discussed here. Since a disk-exposed working electrode often yields such floating capacitance that the DL impedance may not be separated from the Warburg impedance, we use a platinum wire electrode without shielding. Dc-voltage and concentrations of FcTMA are varied in order not only to confirm the Warburg impedance but also to examine participation of adsorption of FcTMA.

Results are different from the preconceived ideas. According to the conceptual diffusion-controlled impedance, the values of the real impedance are smaller than those of the negative imaginary ones owing to the double layer impedance. However, the opposite behaviour is found in the Nyquist plot at which the experimental data fell on the domain of $|-Z_2| < |Z_1|$ in the dc-potential domain for the redox reaction. It can be explained in terms of either extreme enhancement of the DL resistance in the redox potential or generation of inductance at the DL layer caused by the redox reaction. The latter being possible will be discussed on this poster.

Key words

Generation of inductance; interplay of faradaic reaction and double layer capacitance; redox reaction of ferrocenyl derivative; ac impedance with frequency-dependence

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Efficient path integral dynamics on modern many-core hardware

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Dynamic phenomena in quantum systems connected to a dissipative bath have been target of scientific efforts for many years, yet their numerically exact solution still requires large computational efforts. One well-established way to solve the dynamic behaviour of an open quantum system relies on the quasi-adiabatic propagation of Feynman path integrals (QUAPI) in an iterative fashion.¹ Here, the iterative approach drastically reduces the number of necessary paths when propagating beyond the bath memory time. However, the number of paths still increases exponentially during memory time, necessitating further approximations especially for slow bath environments with long memory times.²

We present an efficient OpenCL implementation of the QUAPI methodology¹ with on-the-fly path selection³ that shows favourable scaling on modern multi- and many-core hardware such as Intel Xeon Phi. A new approximate treatment of long memory times achieves a reduction of the number of significant paths by mapping on a non-uniform time grid and merging of paths that coincide on the non-uniform grid. This allows for the investigation of charge and exciton transport in extended systems with up to 7 states characterized by slow bath environments. The accuracy of the method is demonstrated for a variety of benchmark systems reported in the literature⁴ as well as the Fenna-Matthews-Olson complex for which accurate HEOM results are available.⁵

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Electron transfer in organic and biological materials

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Electron transfer events are key phenomena, ubiquitous throughout physics and chemistry. In particular, electron transfer plays a prime role in numerous biochemical mechanisms, especially those mechanisms involving oxidation-reduction reactions, e.g. respiration¹. Electron transfer in liquids, organic materials or soft matter emerges from molecular fluctuations. For those occurring in complicated materials such as biological molecules or organic semi-conductors, experiments often fail to provide a complete microscopic picture of these fluctuations. Molecular simulations can shed some light by describing the system at the atomistic and molecular level. For instance, when electron transfer occurs between distant sites or molecules, Marcus theory (or more elaborated theory) associated with classical molecular dynamics produces a good estimate of the kinetic rate of the transfer². By combining these kinetic rates with a master equation, we can describe the ET process throughout large systems at different time scales. However, this method assumed a hopping mechanism between the sites and the validity of a rate theory (e.g. Marcus theory).

A general treatment of the electron transfer problem requires to take into account electrons explicitly, but faces two main challenges. First, exploring the electron transfer mechanisms necessitates sampling the system dynamics during a long time scale. For this reason, a classical description of the nuclei is mandatory. A number of methods have been developed to propagate the dynamics of a mixed classical-quantum system. In the case of electron transfers, Tully's Surface Hopping approach presents interesting results. The second challenge faced by a direct evaluation of electronic and nuclear trajectory is the calculation at each time step of the relevant purely electronic properties, e.g. the electronic coupling between reactant and product states. Calculating these electronic properties with an explicit electronic structure method is presently extremely expensive and can be done solely for small systems and over short times scales³. We propose to overcome this difficulty by using the recently developed Analytical Overlap Method⁴ in our group, which allows fast calculation of electronic coupling within chemical accuracy. This method is first applied to study electron transfers in a toy-model consisting of a chain of ethylene-like molecules⁵. Our first results highlight the different time scales arising in the electron transfer event and question the domain of validity of the rate theory for this event. In the future, we could apply our approach to much larger systems as proteins or organic semi-conductors.

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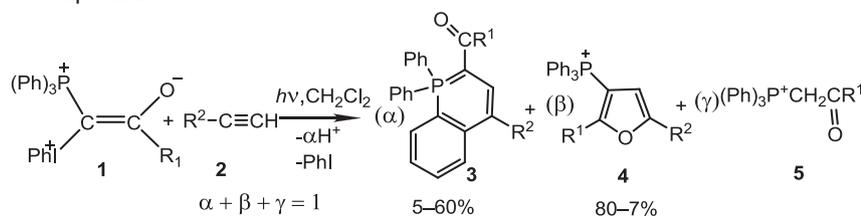
Experimental and theoretical challenges in the study of the mechanism of heterocyclization reaction between mixed phosphonium-iodonium ylides and acetylenes

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Heterocyclization of mixed phosphonium-iodonium ylides and acetylenes (Scheme, counterion BF₄⁻ is omitted) allows for the synthesis of P-containing heterocycles, λ⁵-phosphinoline **3**, and substituted furan **4** in metal-free reaction at room temperature.¹



The ratio of products **3** and **4** depends on acetylene structure: the more electron-rich acetylene the higher yield of furan **4**, and these ratios are 50 : 7, 45 : 30 and 5 : 80 for phenylacetylene, p-methoxyphenylacetylene and 9-phenanthrolylacetylene, respectively.

Reaction proceeds with induction time only in microheterogeneous medium in CH₂Cl₂ at the ylide concentration exceeding 0.01 M (particle size ~800 nm). Addition of acid in concentration not exceeding the ylide concentration decreases the induction time and accelerates the formation of **3**.²

Being iodonium salts, ylides **1** under irradiation undergo decomposition by two routes³: (i) homolytic C–I*Ph bond scission to give PhI^{•+} radical cation and radical from **1** and (ii) heterolytic C–I*Ph bond scission to give PhI and cation from ylide. The reaction mixture is a bouillon containing different types of radicals, radical cations and ions from the reagents and the solvent. Two types of relatively stable (lifetimes of several minutes) paramagnetic particles with different g-factors and hyperfine coupling constants are observed upon irradiation of the ylide in the resonator of ESR spectrometer. In the presence of acetylenes the formation of another radical with hyperfine coupling constants on ³¹P and ¹H atoms of the R² fragment of acetylene is observed. The radicals with acetylenes are secondary intermediates with lifetimes of 20–40 min and are formed in higher concentration.

In the study of the kinetics of product formation by ³¹P NMR, CIDNP phenomenon has been observed on the initial times of the reaction between **1** and p-methoxyphenylacetylene: non-proportional increase in the signal of salt **5** and emission signals of products **3** and **4**. It has been found that salt **5** and furan **4** are formed during the first 3–5 min of the reaction, whereas the formation of phosphinoline **3** occurs during 20–30 min.

The following problems are under discussion: (i) the reasons why the reaction proceeds only in microheterogeneous medium, (ii) the role of H⁺ ions generated in situ or added to the reaction mixture, (iii) the structure and origin of free radicals and their role in the formation of products, (iv) the nature of CIDNP effect and (v) the possibility to vary the ratio between the reaction products by changing the reaction conditions.

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Full- and one-dimensional semiclassical calculations of reaction rate constants

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Semiclassical Transition State Theory (SCTST)¹ is an efficient approach to rate constant calculations. Further gains in efficiency can be achieved by treating only a subset of the system's degrees of freedom (DOFs) in dynamics calculations². We are performing full- and one-dimensional (FD and 1D) SCTST calculations for the H atom abstraction reactions $\text{H}+\text{CH}_4$ and $\text{H}+\text{C}_2\text{H}_6$, and 1D SCTST calculations for the H atom exchange reaction CH_3+CH_4 . In the poster, the following aspects of our calculations will be presented:

Ab initio force constant calculations: The third and fourth potential derivatives required for FD SCTST calculations are obtained via numerical differentiation of Hessian matrices calculated using quantum chemistry³. A method based on Richardson extrapolation⁴ for systematically improving the accuracy of these derivatives using additional Hessian matrix calculations will be discussed. The derivatives along the reaction mode needed for 1D calculations are obtained by differentiating single-point energies.

Implementation of SCTST: Due to the computational expense associated with enumerating over all vibrational states of the transition state in SCTST calculations, the Wang-Landau algorithm is used to sample these states. A correction to SCTST proposed by Wagner⁵ that improves its treatment to tunnelling at low energies is also applied.

Comparison of the cost and accuracy of SCTST calculations: Rate constants calculated using SCTST will be compared to those from other experimental and theoretical studies to evaluate the accuracy. 1D rate constants will be compared to FD rate constants in order to evaluate the effect of reducing the number of DOFs treated, and the computational costs of these methods will also be compared.

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Influence of the excitation light intensity on the rate of bimolecular electron transfer reactions

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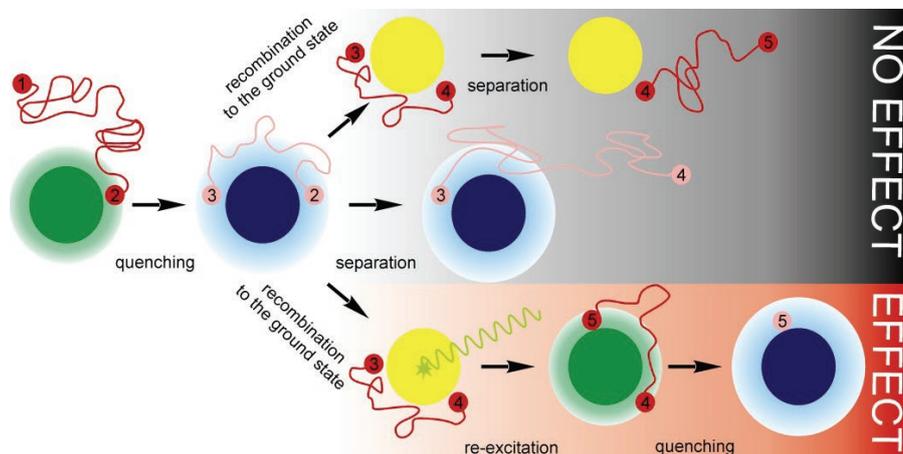
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We have tested experimentally whether excitation intensity - the number of photons per second absorbed by a sample - can affect the kinetics of photo-induced bimolecular reactions in liquid solution. It has been theoretically predicted that an increase of quenching efficiency should be noticed when increasing the excitation intensity¹. However, the level of photons density flux necessary to test this is enormous, and as such is unattainable through the use of lamps installed in commercial fluorimeters. Therefore, in order to test the former prediction we have constructed a dedicated apparatus inspired by fluorescence confocal microscopes and fed by a 1W green CW laser. By varying the amount of light used for excitation and comparing the Stern-Volmer (SV) constants, we have found that the effect is even larger than that anticipated by the existing theories. Nevertheless, the dependencies of the effect with free energy of the quenching reaction and viscosity are in qualitative accordance with the predictions.

In order to verify the previous effect we have performed experiments with fs-excitation in a fluorescence-up conversion set-up. In order to mimic the process responsible for the increase of the SV constant we have devised a dual pulse excitation modification of the set-up with a delay of 1-100 ps between pulses, such that the reacting systems may be re-excited after completing a full cycle of excitation-quenching-recombination.

Interestingly, the extent of the effect depends not only on the energetics and yield of the ionization reaction but also on those of the recombination to the ground state. This opens up the possibility of studying both processes within a single experiment.

The present work may have implications for the interpretation of the kinetics of bimolecular reactions as studied by means of fluorescence microscopy or by techniques employing ultrafast and powerful lasers of high repetition rates.



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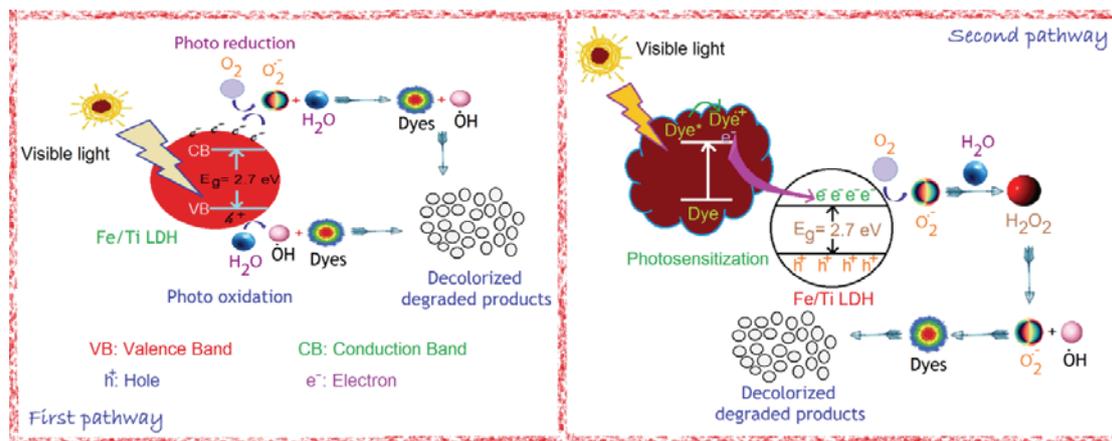
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Interpretation of electron transport with experimental and Markov Chain Monte Carlo simulations across Fe/Ti layered double hydroxide for efficient photocatalytic applications

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2:1 Fe/Ti layered double hydroxide (LDH), synthesized by a single step hydrothermal method, has been characterized by using XRD, XPS, PL, TRES, EIS, TEM, EDX, AFM, UV-visible DRS measurements. The LDH has been shown to possess hexagonal morphology, high surface area, narrow band gap, defect states and oxygen vacancies within its layered framework. It exhibited excellent semiconductor properties with remarkable visible light decolorization potential for cationic and anionic azo dyes like Crystal Violet and Reactive Orange 16 respectively in aqueous medium with higher activity than that observed with commercial catalysts like FeO, Fe₂O₃, TiO₂ and Degussa P25. The photocatalysis proceeds through hopping of e⁻-h⁺ pairs and by dye photosensitized pathways and reaction mechanisms have been established for the degradation of the dyes to less toxic and more eco-friendly molecules on the basis of the identified end-products of photodegradation. The electron transport across the LDH, investigated by photoluminescence and electrochemical impedance spectroscopy, has been co-related theoretically for the first time using Markov Chain Monte Carlo (MCMC) simulation studies. The results have validated electron transport to be the principal mechanism for imparting high photoactivity to the semiconducting LDH, paving way for its large-scale environmental applications. As a whole, the work yields valuable insights into the use of LDH as a photocatalyst and also into the concept of electron transport being associated with photocatalysis, under experimental as well as theoretical approaches. The results have been useful in understanding the fundamental concept of electron transport across novel photocatalysts.



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Investigating the dynamics of the disk- to slab- geometry phase transition

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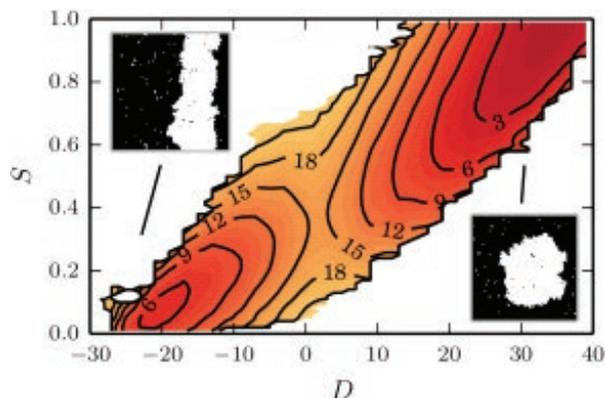
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Geometric phases¹ are found in systems which exhibit phase separation and are characterized by droplet shapes other than spherical that are stabilized by the use of periodic boundary conditions. We investigate the phase transition from a disk- to a slab-shaped cluster in the 2D Ising model in simulations with constant total magnetization and vanishing external field.

Two order parameters describing the structure of the cluster near the connection to its periodic image and the overall shape of the cluster respectively are introduced and their interplay is investigated by comparing the results of commitor calculations to solutions of the backward-Kolmogorov equation².

The observed significant shift of the critical isocommitor lines away from the ridge of the free energy landscape can be traced back to a difference in diffusion constants observed along the two coordinates, similar to what was previously shown by Metzner et al. for random walkers in 2D potential energy landscapes². In order to apply these methods to the collective variables used in this example, the apparent subdiffusion observed along one of the coordinates is treated by choosing an appropriate non-linear coordinate transformation on the basis of the observed time dependence of the mean-square displacement³. This allows for a reliable measurement of diffusion constants and leads to qualitative agreement with the measured commitor data.



Free energy as a function of two order parameters that characterize the cluster shape.

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Kinetics and thermodynamics of heteromolecular filament and cluster assembly

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The self-assembly of molecular building blocks into linear filaments is a common form of self-organisation in nature, and underlies the formation of both functional and pathological supra-molecular polymers in a variety of contexts, including in human biology. To date, theorists' attention has focused mainly on homo-molecular assembly. However, it has become apparent that hetero-molecular assembly is also of significant importance. Here, we present a general kinetic scheme for mixed protein filament formation, and derive closed-form analytical expressions that describe the dynamics of such systems. We next investigate the thermodynamics of filamentous growth and derive the partition function and equilibrium composition for such a system. Finally, oligomeric species have recently been discovered to be intermediates on the pathway to filament formation in certain biological systems, notably in protein filament formation in amyloid diseases such as Alzheimer's. An increasing weight of evidence holds these species responsible for the symptoms of these diseases. We therefore investigate the thermodynamics of small heteromolecular cluster formation, drawing on micelle theory and mean-field theory, and derive an approximate partition function and system composition.

Lindblad approach to quantum transition rate theory

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The generalisation of classical transition rate theory to quantum mechanics is a long-standing problem. A common approach is to interpret Feynman's isomorphism between a quantum-mechanical particle and a periodic ensemble of harmonically interacting classical particles in a dynamical sense, leading for example to the so-called ring-polymer molecular dynamics (RPMD) method. Here we investigate a toy model to shed further light on the connection between this type of semiclassical description for the open quantum dynamics and the results based on the quantum master equation. We study the time evolution of a particle in a double-well potential governed by a Lindblad equation, as a quantum analogue of a classical Langevin equation. We use the quantum state diffusion approach, where the evolution of the density operator is modelled by an ensemble average over stochastic Schrödinger equations. By using a Gaussian ansatz for the wavepacket we show that the classical limit of the pure state dynamics corresponds to a Langevin equation. We investigate the effects of quantum-mechanical tunnelling and coherence in comparison to the classical dynamics and outline how this model can be used to assess the correctness of the RPMD method.

Locating instantons in calculations of tunnelling splittings

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An exact treatment of tunnelling dynamics in molecular systems requires the potential energy surface (PES) that covers all geometries accessible to the nuclear wave function and scales exponentially with the number of degrees of freedom (DOF), so even for small gas-phase systems, it is a challenging computational task. The semiclassical instanton method¹ relies on the approximation in which only the dominant contribution to the quantum partition function is calculated, which comes from the stationary (Euclidean) action path for the motion of nuclear DOF on the PES, the instanton. The use of instantons to obtain accurate tunnelling rates² and tunnelling splittings³ in the polyatomic systems at a relatively low computational cost has recently gained in popularity.

We present an efficient numerical approach⁴ for calculating tunnelling splittings between two symmetric wells in a polyatomic system using the semiclassical instanton method. In the instanton method, the search for the stationary action represents the bulk of computational effort. The instanton trajectory is discretised using a set of equidistant system replicas. Instead of finding instantons at a particular temperature, one can search for instantons at a particular energy, whereby the stationary action path is converted into the minimum action path (MAP)⁵. We employ this idea and adapt the standard methods for finding minimum energy paths (MEP)⁶, such as nudged elastic band, string/quadratic string method and FIRE, for locating instantons with minimal number of system replicas (DOFs) and study the performance of the methods. The critical difference between the MEP and MAP finding is that the orientations of the system replicas with respect to each other are important in the MAP. The approach is general since it uses Cartesian coordinates and has a similar computational cost to the MEP finding, so it is widely applicable.

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Mechanism of tungsten-containing benzoyl-CoA reductase

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Benzoyl-Coenzyme A plays a central intermediate role in anaerobic metabolism of aromatic compounds in living organisms. First step towards aromatic ring degradation in anaerobic microorganisms is two-electron reduction of benzoyl-CoA to cyclohexa-1,5-dienoyl-1-carboxyl-CoA (dienoyl-CoA). Albeit facultative anaerobes utilize two molecules of ATP for this aromaticity disruption, in obligatory anaerobes, where ATP is more scarce, a multi-subunit ATP-independent enzyme complex BamB-I developed instead. In *Geobacter metallireducens* it is composed of eight subunits - BamBCDEFGHI, where BamB is the catalytic subunit, while the rest serve as electron carriers, providing electrons for the difficult reduction by so far unclear mechanism.

In our computational study, we started from crystal structure of BamBC part of the complex. It is a heterotetramer, composed of two big B subunits connected by two small C subunits, that probably link the tetramer to the rest of the complex. Catalytic subunit B contains tungsto-bispterin and [4Fe4S] cluster, each subunit C binds three [4Fe4S] clusters. The substrate is bound in the vicinity of the tungsten, the final electron donor. The tungsten is coordinated by four sulfurs of the pyranopterin cofactors, a sulfur of a cysteine and by a sixth ligand, that could not be reliably resolved in the crystal structure (denoted X). This uncertain ligand X (i.a. inorganic sulphur or cyanide) could, however, play a significant role in catalysis, since it is supposed to be pointing towards the substrate.

In presented study, we first investigated the influence of tungsten oxidation state and ligand X identity on the protonation state of the protein using continuum electrostatic methods. The influence of the ligand X identity and protonation on the catalytic mechanism and the reaction rate was then investigated in the hybrid QM/MM environment.

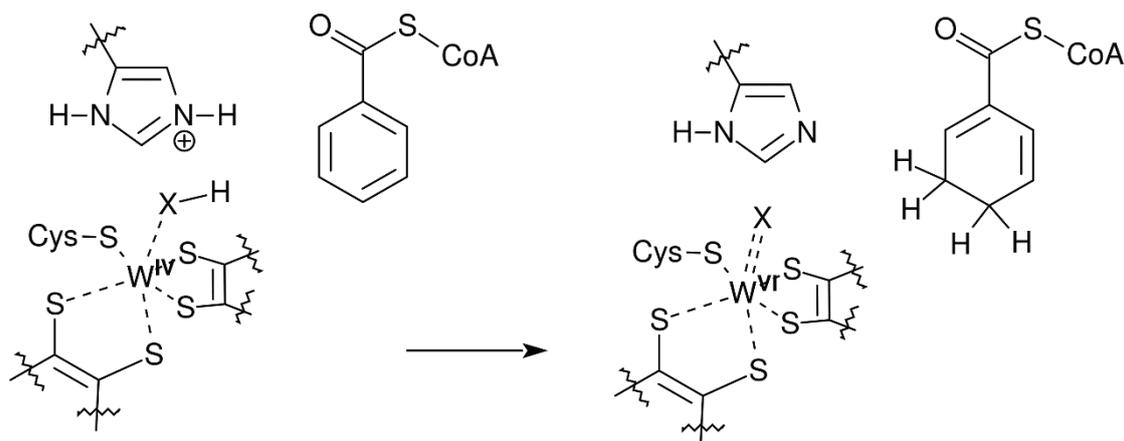


Figure 1. One prospective reaction mechanism of benzoyl-CoA reduction in the active site of BamB

Molecular dynamics simulations for the detection of unfolding pathways and stable conformations of DNA oligonucleotide in the presence of urea

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The formation of specific DNA secondary and tertiary structures has been reported to play a key role in various range of biological processes, such as transcription termination or intermolecular binding. Among them, a pivotal role has been ascribed to DNA i-Motif and G-Quadruplex structures, which due to their biological appearance in telomeric and centromeric DNA are considered as potential targets for various diseases. Recent studies on high-temperature unfolding simulations of the DNA iMotifs have revealed the existence of stable hairpin configurations as an intermediate step in the unfolding pathway of DNA higher-order structures¹. In our study, we investigate a simple 7-nucleotide DNA hairpin structure with the sequence d(GCGAAGC)² to achieve a detailed insight into the stability of DNA hairpin structures and their interaction with the osmolyte urea.

The interaction between DNA and urea in unbiased simulations was analysed according to Kirkwood-Buff theory³. The free energy landscape of unfolding has been approached via Metadynamics^{4, 5} upon the addition of a bias potential. This allows us to get a more comprehensive understanding of the stability of the DNA structures in the presence of urea.

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Molecular dynamics study of reaction kinetics in Li-O₂ systems

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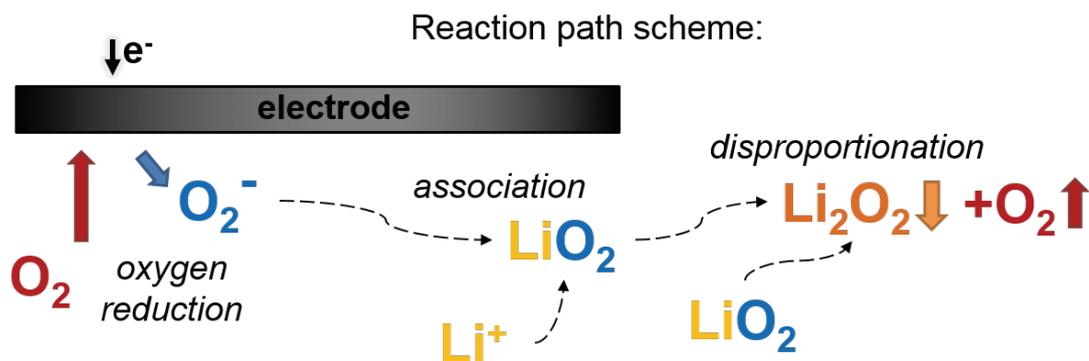
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Li-air (Li-O₂) batteries attract lots of attention over the past few years as it hopefully can enable energy storage with a several times higher specific energy than Li-ion batteries. The development of such systems, however, uncounted a number of problems such as low capacity, low rate-capability and poor rechargability. All those issues are connected to the underlying chemistry of oxygen reduction (ORR) in nonaqueous solutions. The net reaction in a Li-O₂ cell is $2\text{Li} + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$. Nevertheless, several reaction steps including both heterogeneous and homogeneous ones may take place. The overall reaction pathway depends on the relation between kinetic rates of the individual reaction steps.

In this work, we started our theoretical study of Li-O₂ chemistry by applying Marcus theory framework to the ORR in aprotic solutions often used in Li-O₂ experiments, i.e. acetonitrile, DMSO and DME. The molecular dynamics tools were employed to simulate explicitly solvent molecules structuring around either O₂ or O₂⁻. The solvent reorganization energies were calculated and linked to physical and chemical properties of the solvents. The calculated values would be used to estimate electron transfer rate and to determine the current-overvoltage dependencies.

In addition, approach barriers for two reactant pairs (O₂⁻/Li⁺ and LiO₂/LiO₂) involved in chemical reaction steps were estimated through calculation of mean force potential. Although ionic species were demonstrated to own pronounced solvation shells in contrast to neutral LiO₂, the difference in approach barriers was found to be negligible even in highly polar solvent. Thus, the disproportionation reaction should be the slowest and LiO₂ should be the long-living form of the superoxide in the system.



Non-equilibrium quantum correlation functions from Ring-Polymer Molecular Dynamics

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During the last decade the Ring-Polymer Molecular Dynamics (RPMD) approach has proven to be an efficient method to approximately simulate quantum mechanical effects in chemical systems. Based on the path integral formulation, RPMD incorporates quantum effects using classical trajectories in an extended ring-polymer phase space. It exhibits appealing features including preservation of detailed balance, being exact in several limiting cases and it can be run efficiently exploiting techniques known from molecular dynamics. However, the current formalism has been limited to the calculation of correlation functions associated with the equilibrium Boltzmann distribution. In this poster the extension of the RPMD approach to simulate processes with non-equilibrium initial conditions is discussed. Furthermore, the prospects of the approach to study photoexcited processes like excited-state proton transfer is investigated.

Nonadiabatic rate coefficients and dynamics of atmospheric oxidation intermediates: Photolysis of isoprene oxidation intermediates

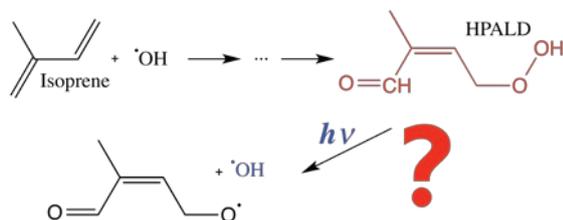
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Earth's atmosphere is the scene of a plethora of chemical reactions involving all sorts of molecules, including complex volatile organic compounds (VOCs). Isoprene is one of the most abundant biogenic VOCs, and its oxidation strongly influences the chemical composition of the troposphere. Despite highly sophisticated and detailed chemical models, a major discrepancy still exists between the predicted and measured concentration of OH radicals upon isoprene oxidation. Different alternative OH production pathways have been proposed, but one central question recently emerged: are photochemical processes important to the mechanism of OH recycling from VOC intermediates? C5-hydroperoxy-aldehydes (C5-HPALD) are isoprene-oxidation intermediates, which could potentially produce OH radicals photochemically.¹ Experiments in the laboratory – conducted on the more stable proxy molecule C6-HPALD – confirmed a photolysis channel leading to OH. However, it remains unclear whether such photochemical OH production channel is viable in atmospheric conditions for the C5 isomer.

In this work, we extensively studied C5-HPALD and C6-HPALD from a theoretical perspective, using nonadiabatic molecular dynamics and microcanonical rate theory. Computed photoabsorption cross-sections (obtained from a wide range of quantum chemical methods) quantitatively reproduce the experimental photolysis rate constant. Characterization of the electronic states of C5- and C6-HPALD indicates that S_2 exhibits dissociative character ($n'(O-O) \rightarrow \sigma^*(O-O)$) in the Franck-Condon region. However, this electronic state cannot be reached by direct sunlight absorption, implying that any photolysis pathway should be initiated from the weakly-allowed transition to S_1 ($n(C=O) \rightarrow \pi^*(O=C-C=C)$), followed by nonadiabatic interactions with S_2 . Using the AIMS (Ab Initio Multiple Spawning) algorithm, we investigated the excited-state dynamics of C5-HPALD in gas phase. We observed long-lived (i.e., picosecond timescale) adiabatic dynamics of C5-HPALD in S_1 , punctuated by strong S_2/S_1 nonadiabatic interactions leading to an OH dissociation. Interestingly, the nonadiabatic interactions have the tendency to trap the molecule in a $n(C=O) \rightarrow \pi^*(O=C-C=C)$ character, and therefore prevent ultrafast OH photolysis, as would be expected from a purely Born-Oppenheimer picture. This extended lifetime of C5-HPALD in S_1 opens a competing deactivation pathway, namely an intersystem crossing to low-lying triplet states, also exhibiting an OH dissociation character.

Based on the mechanistic details extracted from the nonadiabatic dynamics simulations, we refined our electronic-structure calculations and built a microcanonical rate theory model, which describes kinetics across the S_2/S_1 intersection seam. This kinetic model allows us to extrapolate our in vacuo AIMS results to atmospheric conditions, and obtain kinetic rate coefficients in temperature and pressure regimes which are characteristic of the ambient atmosphere.



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Potential energy surfaces in quantum dynamics using Gaussian process regression

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Recent methodological advances in the field of theoretical quantum dynamics have made the study of molecules of non-trivial size feasible^{1,2}, however, the bottleneck in terms of effort is the construction of the potential energy surface (PES) on which the nuclear wavefunction evolves. In order to minimise effort, and make methods usable by non-experts, the PES should ideally be constructed on-the-fly, that is while the nuclear dynamics is proceeding. As quantum dynamics is inherently non-local, this is an issue. One solution is the use of Gaussian functions as the basis of the nuclear wavefunction which allows a local harmonic expansion of the PES around the centres of the dynamic Gaussians to be calculated, from which Shepard interpolation, for example, is used to construct a global representation of the PES³. This method requires, however, the calculation of energy gradients and Hessians, a significant computational effort for large molecules. In this work we will present recent methodological developments in the construction of PESs using Gaussian Process Regression⁴, a method which only requires evaluation of molecular energies, along with illustrative examples.

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Boxed molecular dynamics: Cheap *in silico* screening of medicinal cyclic peptides by estimating rates of cyclization and kinetics of AFM protein unfolding

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Boxed Molecular Dynamics (BXD) is a method of enhanced sampling which drastically speeds up the convergence of classical Molecular Dynamics simulations of free energies and reaction rates.^{1,2} Recently this technique has been used to accurately reproduce experimental data for the mechanical unfolding of proteins³, peptide cyclization² and many other processes occurring on the timescales up to the order of seconds, far beyond the reach of conventional MD simulation.⁴ Two new applications of BXD are presented:

- 1) *In silico* screening of medicinal peptide cyclization with BXD is reported. Cyclic peptides are promising candidates for new antibiotics and anti-cancer drugs. However, the cyclization of a linear peptide is difficult as cyclizable amino acid sequences are found only by trial and error and no successful predictions of the cyclizable sequences have been made so far. BXD was used to predict which sequences could and could not be cyclized and scored 75 percent in a blind test against experimental data, with each prediction converging in a few CPU days. Therefore, an *in silico* tool for finding cyclizable peptide sequences is suggested. This work provides an example of when a biochemical property can be predicted solely from the amino acid sequence⁵. In addition our simulations shed light on the mechanism of enzymatic cyclization.
- 2) AFM protein pulling has been simulated with BXD and the experimental data for a number AFM pulling experiments have been reproduced. Calculations show the presence of the pulling force “humps” previously observed in the experiments and allow the identification of intermediate protein conformations responsible for them.

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Quantum path integral and correlation functions in coherent state representation with the help of classical dynamics in extended phase space

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New techniques for performing quantum calculations in Coherent State representation are presented:

- 1) An algorithm is proposed to evaluate real time Feynman path integral in the Coherent State representation [1].

$A_{fi} = \langle p_f q_f | e^{-i\hat{H}t} | p_i q_i \rangle$ The amplitude between two arbitrary phase space points described by two Coherent States, not necessarily those connected by a classical trajectory, can be evaluated by the steepest descent method. The saddle point, which determines the integral, can be found from a trajectory in extended phase space of the dimensionality equal to the product of that of the actual space of the physical system and the number of the path integral slices. The equations of motion for the saddle point trajectory are derived with the help of parametric continuation technique [2]. It is shown that steepest descent method yields accurate result for quantum amplitude only for a short time.

$$\frac{\text{tr} \left(e^{-\frac{\beta}{2} \hat{H}} e^{-i\hat{H}t} \hat{A} e^{i\hat{H}t} e^{-\frac{\beta}{2} \hat{H}} \hat{B} \right)}{\text{tr} \left(e^{-\beta \hat{H}} \right)}$$

- 2) An algorithm to calculate correlation functions is presented, which is also based on trajectories in the extended phase space driven by an effective Hamiltonian. The approach exploits the isomorphism between quantum dynamics and classical dynamics in extended phase space noted in [3]. A formally exact expression for the correlation function is derived. Its structure is very similar to that of Ring Polymer Molecular Dynamics (RPMD) [4] and RPMD can be obtained as a well-defined approximation to the exact result.

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Reaction coordinate, free energy and rate for the key proton transfer reaction in human carbonic anhydrase II

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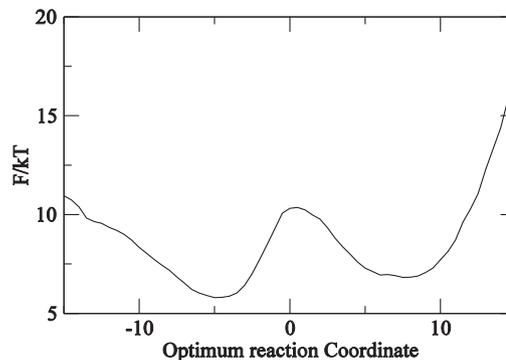
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For an enzyme catalysed reaction, a direct comparison of its experimentally measured rate and free energies to those estimated from molecular simulations still remains a challenge. In this article, we adopt transition path sampling simulation to obtain an optimum reaction coordinate for the key reaction from an ensemble of unbiased, reactive transition paths across a high free energy barrier. The free energy profile and rate of transfer are also estimated along the reaction coordinate.

The proposed method is applied to human carbonic anhydrase II (HCA II), one of the most efficient enzymes known. It is a zinc based metallo-enzyme comprised of 259 amino acid residues and catalyses the reversible hydration of CO_2 in the micro-second timescale. The rate determining step in the catalysis is known to involve deprotonation of a zinc-bound water molecule at the active site followed by the transfer of an excess proton to the sidechain of the residue His-64 via 2-3 water molecules.

We model this step starting with a high resolution crystal structure followed by optimization of the active site using two Layer ONIOM (HF/6-31G*/AMBER)¹. However, the desired proton transfer is observed only by using steered molecular dynamics² combined with SCC-DFTB (QM/MM)³. These biased trajectories are subsequently used as seeds in harvesting an ensemble of unbiased, reactive transition paths with aimless shooting⁴. The method of forward-trajectory likelihood maximisation [7,8] used in conjunction with a Bayesian information criterion method analyses 33 candidate collective variables and yields an optimum reaction coordinate⁵. The latter is found to derive contributions not only from the variation in bond distances while being broken and made, but also from active site residues such as His-64, Asp-62, Asp-67 and Glu-106. The resultant free energy profile (shown on the right) correctly reproduces the experimentally known free energy barrier of about 9 kcal/mol[9]. Implication of these results for the estimation of rate is also discussed.



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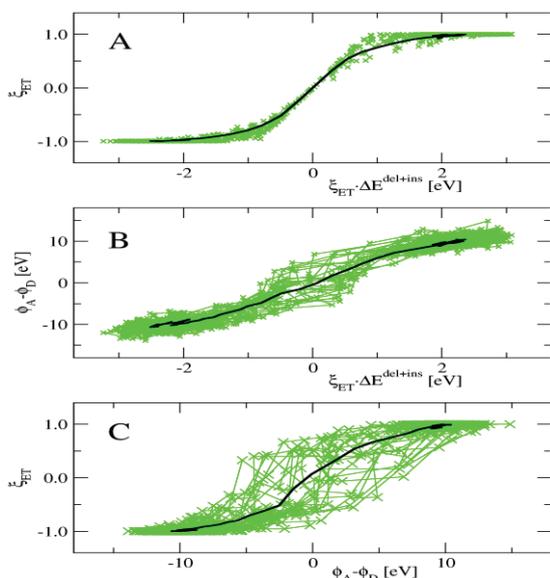
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Reactive trajectories of the $\text{Ru}^{2+/3+}$ self-exchange reaction and the connection to Marcus' theory

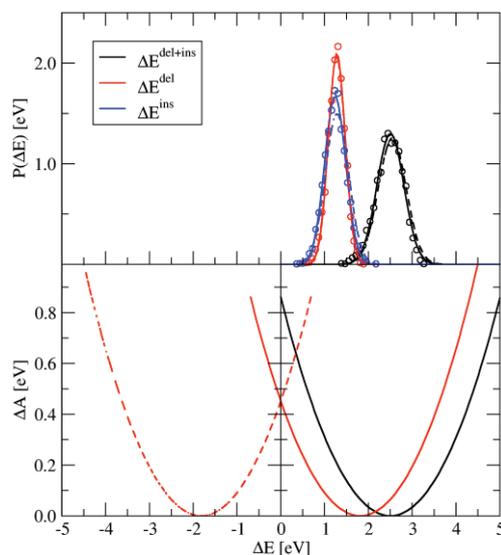
Tiwari, Ambuj and Ensing, Bernd
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Outer sphere electron transfer between two ions in aqueous solution is a rare event on the time scale of first principles molecular dynamics simulations. We have used transition path sampling to generate an ensemble of reactive trajectories of the self-exchange reaction between a pair of Ru^{2+} and Ru^{3+} ions in water. To distinguish between the reactant and product states, we use as an order parameter the position of the maximally localised Wannier center associated with the transferring electron. This allows us to align the trajectories with respect to the moment of barrier crossing and compute statistical averages over the path ensemble. We compare our order parameter with two typical reaction coordinates used in applications of Marcus theory of electron transfer: the vertical gap energy and the solvent electrostatic potential at the ions.

Until now, the main approach to study this prototypical self-exchange reaction at the DFT level of theory was by means of the half-reaction approach. Here instead we performed equilibrium DFT-MD simulations of a pair of donor and acceptor ions in solution. As it is not possible for the full reaction to sample the vertical gap energy, ΔE , of transferring the electron from the donor ion to the acceptor ion, the gap energy was probed indirectly as the sum of the energy needed to delete an electron from the donor ion, ΔE^{del} , and the energy required to insert an electron at the acceptor ion, ΔE^{ins} . This allowed us to compute the free energy profiles of the full diabatic electron transfer reaction.



Correlation between the three reaction coordinations used here to describe the electron transfer reaction. Green crosses and lines denote the points visited along the reactive trajectories; The black lines show the average over all accepted paths



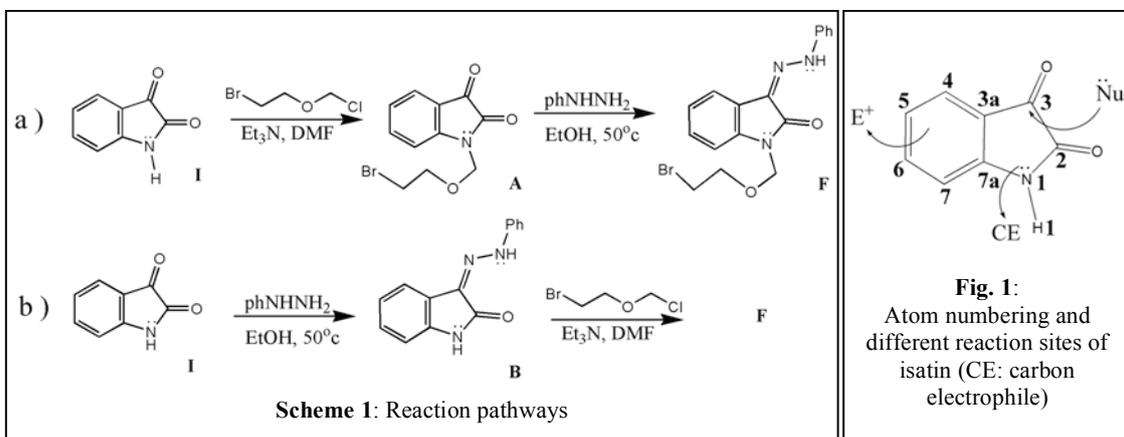
Top panel: Distributions of $\Delta E^{\text{del+ins}}$, ΔE^{ins} , and ΔE^{del} + ΔE^{ins} , computed for the $\text{Ru}^{2+} + \text{Ru}^{3+}$ system. Bottom panel: parabolic free energy curve obtained from the Gaussian fit function (solid black line) and the final free energy curves (red) that are shifted based on $\lambda^{\text{del+ins}}$

Slow and low yield *N*-alkylation of 3-(2-phenylhydrazono)indolin-2-one, compared to that of 1*H*-indole-2,3-dione; reasons by theoretical investigation

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Synthetic strategies of an important derivative of isatin's (1*H*-indole-2,3-dione, see Fig. 1 for atom numbering and its different reaction sites) Schiff bases, which have been reported to possess important pharmaceutical activities¹⁻⁵, are focused in the present study. Two synthetic procedures⁶ (Scheme 1) are reported to obtain 3-(2-phenylhydrazono)-1-((2-bromoethoxy) methyl) indolin-2-one (**F**) from isatin (**I**). The first pathway is the direct condensation of **I** in the presence of strong base Et₃N with 2-bromoethoxymethyl chloride (RX as electrophile for *N*-alkylation) that gives acyclic nucleoside 1-((2-bromoethoxy) methyl) indole-2,3-dione (**A**). Compound **A** subsequently converted to its hydrazone analogue **F**, using phenylhydrazine solution in EtOH. The second pathway to obtain compound **F**, i.e. direct condensation of 3-(2-phenylhydrazono) indolin-2-one (**B**) with RX, has been shown to be slow and give very poor yield of **F**. Since the RX used is a very strong electrophile, the poor yield of this reaction should be because of vanishing nucleophilic character of N1 atom of intermediate **B**. Some previous studies⁶ suggest this could be attributed to the formation of intramolecular hydrogen bonding (IHB) in the lactim form of compound **B**, in which there is no adjacent H1 atom to the atom N1, and so the nucleophilic power of N1 diminishes. Different DFT levels of calculation, using GAUSSIAN 09W and GENNBO 5.0 programs, have been used to illustrate the possible explanations of diminishing nucleophilic nature of N1 in compound **B**. According to the relative stabilities at all used levels, the presence of lactim tautomers of **I** and **B** is improbable. Therefore the H1 engaged in IHB as the reason for the problem was rejected. Based on the NBO analyses, reactants **I** and **B** show no remarkable difference in nucleophilic property of N1. So, assuming two-step reactions of **B** and **I** with RX in presence of base, the anions **B**⁻ and **I**⁻ were considered as nucleophiles. Optimizations and NBO analyses showed that in **B**⁻, the atom N1 has two σ-bonds and a π-bond (N1-C7a), while there are only two σ-bonds in **I**⁻, without any π-bond. Instead, **I**⁻ has two free lone pairs on N1, while there is just one lone pair in **B**⁻. So, turning a lone pair in **I**⁻ to a π-bond in **B**⁻ could be the main reason of diminishing nucleophilic character of N1 in **B**⁻. Detailed studies of NBO analyses and comparing **B** with **B**⁻, and **I** with **I**⁻, result in more satisfactory findings.



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State space path integrals and mean field dynamics for nonadiabatic reaction rates

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We present an imaginary-time, state-space path integral method for calculating electron transfer rate constants for multi-state, multi-electron processes in the condensed phase. Our approach involves computing a transition state theory rate estimate using an exact path integral in discrete electronic states and continuous Cartesian nuclear coordinates. A dynamic correction to the transition state theory estimate is then obtained using mean field ring polymer molecular dynamics. We establish the numerical accuracy of our approach for a wide range of system-bath models, varying parameters including driving force, electronic coupling, and bath friction. Further, we explore and identify good reaction coordinates for the different regimes of Marcus theory; in particular, we show that using a reaction coordinate based on electronic state populations allows us to capture the turnover in rates of electron transfer in the Marcus inverted regime.

Stochastic model of multistage non-equilibrium electron transfer reaction in polar solvents with several relaxation timescales

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Electron transfer (ET) reactions in polar media are known to be strongly coupled to solvent polarization around the reactants. In solvents with relaxation timescales, single-step intermolecular ET is commonly described in terms of solvent coordinates, with each coordinate representing separate solvent relaxation mode¹. However, many multistage photoinduced ET processes in large supramolecules cannot in general be described using this 2-state/-mode approach until these processes involve ultrafast ET steps between distant donor and acceptor centers. Such reactions often proceed under non-equilibrium conditions and are strongly affected by dynamics of solvent polarization at previous ET steps.

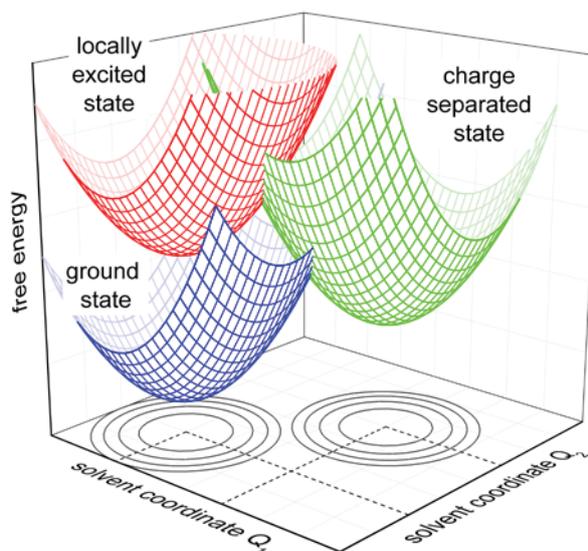
Here we report the development of a general model of ultrafast electron transfer reaction, taking into account both multimode relaxation of solvent and multiple non-equilibrium electronic transitions within a supramolecule. The approach is based on construction of two coordinate subspaces: 1) the subspace of "spatial" coordinates (Q_s), where is the number of electron localization centers within a supramolecule), and 2) the subspace of "relaxation" coordinates (Q_r). Configuration space of the model is then constructed as a direct product of these subspaces. Validity of this approach is discussed.

We also propose a method for constructing parabolic free energy surfaces (FES) for electronic states of the molecular system using known values of solvent reorganization energies for transitions (λ). A set of differential equations for the probability distribution functions of particles on these FES is written. Efficient algorithms for numerical solution of these equations based on the Brownian simulation technique^{2,3} are discussed.

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Studying complex reactive systems with accurate Potential Energy Surfaces

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Potential Energy Surfaces (PES) are mainly used to study the rate of elementary bimolecular reactions and their dynamics, being useful to compute state to state rate constants. When we have a complex reactive system, many elementary reactions are involved and the overall study becomes difficult. Complex reactive systems are usually treated by kinetic models, which suppose thermal equilibrium between reactants, intermediates and products present in the mixture.

In a gas phase combustion or explosion, as well as in interstellar chemistry, reactants and intermediates can be far from thermal equilibrium, i.e., the number of non-reactive collisions can be small and the energy distribution of the intermediate species can be far from the Boltzmann distribution. As the efficiency of the collisional energy transfer is different for vibrational, rotational and translational energies, it can occur that a molecular species presents different temperature distributions for each kind of energy.

In order to circumvent this problem, a new algorithm to model complex reactive systems using accurate PESs has been proposed and successfully applied to combustion chemistry¹. There, we proposed to model the overall process integrating the equations of motion in a global PES (gPES) surface built from PESs corresponding to each of the most important elementary reactions present in the system. This gPES is constructed by assigning each atom to a PES defined by the electronic partition function of the colliding partners. In addition we include long-range attractive forces and short-range repulsive potentials to account for non reactive collisions.

The presence of PESs from different authors than can introduce energy conservation problems. The introduction of switching functions², when changing from different PESs, has shown to circumvent this problem.

In this poster, we present preliminary results for the energy distribution of the OH radical present in a combustion of a hydrogen and oxygen mixture. They shown that, despite the large number of collisions, the OH radical is vibrationally excited, when compared with the rotationally and translational energy distributions. This result reinforces the value of molecular simulations to study fast gas phase reaction systems such as combustion.

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Studying the pressure dependence of the termolecular reaction

$$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$$

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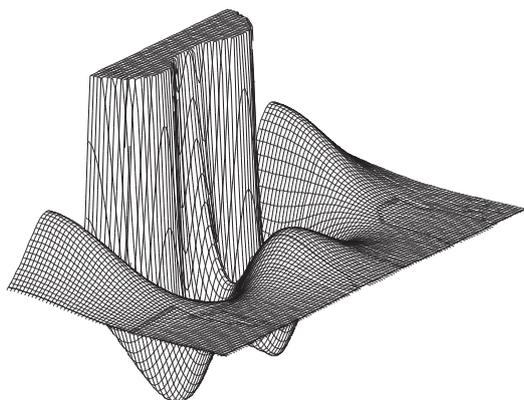


Figure 1 An H atom around an O₂ molecule.

The pressure dependence of the termolecular reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ is one of the main sources of uncertainty when modelling hydrogen combustion chemistry¹. This reaction is initiated by a $\text{H} + \text{O}_2$ collision giving a long lived excited HO_2^* radical that can react to products, $\text{O} + \text{OH}$, which is endothermic, dissociate back to reactants, $\text{H} + \text{O}_2$, or be stabilized by collision.

The long-lived nature of this radical is a result of its electronic structure. At collinear and perpendicular geometries this radical correlates with a hydrogen atom in a 2p state. By this way, the dissociation back to $\text{H} + \text{OH}$ has energy barriers in these directions. In Figure 1, we display the energy of a hydrogen atom around an oxygen molecule at its equilibrium geometry.

Being a termolecular reaction, it cannot be studied using normal classical trajectory programs. We have adapted the program MReaDy² to study this reaction at 2 000K and pressures of 10, 20 and 50 atm. With this program we can take into account the energy transfer by collision. Following the HO_2^* radicals formed, we are able to evaluate its stabilization. In Figure 2 we display preliminary results for this process showing a clear increase of the rate constant with pressure.

In this poster we present a kinetic study of this process.

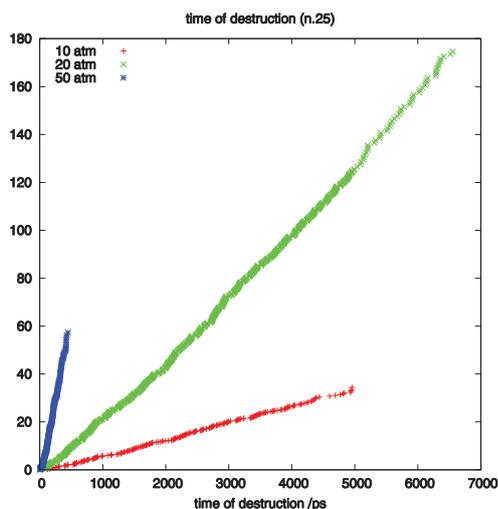


Figure 2 Number of HO₂ radicals stabilized by collision at 10, 20, and 50 atm.

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The dynamical coupling of electrons and nuclei within the nuclear velocity perturbation theory

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The calculation of the dynamical coupling between electrons and nuclei beyond the Born-Oppenheimer (BO) approximation builds a computationally expensive task and is a priori not feasible for large systems. Therefore, to calculate the non-adiabatic effects in physically or chemically interesting systems the unfortunate scaling of the problem dimensionality with the system size has to be overcome.

We have developed a Nuclear Velocity Perturbation Theory (NVPT) for perturbatively including non-adiabatic effects in the equations of motion for electrons and nuclei.¹ Based on the exact factorisation of the electron-nuclear wavefunction, the new formalism offers an exact starting point to include correction terms to the BO form of the molecular wave function.^{2,3} The corrections depend on a small parameter that in a classical treatment of the nuclei is identified as the nuclear velocity.

Whereas the electronic motion induced by nuclear dynamics is identically zero within the BO framework, the NVPT allows the evaluation of electronic currents along molecular trajectories and reaction paths. The approach can straightforwardly be combined with molecular dynamics simulations and free energy methods.

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Unexpected behavior of hydrogen tunneling on transition metal surfaces

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The diffusion of adsorbed particles is of fundamental importance to chemical and physical processes on surfaces, including film or crystal growth, associative desorption, and heterogeneous catalysis. Fundamental understanding of hydrogen (H) diffusion is important to future catalyst design and experimental work in surface science. We show that on the 110 surface of some FCC transition metals, a flat-top shape barrier for H diffusion exists. To understand the general behavior of these type of barrier and their uniqueness compared with other shape barriers, we constructed 4 1D barrier with different shape and compared the tunneling behavior on these barriers. We found that on the flat-top barriers, the transition between classical over the barrier hopping to deep quantum mechanical tunneling happens in a very narrow temperature window, in which both classical and deep tunneling happens equally likely. Such behavior deviates from the typical behavior and is a challenge for the current theories. We tested different theoretical approaches on this the square shape barriers and the improved instanton theory have good performance.

Towards a microcanonical tunnelling theory

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The phenomenon of quantum tunnelling is crucial in order to make accurate predictions for chemical reaction rates, particularly for those involving the transfer of light atoms such as hydrogen. This is especially true for reactions that take place in extremely cold environments as for instance in molecular clouds in interstellar space.

A widely used method to describe tunnelling effects in large systems is the use of instanton theory in the canonical ensemble which allows the calculation of reaction rates at well-defined temperatures. For reactions in the gas phase, however, a formulation of instanton theory depending on (collision) energies rather than temperature is needed.

In order to obtain such a formulation of instanton theory a semiclassical approximation¹ of the density operator in the microcanonical ensemble is achieved using the Feynman path integral formulation of quantum mechanics in order to obtain the cumulative reaction probability^{2,3}.

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Tracking solvent controlled photoinduced electron transfer using broadband fluorescence up-conversion

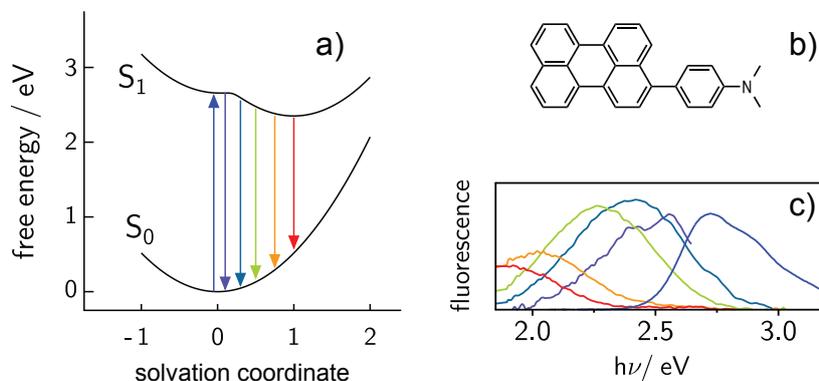
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Solvation dynamics is crucial for understanding the charge transfer reactions in liquids.[1] Here we revisit the kinetics of a donor-acceptor molecule [2] in several solvents of varying static and dynamic dielectric properties, measured by means of femtosecond broadband fluorescence up-conversion [3]. We have tried to rationalize the data using several different theoretical approaches based on the Generalized Smoluchowski Equation equation [4], the Sumi-Marcus model and an adapted Generalized Langevin Equation model. The potential energy surfaces have been reconstructed from the stationary absorption and fluorescence data and the friction over them determined experimentally by using a none reacting probe. The merits and demerits of each of these models will be discussed in the poster.



a) Representation of the free energy surface for the LE/CT transition of (b). c) Broadband fluorescence spectra at consecutive times, allowing to track the reaction progress.

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Tunnelling rates in reduced instanton theory

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The calculation of accurate reaction rates in canonical instanton theory suffers from two inherent restrictions. The first of these restrictions occurs near the crossover temperature, where instanton theory tends to overestimate rates. The second is a problem of computational scaling, reactions involving many degrees of freedom require the diagonalisation of a potentially very large matrix.

We have implemented a version of reduced instanton theory in DL-FIND¹ based on the theory developed by Kryvohuz². The rates calculated by canonical instanton theory and reduced instanton theory are compared back-to-back. Our test cases are the tunnelling of a hydrogen atom on the Müller-Brown surface, the reaction of methylhydroxycarbene to acetaldehyde and the reaction of H₂ with OH.

At temperatures close to the crossover temperature and above, we show that reduced instanton theory exhibits none of the divergent behaviour of canonical instanton theory. We further show that it is equally as accurate as canonical instanton theory down to moderately low temperatures while being significantly less computationally expensive.

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Variational free energy flooding for nucleation rates calculation

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We compute the vapor-liquid nucleation rate of a Lennard-Jones fluid at moderate supersaturation. For these supersaturations the time scale of the transition greatly exceeds that of a typical molecular dynamics simulation. Therefore we employ a recently introduced method^[1] to construct a bias potential that floods the free energy surface up to a predefined energy level (see Figure 1). The resulting bias potential accelerates the transition to the liquid phase while leaving the transition region untouched. In this way accurate nucleation rates can be efficiently extracted from biased simulations. At variance with previous applications of this methodology, in this work we use the physical model of the classical theory of nucleation to construct the bias potential^[2]. The parameters of the model are variationally optimized^[3] to satisfy the aforementioned conditions. The procedure described in this work can also be employed to calculate nucleation rates in more complex systems.

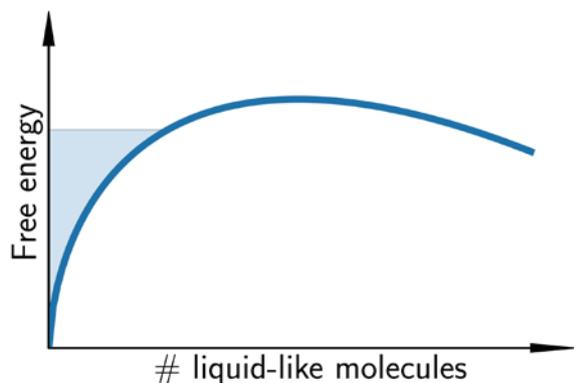


Figure 1: Hypothetical nucleation free energy profile illustrating the flooding method applied to nucleation problems.

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Reduction mechanism of a coordinated superoxide by benzyl alcohol and 2-propanol

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In aqueous acetate buffer media, Benzyl alcohol and 2-propanol reduces the bridging superoxide in $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}(\text{NH}_3)_5]^{5+}$ (**1**) to corresponding peroxide in the complex, $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2\text{H})\text{Co}^{\text{III}}(\text{NH}_2)(\text{NH}_3)_4]^{4+}$ (**2**), the reductants being oxidized to benzaldehyde and acetone respectively. The complex **2** thus produced decomposes rapidly to the final products, Co^{II} , NH_3 , etc. instead of reacting with a second molecule of hydrogen peroxide. In the presence of excess reductants over **1**, the reaction obeyed first-order kinetics and exhibited inverse proton dependence. $[(\text{NH}_3)_5\text{Co}^{\text{III}}(\text{O}_2)\text{Co}^{\text{III}}((\text{NH}_2)(\text{NH}_3)_4)]^{4+}$ (**3**), a conjugate base of **1**, seems to be the kinetically reactive species and the cause for the observed inverse proton dependence. Reaction rate with hydrogen peroxide significantly decreases with increasing proportion of D_2O replacing water in the solvent and the rate-limiting step seems to be an H-atom transfer.

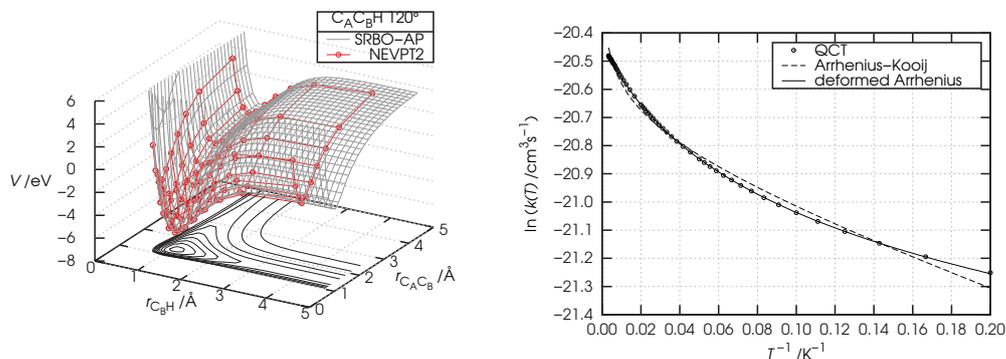
On the temperature dependence of the rate coefficient of formation of C_2^+ from $C + CH^+$ on a new bond-order based potential energy surface

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We carried out quasi-classical trajectory calculations for the $C + CH^+ \rightarrow C_2^+ + H$ reaction on an ad hoc computed high-level ab initio potential energy surface¹ obtained through an optimal bond-order based configuration-space sampling.² Thermal rate coefficients at the temperatures of relevance in cold interstellar clouds were derived and compared with the assumed, temperature-independent (Langevin model) estimates publicly available in kinetic databases KIDA and UDfA. For a temperature of 10 K the database value overestimates by a factor of two the one obtained by us (thus improperly enhancing the destruction route of CH^+ in astrochemical kinetic models) which is seen to double in the temperature range 5–300 K with a sharp increase in the first 50 K. The computed values were fitted via the popular Arrhenius–Kooij formula and best-fitting parameters to be included in the online mentioned databases are provided. Further investigation showed that the temperature dependence of the thermal rate coefficient better conforms to the recently proposed so-called ‘deformed Arrhenius’ law by Aquilanti and Mundim.^{3,4}



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Effect of oxide promoters on the total oxidation functionality of nanocomposite MnO_x catalysts: Mechanism and kinetics of the CO oxidation reaction

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Oxidation catalysis is an essential class of chemical reactions finding widespread application in manufacturing and environmental processes; in fact, chemicals' synthesis reactions mostly rely on the selective oxidation pattern of transition metal oxide catalysts to produce basic chemicals like epoxides, diolefins, aldehydes, acids, anhydrides, etc., while environmental safeguard technologies take advantage of the high oxygen activation capacity of noble-metals to drive the combustion of organic pollutants in both liquid and gas streams [1]. Then, it is evident that the discovery of low-costly catalyst formulations, alternative to expensive noble-metals based ones, could significantly stimulate worldwide the development of environmental prevention and remediation technologies. Although various probe molecules have been used to investigate the functionality of metal and oxide catalysts, CO oxidation deserves a special consideration for both practical and theoretical reasons; indeed, CO is a highly toxic pollutant, also acting as precursor of "ground-level" ozone [2] and it is a poison of various catalytic technologies (ammonia synthesis, Fuel Cell, etc.) [3,4] while its oxidation is, de facto, a very simple reaction helpful to shed light on the functionality of metal and oxide catalysts [1,3,4].

Therefore, this work is aimed at assessing the effects of Ce and Fe addition on the CO oxidation functionality of nanocomposite MnO_x catalysts obtained via the redox-precipitation method [5,6], while an exhaustive kinetic study highlights the factors controlling the reactivity of the active MnO_x phase.

Although larger surface area values than each oxide component signal remarkable structural effects of Ce and Fe promoters in all composite systems [5], temperature programmed catalytic reaction tests in the range of 293-533K ($p_{\text{CO}}=p_{\text{O}_2}$, 0.025) uncover activity levels depending on the MnO_x content and unchanging apparent activation energy values (E_{app} , 49 ± 2 kJ/mol) that exclude significant electronic effects on the functionality of the active MnO_x phase. Furthermore, in-depth characterization studies of the surface properties and reactivity by IR and TPRS of adsorbed methanol, XPS and CO-TPR techniques shed light on nature and abundance of active sites on the surface of nanocomposite MnO_x catalysts.

A systematic kinetic study of the CO oxidation reaction on the composite $\text{Mn}_{0.83}\text{Ce}_{0.17}\text{O}_x$ catalyst ($\text{Mn}_{\text{at}}/\text{Ce}_{\text{at}}$, 5), varying p_{CO} and p_{O_2} in the range of 0.00625-0.025, discloses constant empiric orders of 0.55 and 0.35 on p_{CO} and p_{O_2} , respectively. Pulse CO oxidation tests (363K) suggest the occurrence of a Mars-van Krevelen path triggered by the enhanced oxygen mobility of the active MnO_x phase [5,6], although a formal reaction mechanism uncovers the role and influence of each elementary step on the reaction kinetics. Hence, a linearization method of the formal kinetic equation provides consistent estimates of the catalyst reduction and oxidation rates [1], predicting the steady-state condition and the CO oxidation kinetics of nanocomposite MnO_x catalysts in a wide range of temperature (293-533K) and fully explaining the origin of the above empiric kinetic parameters.

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Spectacular rate enhancements of the diels-alder reaction at the ionic liquid/*n*-hexane interface

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Use of the ionic liquid/*n*-hexane interface, a new class of reaction medium to carry out the Diels-Alder reaction has resulted in exceedingly large rate enhancements, of the orders of 10^6 to 10^8 times and very high stereoselectivities,¹ as compared to those in homogeneous medium.^{2,3} The rate accelerations were found to be even larger than those obtained for 'on water' reactions.⁴ A rate law based on the solubility of reactants has been derived to calculate the interfacial rate constants (k_i) of a trans-phase bimolecular reaction. Furthermore, a model has been designed to get the concentration reduced interfacial rate constant ($k_{i,r}$) and homogenous rate constant (k_h) for the comparison of the interfacial rate constants with homogeneous rate constant. The model used for the calculation of concentration reduced interfacial rate constants has the form of following equation

where, $C_{n-hexane}$ signifies the molar concentration of *n*-hexane in the reaction mixture, n is the coordination number for trans-phase interfacial reaction, $n = 1$. $V_{n-hexane}$ and $V_{ionic\ liquid}$ represent the respective volume of *n*-hexane and ionic liquid phases, respectively in the reaction mixture. $r_{ionic\ liquid}$ has been taken as the radius of ionic liquid droplet, whereas $r_{n-hexane}$ and $r_{ionic\ liquid\ molecule}$ indicate the radius of *n*-hexane and ionic liquid molecules, respectively. The rate enhancements have been attributed to the H-bonding abilities and polarities of ionic liquids, whereas, the hydrophobicity of ionic liquids was considered to be the factor controlling stereoselectivity.

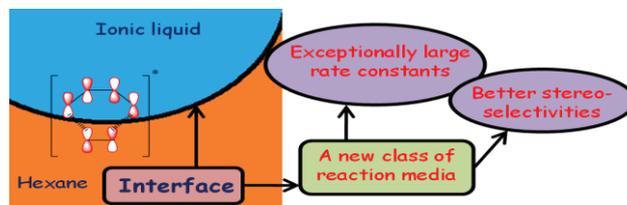


Figure: Spectacular rate enhancements and better stereo-selectivities obtained at the ionic liquid/*n*-hexane interfaces for a Diels-Alder reaction.

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On the short-time behavior of Mapping Variable Ring Polymer Molecular Dynamics

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Charge transfer reactions (CTRs) exemplify the economy of naturally occurring chemistry. They remain a subject of modern research due in part to their desirable efficiency. To accurately model CTRs a kinetic theory must respect the short-time limits inherent to these sub-femtosecond reactions while properly imposing the constraint of discrete quantum states in the condensed phase. Mapping Variable Ring Polymer Molecular Dynamics (MV-RPMD) was originally devised to meet these challenges¹. The MV-prescription extends the standard formalism of RPMD (thereby retaining its advantages in classical rate theory), but correctly discretizes the continuum of extended phase space. To date MV-RPMD has shown some promise, but its phase space structure, dynamics in various system regimes, and time-order accuracy have yet to be given a systematic analysis.

In this study we address the short-time limit of MV-RPMD. Following the original investigation of RPMD's short-time behavior^{2,3}, we examine moments of the Boltzmann distribution for successive orders in time. Specifically, we focus on a simple two level system for which the population autocorrelation function is exactly solvable. Zeroth order moments corroborate with exact quantum results. For higher order, non-integrable moments we proceed by comparing integrands of the moments via the recently derived quantum MV-liouvillian⁴. We apply this program to a series of established population estimators^{5,6} in addition to several hybrid estimators.

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Quantum dynamics on time-independent and time-dependent PES's

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Quantum dynamical studies on many elementary chemical reactions will be presented. Time-dependent wave packet calculation¹ for the atmospherically important reaction: $S(^1D) + H_2(X^1\Sigma_g^+) \rightarrow SH(X^2\Pi) + H(^2S)$ has been carried out, using double many-body expansion potential energy surface (PES), to understand the detailed mechanism of this reaction. Effect of rotation and more importantly orientation will be discussed².

Second part will be on the possibility of preferentially breaking of one of the chemical bonds of a molecule using few-cycle, intense laser pulse to obtain desired products. We found a 3-fold enhancement for bond-selective fragmentation in HOD upon application of intense, 2-cycle, 800nm CEP-stabilized laser pulse³. Also the dependence of dissociation dynamics of HOD^{2+} on the initial vibrational state of HOD will be presented⁴.

With the advent of attosecond experimental technologies, it becomes mandatory to solve the coupled electron-nuclear time-dependent Schrödinger equation to take into account the complex correlation between electronic and nuclear degrees of freedom. The computational demand for exact numerical solution provides a challenge and till now it has only been done to the very simplest of molecules. Final part will be on the dynamical behaviour of H_2^+ in presence of intense ($I = 10^{14} \text{ W/cm}^2$), ultrashort (5fs), infrared ($\lambda = 800\text{nm}$) laser field⁵ using time-dependent Born Oppenheimer approximation, proposed by Cederbaum⁶ as it seems to be promising for further implementation to polyatomic molecules.

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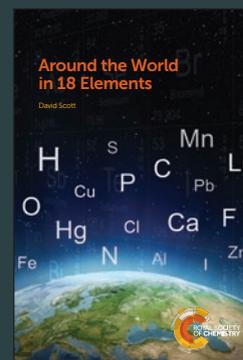
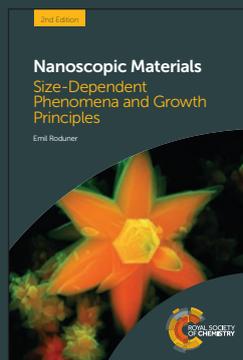
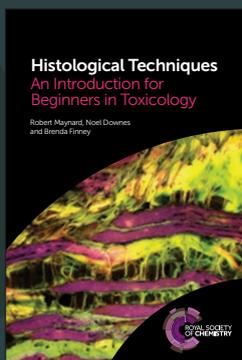
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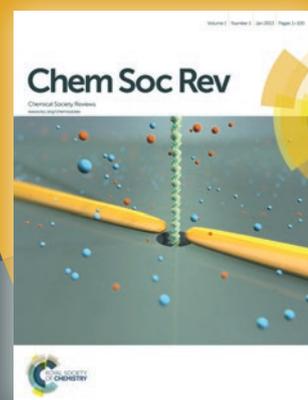
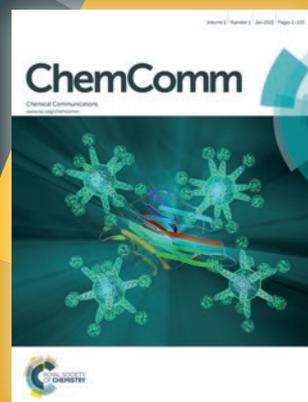
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