

# PhysChem 2013

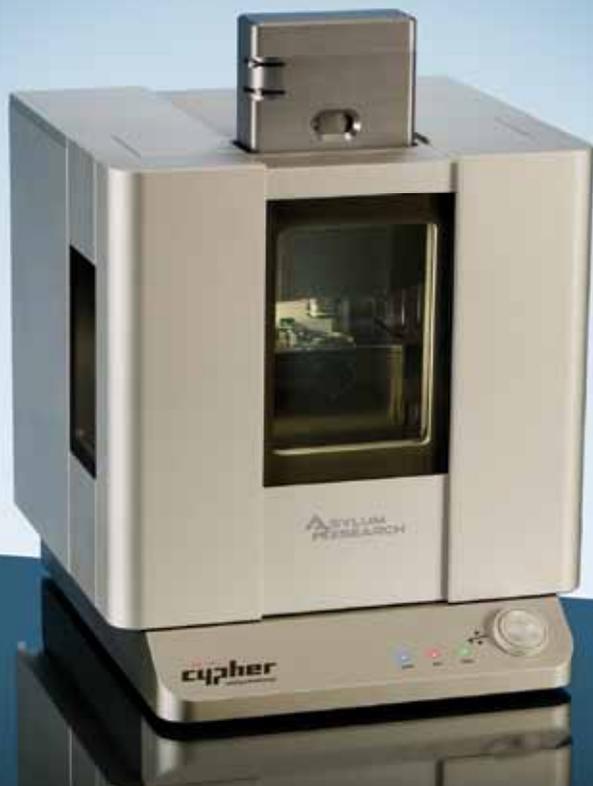


Pre Conference Workshop 3 December  
Conference 4-6 December  
Hobart Waterfront  
[www.physchem2013.com.au](http://www.physchem2013.com.au)

## Conference Handbook



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## Contents

Welcome .....	4
Conference General Information .....	5-6
Pre-Conference Workshop .....	7-9
Conference Program .....	10-17
Social Program .....	18-19
Abstracts and Biographies .....	21-75
Poster Presentations .....	76-162
Sponsorship & Exhibition .....	163-169

## Conference Organising Committee

**Dr Tak W. Kee**

University of Adelaide

**Dr Adam Trevitt**

University of Wollongong

**Prof Evan Bieske**

University of Melbourne

**Prof Jeff Reimers**

University of Sydney

**Dr David Huang**

University of Adelaide

**Dr Duncan Wild**

University of Western Australia

**Dr Angus Gray-Weale**

University of Melbourne

## Conference Managers



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## Welcome

Welcome to the Royal Australian Chemical Institute conference, PhysChem 2013, and to beautiful Hobart.

This meeting promises to be an exciting event. The conference organising committee would particularly like to welcome our international plenary speakers to Australia, and thank them for their contributions throughout the meeting. They headline an exciting program, with an outstanding line-up of speakers and poster presenters. We would like to thank you all for contributing to this line-up, and hope that you enjoy the program ahead.

A warm welcome and thank you are also extended to our sponsors and exhibitors. We deeply appreciate your support of this meeting and your commitment to the RACI Physical Chemistry Division and the physical chemistry community.

If you can, spend a day or two to enjoy Hobart, and beautiful Tasmania (not during conference session times!). There are many things that make Tasmania special. Outstanding wilderness areas, beautiful beaches, dramatic seascapes, a rich history, weird art, and some of the best beer and wine available in Australia to complement fine food served in a relaxed atmosphere.

It's our pleasure to welcome you to RACI PhysChem 2013, on behalf of the conference organising committee. We look forward to your participation.

### **Dr Tak W. Kee**

School of Chemistry  
& Physics  
University of Adelaide



### **Prof Evan Bieske**

School of Chemistry  
University of Melbourne



Co-Chairs  
RACI PhysChem 2013

# Conference General Information

## Registration Desk

The Registration Desk will be located in the main foyer of the Tasmanian School of Art, Hunter Street and will be open at the following times:

## Registration Desk opening Times:

Wednesday 4 December 2013:

**8:00am – 6:00pm**

Thursday 5 December 2013:

**8:00am – 6:00pm**

Friday 6 December 2013:

**8:00am – 6:30pm**

## Accommodation

If you have any queries relating to your accommodation booking first speak to the staff at your hotel or alternatively Leishman Associates staff at the Registration Desk.

Your credit card details were supplied to the hotel you have selected, as security for your booking. If you have arrived 24 hours later than your indicated arrival day you may find that you have been charged a fee. You will be responsible for all room and incidental charges on check out and may be asked for an impression of your credit card for security against these charges. This is standard policy in many hotels.

## Conference Name Badges

All delegates, speakers, sponsors and exhibitors will be provided with a name badge, which must be worn at all times within the conference venue, as it is required for access to all the conference sessions and social functions.

## Conference Proceedings

The conference abstracts will be available on the RACI PhysChem website following the conclusion of the conference. To obtain copies of presentations during the conference, please contact the speakers directly.

## Dress

Dress throughout the day and social events is smart casual.

## Internet

There will be wireless internet available in the conference venue for the duration of the conference. You will be supplied with an internet code upon registration.

## Mobile Phones

As a courtesy to other delegates, please ensure that all mobile phones are turned off or in a silent mode during all sessions and social functions.

## Photographs, Videos, Recording of Sessions

Delegates are not permitted to use any type of camera or recording device at any of the sessions unless written permission has been obtained from the relevant speaker.

## Speakers

Speakers will be asked to bring their presentations with them on a CD or USB stick, then load their presentations onto the computer in the theatre. This must be done AT LEAST by the break prior to your presenting time – this may mean the day before your presentation. There will be dedicated speakers assistants to provide help uploading your file. All speakers are responsible for ensuring their presentation is uploaded and ready for their session. Please see the staff at the Registration Desk for further information.

## Special Diets

All catering venues have been advised of any special diet preferences you have indicated on your registration form. Please identify yourself to venue staff as they come to serve you and they will be pleased to provide you with all pre-ordered food. For day catering, there may be a specific area where special food is brought out, please check with catering or conference staff.

## Disclaimer

The 2013 RACI PHYSCHEM conference reserves the right to amend or alter any advertised details relating to dates, program and speakers if necessary, without notice, as a result of circumstances beyond their control. All attempts have been made to keep any changes to an absolute minimum.



# Pre - Conference Computational Chemistry Workshop

**Date:** Tuesday 3 December 2013

**Location:** Room 327, Chemistry Building, UTAS, Sandy Bay Campus

**Workshop Fee:** \$80.00

Please note that attendees need to make their own way to and from the pre-conference workshop.

The one-day workshop will be held the day before the start of the conference. It will provide an introduction to computational chemistry methods, including molecular orbital methods, semi-empirical theories, density functional theory (DFT), molecular dynamics and Monte Carlo simulations, integral equation theories of liquids, and computational spectroscopy.

The workshop will consist of two parallel streams: an introductory stream aimed at teaching

participants less familiar with computational methods how to apply these methods to standard problems and an advanced stream comprising master classes by guest lecturers focussing on particular computational problems or methods. Participants can choose which sessions from the two streams they attend

**The pre-conference workshop is an optional delegate activity. You must pre-purchase a ticket to attend this workshop. Please note that spaces are limited.**



# Pre - Conference Workshop

Tuesday 3 December 2013

<b>Optional Pre - Conference Computational Chemistry Workshop</b> University of Tasmania, Sandy Bay Campus		
9:00 am – 9:20 am	<b>Welcome and Introduction</b> C2 Lecture Theatre, Room 329	
9:20 am – 10:00 am	<b>Session 1: Quantum chemistry</b> <b>A/Prof Meredith Jordan</b> , <i>The University of Sydney</i> C2 Lecture Theatre, Room 329	
10:00 am – 10:20 am	<b>Morning Refreshments</b> Chemistry Staff Room, Room 208	
<b>Stream 1 - Introduction to Computational Chemistry</b> Computer Lab, Room 327		<b>Stream 2 - Master Classes</b> C2 Lecture Theatre, Room 329
10:20 am – 12:00 pm	<b>Session 1 (continued)</b>	10:20 am – 11:10 am <b>Explicit correlation: accelerating basis set convergence</b> <b>Dr Jo Lane</b> , <i>The University of Waikato</i>
		11:10 am – 12:00 pm <b>Dynamics of open quantum systems</b> <b>A/Prof Kenneth Brown</b> , <i>Georgia Institute of Technology</i>
12:00 pm – 12:50 pm	<b>Lunch</b> Chemistry Staff Room, Room 208	
1:00 pm – 2:40 pm	<b>Session 2: Classical molecular simulations</b> <b>Dr David Huang</b> , <i>The University of Adelaide</i>	1:00 pm – 1:50 pm <b>Molecular dynamics simulation of non-equilibrium systems</b> <b>Prof Debra Bernhardt</b> , <i>The University of Queensland</i>
		1:50 pm – 2:40 pm <b>Quantum mechanics for condensed phases</b> <b>Prof Julian Gale</b> , <i>Curtin University</i>

2:40 pm – 3:00 pm	<b>Afternoon Refreshments</b> Chemistry Staff Room, Room 208	
3:00 pm – 5:30pm	<b>Session 3: An introduction to the statistical mechanics of solvation and interfaces</b> <b>Dr Angus Gray-Weale,</b> <i>The University of Melbourne</i>	3:00 pm – 3:50 pm <b>Computational electronic and vibrational spectroscopy</b> <b>A/Prof Tim Schmidt,</b> <i>The University of Sydney</i>
		3:50 pm – 4:40 pm <b>Sampling rare but important trajectories</b> <b>Prof Phillip Geissler,</b> <i>University of California, Berkeley</i>
		4:40 pm – 5:30 pm <b>Exploring conformational space and conformational averaging</b> <b>Prof Michelle Coote,</b> <i>Australian National University</i>
5:30 pm – 5:50 pm	<b>Closing Remarks</b> C2 Lecture Theatre, Room 329	

**PhysChem**  
**2013**



**Conference Program**

## Wednesday 4 December 2013

The Tasmanian School of Art, Hunter Street

8:00 am	<b>Registration Desk Opens</b>	The Main Foyer
8:45 am	<b>Official Conference Opening Remarks</b>	The Dechaineux Theatre
<b>Plenary Session</b>		The Dechaineux Theatre
9:00 am	<b>How complicated can crystal growth really be?</b> <i>Prof Julian Gale, Curtin University</i>	
<b>Contributed Papers</b>		
9:45 am	<b>Do Classical Electrostatics Determine the Magnetic Anisotropy of Low-Symmetry Dysprosium Complexes?</b> <i>Dr Alessandro Soncini, The University of Melbourne</i>	
10:00 am	<b>Classical density functional theory of solvation, interfaces, and surfactant assembly</b> <i>Dr Angus Gray-Weale, The University of Melbourne</i>	
10:15 am	<b>Beryllium Chemistry the Safe Way – A Quantum Chemical Investigation</b> <i>Dr David Wilson, La Trobe University</i>	
10:30 am	<b>Morning Refreshments</b>	The Main Foyer
<b>Keynote Session</b>		The Dechaineux Theatre
11:00 am	<b>High-Coherence Electron and Ion Bunches from Laser-Cooled Atoms</b> <i>A/Prof Rob Scholten, The University of Melbourne</i>	
<b>Contributed Papers</b>		
11:30 am	<b>Can Molecular Dynamics Reveal the Active Conformation of Insulin?</b> <i>Dr Naomi Haworth, Monash University</i>	
11:45 am	<b>How do cryoprotective agents damage cell membranes at high concentration? A molecular dynamics simulation study</b> <i>Prof Ricardo Mancera, Curtin University</i>	

<b>Keynote Session</b>		The Dechaineux Theatre
12:00 pm	<b>pH Switching Radical Stability and Orbital Conversion</b> <i>Prof Michelle Coote, Australian National University</i>	
<b>Contributed Papers</b>		
12:30 pm	<b>Density functional theory calculations of organo-modified silicene</b> <i>Dr Michelle Spencer, RMIT University</i>	
12:45 pm	<b>Molecular Meccano and Neurodegeneration: The Computational Challenges</b> <i>Dr Cyril Curtain, Mental Health Research Institute of Victoria</i>	
1:00 pm	<b>Lunch</b>	The Main Foyer
1:55 pm	<b>Welcome Address from the Major Sponsor</b>  <i>Dr Shane Huntington, Director, The Innovation Group Pty Ltd</i>	The Dechaineux Theatre
<hr/> <p>Delivering excellence in SPM and Profilometry through Partnership</p> <div style="display: flex; justify-content: space-around; align-items: center;">     </div>		
<b>Plenary Session</b>		The Dechaineux Theatre
2:00 pm	<b>Line 'em all up: assembly at complex liquid interfaces</b> <i>Prof Geraldine Richmond, University of Oregon, USA</i>	
<b>Contributed Papers</b>		
2:45 pm	<b>Conjugated Polymer Films Imaged at High Spatial and Temporal Resolution</b> <i>A/Prof Trevor Smith, The University of Melbourne</i>	
3:00 pm	<b>Molecular Approaches to Next Generation Photovoltaics</b> <i>A/Prof Timothy Schmidt, The University of Sydney</i>	
3:15 pm	<b>Controlling Resonance Energy Transfer between Dyes on a Co-Sensitised Metal-Oxide Surface</b> <i>Dr Viktoras Dryza, The University of Melbourne</i>	
3:30 pm	<b>Afternoon Refreshments</b>	The Main Foyer

<b>Keynote Session</b>		The Dechaineux Theatre
4:00 pm	<b>Remote but not disinterested: Measuring the effect of charge on radical stabilisation in distonic radical anions</b> <i>Prof Stephen Blanksby, University of Wollongong</i>	
<b>Contributed Papers</b>		
4:30 pm	<b>NMR Chemical Shift in molecules with a (quasi)-degenerate Ground State</b> <i>Dr Willem Van Den Heuvel, The University of Melbourne</i>	
4:45 pm	<b>The THz/Far-IR Beamline at the Australian Synchrotron</b> <i>Dr Courtney Ennis, Synchrotron Light Source Australia</i>	
5:00 pm	<b>Electronic energies, molecular structures and frequencies by systematic molecular fragmentation</b> <i>Prof Michael Collins, Australian National University</i>	
5:15 pm	<b>Super-resolution localization microscopy of transfected cells, starved cells and mitochondria</b> <i>Dr Toby Bell, Monash University</i>	
5:30 pm	<b>Session Close</b>	
6:00 pm-9:00 pm	<b>Welcome Reception and Poster Session 1</b> The Tasmanian School of Art, Hunter Street	The Main Foyer

<b>Thursday 5 December 2013</b>		
The Tasmanian School of Art, Hunter Street		
8:00 am	<b>Registration Desk Open</b>	The Main Foyer
<b>Plenary Session</b>		The Dechaineux Theatre
9:00 am	<b>Ultrafast Studies of Single Metal and Semiconductor Nanostructures</b> <i>Prof Greg Hartland, University of Notre Dame, USA</i>	
9:45 am	<b>Student Award Winner</b> <b>The Photon of Persuasion: Influencing Branching Fractions in the Photodissociation of H<sub>2</sub>CO</b> <i>Mitchell Quinn, The University of Sydney</i>	
<b>Contributed Papers</b>		

10.00 am	<b>'Hot' Photo-induced Electron Transfer</b> <i>Prof Ken Ghiggino, The University of Melbourne</i>
10.15 am	<b>Modelling Nano-Scale Structure and Energy Transfer in Conjugated Polymers</b> <i>Dr David Huang, The University of Adelaide</i>
10:30 am	<b>Morning Refreshments</b> <span style="float: right;">The Main Foyer</span>
<b>Keynote Session</b> <span style="float: right;">The Dechaineux Theatre</span>	
11.00 am	<b>Shearing nanoconfined fluids</b> <i>Prof Debra Bernhardt, The University of Queensland</i>
<b>Contributed Papers</b>	
11:30 am	<b>Adiabatic energy surfaces: the interplay between electronic coupling and electron-vibrational coupling that controls chemical reactivity, spectroscopy, and the development of entanglement</b> <i>Prof Noel Hush, The University of Sydney</i>
11:45 am	<b>Spin-system crossing points in reaction mechanisms</b> <i>Prof Brian Yates, University of Tasmania</i>
<b>Keynote Session</b> <span style="float: right;">The Dechaineux Theatre</span>	
12.00 pm	<b>Are bond critical points really critical for hydrogen bonding?</b> <i>Dr Joseph Lane, The University of Waikato, New Zealand</i>
12:30 pm	<b>Lunch</b> <span style="float: right;">The Main Foyer</span>
<p><b>The remainder of the afternoon is free for independent exploration of Hobart!</b></p> <p>What to see and do? Visit the website for more information <a href="http://www.physchem2013.com.au">www.physchem2013.com.au</a></p> <p>Want to visit the world famous MONA? Ferry departs at 1:15 pm. Pre-book your tickets @ <a href="http://www.mona.net.au">www.mona.net.au</a></p>	
6:00 pm – 9:00 pm	<b>Poster Session 2</b> <span style="float: right;">The Main Foyer</span> The Tasmanian School of Art, Hunter Street

## Friday 6 December 2013

The Tasmanian School of Art, Hunter Street

8:00 am	<b>Registration Desk Open</b>	The Main Foyer
<b>Plenary Session</b>		The Dechaineux Theatre
9:00 am	<b>Probing Actinide Bonding using Multiphoton Excitation and Photoelectron Spectroscopy</b> <i>Prof Michael Heaven, Emory University, USA</i>	
<b>Contributed Papers</b>		
9:45 am	<b>Assignment of the Q-Bands of the Chlorophylls: Coherence Loss via Qx-Qy Mixing</b> <i>Prof Jeffrey Reimers, The University of Sydney</i>	
10:00 am	<b>Quantum enhancement of steady-state light harvesting in sunlight</b> <i>Dr Ivan Kassal, The University Of Queensland</i>	
10:15 am	<b>Morning Refreshments</b>	The Main Foyer
<b>Keynote Session</b>		The Dechaineux Theatre
10:45 am	<b>Harnessing the Power of the Sun – Self-Assembled Porphyrin-fullerene Complexes as Functional Components</b> <i>A/Prof Cather Simpson, The University of Auckland, New Zealand</i>	
<b>Contributed Papers</b>		
11:15 am	<b>Reactivity of Gallium Nano-clusters</b> <i>Dr David Henry, Murdoch University</i>	
11:30 am	<b>Metal Clusters on Oxide Surfaces for Catalysis</b> <i>A/Prof Gunther Andersson, Flinders University</i>	
<b>Keynote Session</b>		The Dechaineux Theatre
11:45 am	<b>Photodissociation of small aromatic species in the gas-phase and liquid-phase microdroplets</b> <i>Dr Adam Trevitt, University of Wollongong</i>	
<b>Contributed Papers</b>		

12:15 pm	<b>Ligand-mediated control of the surface plasmon resonance in metal nanoparticles generated by laser ablation</b> <i>Prof Mark Buntine, Curtin University</i>
12:30 pm	<b>Roaming, roaming everywhere</b> <i>Prof Scott Kable, The University of Sydney</i>
12:45 pm	<b>Lunch</b> <span style="float: right;">The Main Foyer</span>
<b>Plenary Session</b> <span style="float: right;">The Dechaineux Theatre</span>	
1:45 pm	<b>Probing molecular ions with laser-cooled atomic ions</b> <i>A/Prof Kenneth Brown, Georgia Institute of Technology, USA</i>
<b>Contributed Papers</b>	
2:30 pm	<b>Resonance and Photoisomerization in Fluorescent Protein Chromophores: Reversible Photobleaching Rate and Proximity to the Cyanine Limit</b> <i>Dr Seth Olsen, The University of Queensland</i>
2:45 pm	<b>Reactive Simulations of Carbonates in Water</b> <i>Dr Paolo Raiteri, Curtin University</i>
3:00 pm	<b>Effective and ineffective transition metal catalysis in reversible hydrogen storage</b> <i>Dr Terry Frankcombe, Australian National University</i>
3:15 pm	<b>Afternoon Refreshments</b> <span style="float: right;">The Main Foyer</span>
<b>Keynote Session</b> <span style="float: right;">The Dechaineux Theatre</span>	
3:45 pm	<b>Ultrafast Probes of Free Charge Photogeneration in Organic Photovoltaics</b> <i>Dr Justin Hodgkiss, Victoria University of Wellington, New Zealand</i>
<b>Contributed Papers</b>	
4:15 pm	<b>Aerosol icing on the cake: IR spectroscopy of nanoscale particles</b> <i>Dr Evan Robertson, La Trobe University</i>
4:30 pm	<b>Helium Nanodroplet Isolation Spectroscopy of Hydridotrioxigen and of its Complexes with Dioxygen</b> <i>Dr Paul Raston, The University of Adelaide</i>

4:45 pm	<b>Can dianions make strong gas phase bases?</b> <i>Dr Berwyck Poad, University of Wollongong</i>
5:00 pm	<b>Rotational spectroscopy of PANH and cyano substituted PAH species</b> <i>Prof Donald McNaughton, Monash University</i>
5:15 pm	<b>Understanding electronic structures of molecules from gamma-ray spectroscopy</b> <i>Dr Feng Wang, Swinburne University of Technology</i>
<b>Keynote Session</b> <span style="float: right;">The Dechaineux Theatre</span>	
5:30 pm	<b>Ab initio molecular dynamics of molecules in strong laser fields</b> <i>Prof H. Bernhard Schlegel, Wayne State University, USA</i>
6:00 pm	<b>Conference Closing Remarks</b>
7:00 pm – 10:00 pm	<b>Conference Dinner</b> The Mill on Morrison, Hobart

# Conference Social Program

## Welcome Reception & Poster Session 1

Proudly sponsored by Innovation Group / NewSpec



**Venue:** University of Tasmania,  
Fine Arts Building, Hobart  
**Date:** Wednesday 4 December 2013  
**Time:** 6:00pm – 9:00pm  
**Dress:** Smart Dress

Inclusive function  
Additional tickets are available  
for \$80.00

*Join us for the official welcome reception and poster session. Authors will be available to speak about their posters during this session and it is a great opportunity to network with new colleagues and to catch up with friends. The evening will included canapés and beverages in a relaxed environment.*

## Poster Session 2

**Venue:** University of Tasmania,  
Fine Arts Building, Hobart  
**Date:** Thursday 5 December 2013  
**Time:** 6:00pm – 9:00pm  
**Dress:** Smart Dress

Inclusive function  
Additional tickets are available  
for \$80.00

*Join us for the second poster session for RACI PhysChem 2013. Authors will be available to speak about their posters during this session. Light food and beverages will be served.*



## Conference Dinner

Proudly sponsored by Innovation Group /  
NewSpec



**Venue:** The Mill on Morrison,  
11 Morrison Street, Hobart  
**Date:** Friday 6 December 2013  
**Time:** 7:00pm – 10:00pm  
**Dress:** Smart Dress

Inclusive Event.  
Additional tickets are available  
for \$130.00

*Come and join us on the last night of  
the conference program for another  
chance to network and meet with  
colleagues, whilst enjoying a great  
night of food and wine at The Mill on  
Morrison.*

*Transport is not provided for the  
conference dinner. Instead a  
walking map will be provided upon  
registration at the conference venue.*





# A bright future, defined by a rich past.

The University of Tasmania was founded over 123 years ago, making it one of Australia's oldest universities.

Today we're recognised as an international leader, ranked in the top 2% of universities in the world.\*

It's that merging of rich heritage with strength of character that guarantees our greatest achievements are still to come.



**TOP 2%**  
OF UNIVERSITIES  
WORLDWIDE

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The background features a light blue gradient with several overlapping, semi-transparent geometric shapes in various shades of blue. A large white diamond shape is centered on the page, containing the main text.

# **Abstracts & Biographies**

**Wednesday 4  
December 2013**

## Plenary Session

**9:00am-9:45am**

### How complicated can crystal growth really be?

**Prof Julian Gale**  
Curtin University

#### Biography

Julian Gale was awarded his first degree from University of Oxford where he also obtained his DPhil in the Dept. of Chemical Crystallography. After a post-doctoral position at the Royal Institution of Great Britain he moved to Imperial College London to take up a Royal Society University Research Fellowship in the Department of Chemistry, where he subsequently became Reader in Theoretical and Computational Chemistry. In 2003, Julian moved to Curtin University as one of two inaugural Premier's Research Fellows awarded by the Government of Western Australia where he also served as acting director of the Nanochemistry Research Institute and as a member of the Premier's Science and Innovation Council. Currently he is an ARC Professorial Fellow in the Department of Chemistry with Curtin's Resources and Chemistry Precinct.

#### Authors

Raffaella Demichelis<sup>1</sup>, Paolo Raiteri<sup>2</sup>,  
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#### Abstract

Crystal growth is ubiquitous, both in the laboratory and the natural world. As a result there have been theories to explain crystallisation that go back over a century, and have evolved along with our atomic view of matter. Even after all this time, this field of research is still presenting challenges to our understanding. In the case of calcium carbonate (CaCO<sub>3</sub>), one of the most widespread minerals at the Earth's surface, there has been considerable debate regarding the nucleation and growth mechanisms.

Firstly, it was recognised that in many natural systems crystalline polymorphs form via an amorphous precursor phase, rather than by direct nucleation. Secondly, and most recently, the existence of stable pre-nucleation clusters was proposed by Gebauer et al [1], in apparent contravention of classical nucleation theory.

In this presentation computer simulation, based on molecular dynamics with a thermodynamically accurate force field, will be used to probe the early and late stages of growth of calcium carbonate from aqueous solution. In particular, the question of why the initial ion association is stable, and what the form of these prenucleation clusters is, will be examined [2]. It will be shown that through careful determination of the free energy landscape [3] it is possible to gain new insights into the complex emergence of crystalline materials via multiple amorphous and liquid-like precursor states [4], as well as how they grow subsequent to nucleation.

[1] D. Gebauer et al, *Science*, 322, 1819 (2008)

[2] R. Demichelis et al, *Nature Commun.*, 2, 590 (2011)

[3] A.G. Stack et al, *J. Am. Chem. Soc.*, 134, 11 (2012)

[4] A.F. Wallace et al, (in press)

#### Key Words

Crystal growth; simulation; calcium carbonate; molecular dynamics; nucleation

**9:45am-10:00am**

## Do Classical Electrostatics Determine the Magnetic Anisotropy of Low-Symmetry Dysprosium Complexes?

#### Authors

**Dr Alessandro Soncini**<sup>1</sup>, Nicholas Chilton<sup>2</sup>, Prof David Collison<sup>2</sup>, Prof Eric McInnes<sup>2</sup>, Prof Richard Winpenny<sup>2</sup>,

1. The University of Melbourne
2. The University of Manchester

#### Biography

*Dr Soncini is a theoretical chemist, with interest in the theory of electronic structure, magnetic and conduction properties of molecules and molecule-based materials. Before coming to the University of Melbourne in 2011 as a lecturer, he held positions in Italy, in the UK, in Belgium and Norway.*

#### Abstract

Understanding the anisotropic electronic structure of lanthanide complexes is important in areas as diverse as magnetic resonance imaging, luminescent cell labelling and quantum computing. We present an intuitive theoretical model based on a classical electrostatic picture, capable of predicting the magnetic anisotropy of dysprosium(III) complexes, even in low symmetry. The strategy relies only on knowing the X-ray structure of the complex and the well-established observation that, in the absence of high symmetry, the ground state of dysprosium(III) is a doublet quantized along the anisotropy axis with an angular momentum quantum number  $m_J = \pm 15/2$ . The magnetic anisotropy axis of fourteen low symmetry monometallic

dysprosium(III) complexes computed via high-level ab initio calculations are very well reproduced by our electrostatic model. Furthermore, we show that the magnetic anisotropy is equally well predicted in a selection of low symmetry polymetallic complexes.

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**10:00am - 10:15am**

## Classical density functional theory of solvation, interfaces, and surfactant assembly

### Authors

Cameron Ritchie<sup>1</sup>, Maoyuan Liu<sup>1</sup>,  
Quinn Besford<sup>1</sup>, **Angus Gray-Weale<sup>1</sup>**

1. The University of Melbourne

### Abstract

Classical density functional theory (CDFT) provides a method for the systematic calculation of fluid structure at interfaces and around solutes, and of related the thermodynamic properties. It suffers from few or none of the problems of accuracy and consistency that come with mean-field or continuum methods such as 'polarisable continuum' or Poisson-Boltzmann methods. The difficulty of obtaining solutions to the CDFT equations has limited its use to crude models. Here we discuss the application of these methods to polar and associating liquids, especially water, without the need for ad hoc assumptions. We look at solvation structure, interfacial structure, and the tendency of surfactants to assemble in various solvents.

We focus on the longest range correlations between solvent molecules, and find a dispersion force arising from correlations between the thermally rotating dipole moments. This force, which attracts each pair of molecules, has usually been assumed negligible, and so it seems in a mean-field treatment that regards other waters near the two in question as a dielectric continuum. Using exact results for the correlations between permanent moments, we show that this attraction is stronger than expected, and that it has a surprising temperature dependence that coincides with the observed temperature dependence of the hydrophobic effect. Our treatment is consistent with the observed cold denaturation of proteins, estimates well the vaporisation entropies of many polar fluids, and captures hydrophobes' signature, temperature-dependent, interfacial, solvation, and protein-unfolding thermodynamics.

We discuss the pH-dependence of the surface tension of water as an example of an interfacial measurement that may be used to test theories of interfacial structure and thermodynamics, and use this example to point out the failings of methods based on the Poisson-Boltzmann method.

Finally, we use an exact result for the strength of dispersion forces between fluids of thermally rotating dipole moments to predict which solvents support the assembly of surfactants into micelles. This prediction performs as well as the best known empirical prediction method, but is derived from exact results on the free energy of a polar liquid.

## Key Words

classical density functional theory, dispersion forces, interfaces, surfactant assembly

**10:15am - 10:30am**

## Beryllium Chemistry the Safe Way – A Quantum Chemical Investigation

### Authors

**Dr David Wilson**, Dr Jason Dutton  
La Trobe University

### Biography

David Wilson obtained his PhD in 2003 from the University of Newcastle, Australia. He then took up a 2-year postdoctoral fellowship with Prof. Trygve Helgaker at the University of Oslo, Norway, working on the Dalton program and studying magnetic and electric properties. In 2005 he gained an appointment at La Trobe University, Australia. His current research is centred around applying quantum chemistry to systems with novel bonding environments.

### Abstract

As part of a study of the binding and electronic structure of low-oxidation state elements ("molecular allotropes") stabilised by donor ligands such as N-heterocyclic carbenes (NHCs), we have investigated the properties of Be and Be<sub>2</sub> in a 0 oxidation state [1]. Standard undergraduate teaching of Mos suggests that neutral Be<sub>2</sub> should have a bond order of zero and thus be unstable. Here we report a means to stabilise Be<sub>2</sub> to make a viable molecule. Results will also

be presented for the Be analogue of the important Mg(I)–Mg(I) dimer supported by the β-diketimate ligand. The study of "molecule allotropes" state has recently become a topic of importance in p-block chemistry [2-3]. In this case, our results demonstrate that the Be(0) complexes are far more stable than the analogous Mg(0) complexes, highlighting the opportunities afforded in Be chemistry, despite the challenges presented by the toxicity of Be compounds. Advanced bonding analysis, including energy decomposition analysis (EDA) sheds light on the bonding and electronic structure of these novel species.

Be has also been reported to undergo ring insertion into NHCs, a phenomenon that has also been observed for B and Si species. Results will be presented for a study of the mechanism of ring formation, in which similarities between then three systems will be outlined.



## Keynote Session

11:00am - 11:30am

### High-Coherence Electron and Ion Bunches from Laser-Cooled Atoms

**A/Prof Rob Scholten**

The University of Melbourne

#### Biography

*Robert Scholten is a Professor of Physics at The University of Melbourne, where he leads the Ultracold Plasma high-brightness electron source Project of the ARC Centre of Excellence in Coherent X-ray Science. His research career began with studying electron collisions from laser-excited atoms, where laser polarisation was used to control the quantum state of the target atoms. His interest in laser-atom interactions formed the basis of later research, for example using atom-optics techniques for nanofabrication as a Fulbright Postdoctoral Research Fellow at NIST in the USA. He has also developed novel approaches to optical imaging of cold atoms, is currently working on quantum sensing using colour centres in diamond, and has created a high-tech start-up company (MOGLabs) based on lasers and laser electronics.*

#### Authors

**RE Scholten**, BM Sparkes, D Murphy, DJ Thompson, R Speirs, J Torrance, R Taylor  
ARC Centre of Excellence for Coherent X-ray Science, School of Physics, The University of Melbourne, Australia.

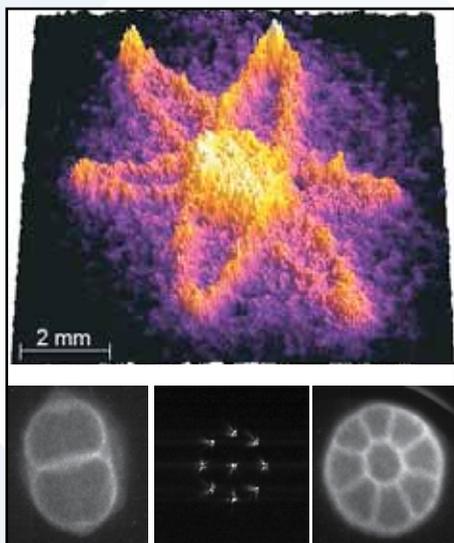
#### Abstract

Cold atom electron and ion sources based on photoionisation of laser

cooled atoms offer a new approach to generating high brightness and high coherence charged particle beams for applications including ultrafast electron diffractive imaging of dynamic processes at the nanoscale. The effective brightness of electron sources has been limited by non-linear divergence caused by repulsive interactions between the electrons, known as the Coulomb explosion. It has been shown that electron bunches with ellipsoidal shape and uniform density distribution have linear internal Coulomb fields [1], allowing reversal of the Coulomb explosion using conventional optics. A cold atom electron source can create bunches shaped in three dimensions and in principle achieve the transverse spatial coherence and brightness needed for picosecond diffractive imaging with nanometre resolution.

We have demonstrated [2] arbitrary shaping of the cold atom cloud (Fig. 1), and hence of the extracted electron bunches, and used the shaping capability to allow detailed measurement of the spatial coherence properties of the cold electron source [3]. We also show remarkable ion bunch shape formation and evolution, with direct visualisation made possible by the very low (milliKelvin) temperature of the ions. Using a counter-intuitive two-step femtosecond excitation and nanosecond ionisation scheme, we have generated electron bunches with durations of a few hundred picoseconds [4]. Diffraction experiments of simple crystalline materials are currently in progress, to demonstrate application of the high coherence of the novel source. Future development of the cold

atom electron source will increase the bunch charge and charge density, demonstrate reversal of Coulomb explosion and picosecond pulse durations, and ultimately, ultrafast coherent electron diffractive imaging.



**Figure 1:** (a) A bunch of electrons (left) has been produced with a complex spatial distribution, and because of the low electron temperature (10 K) the bunch has retained its shape after propagating 24cm. (b) Images of propagated ion bunches (right) show two adjacent expanding ion bunches; excitation laser beam intensity profile for an array of miniature ion-bunches, and far right, complex pattern formed by Coulomb effects between the bunches during propagation.

#### References

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[2] A. J. McCulloch, D. V. Sheludko, M. Junker, S. C. Bell, S. D. Saliba, K. A. Nugent, and R. E. Scholten, Nature Physics 7, 785 (2011).

[3] S. D. Saliba, C. T. Putkunz, D. V. Sheludko, A. J. McCulloch, K. A. Nugent, and R. E. Scholten, Optics Express 20 (4) 3967 – 3974 (2012).

[4] A. J. McCulloch, D. V. Sheludko, M. Junker and R. E. Scholten, High coherence picosecond electron bunches from cold atoms, Nature Communications 4 1692 (2013).

## 11:30am - 11:45am

### Can Molecular Dynamics Reveal the Active Conformation of Insulin?

#### Authors

**Dr Naomi Haworth**<sup>1</sup>, Briony Forbes<sup>2</sup>, A/Prof Andrea Robinson<sup>1</sup>.

1. Monash University,
2. Flinders University

#### Biography

Dr Haworth completed her BSc(Hons) in Chemistry at Quantum Physics at the University of Melbourne followed by a PhD in Theoretical Chemistry at the University of Sydney under the supervision of Dr George Bacskay. She has worked as a postdoctoral researcher in the groups of Professor Leo Radom at the University of Sydney and Professor Tim Clark in Erlangen Germany (as a Humboldt Fellow) as well as holding research positions with the Victor Chang Cardiac Research Institute, Deakin University and Monash University.

## Abstract

Insulin is an essential hormone which is responsible for controlling the metabolism of carbohydrates and fats. Failure of the body to adequately produce and/or respond to insulin results in diabetes mellitus, one of the major health challenges facing Australia in the 21st century. Current insulin analogues used in diabetes treatment have significant drawbacks. They require patients to undergo regular injections, can be unstable unless stored and transported with care and have the potential to cause undesirable side effects. However, the targeted development of alternative insulin therapies requires a good understanding of the behaviour of insulin in the body, in particular how it binds to the insulin receptor (IR) and signals the initiation of the glucose metabolism pathway. While steady progress is being made in this field, the "active" conformation of insulin required for IR binding and the details of the insulin-IR interactions are still unknown.

Insulin consists of two polypeptide chains (A and B) linked by two disulfide bonds (A7-B7 and A20-B19). A third disulfide connects residues 6 and 11 of the A chain. Recently this intrachain disulfide has become a target for modifications seeking to improve insulin stability. A particularly interesting variant involves replacement of the disulfide with a carbon-carbon double bond linkage (a "dicarba" bridge). Two possible isomers can be formed, involving either E or Z stereochemistry around the double bond. Crucially, one of these isomers has almost identical biological activity to wild-type insulin, while the other is inactive.

We have used molecular dynamic simulations to probe the effects of replacing the A6-A11 disulfide of wild-type human insulin with both E and Z dicarba linkages. Starting geometries were taken from four independent insulin crystal structures, each having different disulfide bond conformations. All simulations of both wild-type insulin and of the active dicarba insulin isomer converge to a single conformation (the "positive" conformation). In contrast, simulations for the inactive isomer converge to one of two structures, neither of which aligns well with that of the active isomer. While these two "negative" conformations occupy neighbouring regions of conformational space to the "positive" conformation, important components of the insulin structure which are known to be essential for IR binding and activation have been displaced. These include the N-terminus of the A chain (GlyA1) and the sidechain of residue GluA4. It is hoped that these results will provide valuable insights in the search for the elusive "active" conformation of insulin.

11:45am - 12:00pm

## How do cryoprotective agents damage cell membranes at high concentration? A molecular dynamics simulation study

### Authors

**Prof Ricardo Mancera**, Dr Zak Hughes,  
Chris Malajczuk  
Curtin University

### Biography

*Ricardo Mancera is Professor of Biomolecular Modelling at Curtin University in Perth. He obtained his PhD at the University of Cambridge and then held research and academic positions in Cambridge and then at Curtin University, where he is currently the Head of the Biomolecular Modelling Group. Ricardo has diverse research interests in protein structure, dynamics and interactions; biomolecular hydration; cell membranes; aqueous solutions; ligand-protein interactions; drug discovery and molecular modelling methods.*

### Abstract

Cryopreservation allows the storage of biological tissues at liquid nitrogen temperatures through the use of cryoprotective agents (CPAs) that promote the formation of the vitrified state of water and minimise the deleterious formation of ice crystals. In these conditions all physical, chemical and biological processes are arrested and cells and tissues can be preserved for decades. Penetrating CPAs can cross cell membranes, dehydrate cells and promote the vitrification of water upon rapid cooling, with DMSO and

polyols (such as glycerol, ethylene glycol and propylene glycol) being frequently used in mixtures referred to as vitrification solutions. These agents have good cryoprotective abilities but can be toxic to cells at high concentration. We have conducted a large number of molecular dynamics simulations to investigate the mechanism of damage of these agents on model cell membranes composed of different types of phospholipid bilayers and sterols.

DMSO induces the expansion and thinning of both DPPC and DOPC bilayers (1). Above a critical concentration, pores in the membranes form spontaneously and, if the concentration increases further, the bilayer structure is completely destroyed (1). DOPC bilayers are more resistant to these deleterious effects as the free energy barrier for the diffusion of DMSO is higher due to the longer acyl chains (1). Addition of sterols stabilises DOPC bilayers, reducing the area per lipid, increasing bilayer thickness and the order of the phospholipid acyl chains (2). Sterols make membranes more resistant to the deleterious effects of DMSO and prevent the formation of pores (2). Polyols induce a similar lateral expansion and lipid disordering on DPPC, DOPC and DOPC/sterol bilayers (3, 4). Propylene glycol and DMSO damage membranes the most (including the formation of pores) due to their higher hydrophobicity (3, 4). The increase in concentration of polyols induces the formation of a cross-linked CPA layer across the surface of the bilayers, especially with glycerol due to its higher ability to cross-link lipid headgroups and order membranes (3). Sterols diminish the deleterious effects of polyols

in a similar fashion to DMSO, in this case by reducing hydrogen-bonding between the bilayer and the CPAs as well as headgroup cross-linking (4). Mixtures of these agents induce bilayer thinning to a much lower degree than DMSO at the same overall concentration, explaining the synergistic effects and reduced toxicity of vitrification solutions.

#### References

- [1] Hughes, Mark & Mancera, J Phys Chem B, 2012, 116, 11911.
- [2] Hughes & Mancera, Soft Matter, 2013, 9, 2920.
- [3] Malajczuk, Hughes & Mancera, BBA - Biomembranes, 2013, 1828, 2041.
- [4] Hughes, Malajczuk & Mancera, J Phys Chem B, 2013, 117, 3362.

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## Keynote Session

12:00pm – 12:30pm

### pH Switching Radical Stability and Orbital Conversion

**Prof Michelle Coote**

Australian National University

#### Biography

*Professor Michelle Coote is a graduate of the University of New South Wales, where she completed a B.Sc. (Hons) in industrial chemistry (1995), followed by a Ph.D. in polymer chemistry (2000). Following postdoctoral work at the University of Durham, UK, she joined the Research School of Chemistry, Australian National University in 2001, initially*

*as an ARC postdoctoral fellow with Professor Leo Radom. She established her own research group in 2004 and is currently an ARC Future Fellow. She has published extensively in the fields of polymer chemistry, radical chemistry and computational quantum chemistry, and received many awards including the 2001 IUPAC prize for young scientists, the RACI Cornforth medal (2000), Rennie medal (2006) and David Sangster Polymer Science and Technology Achievement Award (2010), and the Le Favre Memorial Prize of the Australian Academy of Science (2010).*

#### Authors

Ganna Gryn'ova, and **Michelle L. Coote**

#### Abstract

The electronic configuration of an atom or a molecule is normally defined according to the aufbau principle: 'a maximum of two electrons are put into orbitals in the order of increasing orbital energy'. However, a limited number of recent publications have reported non-aufbau occupation of molecular orbitals in radicals, where the molecular orbital accommodating the unpaired electron (the singly-occupied molecular orbital, or SOMO) is no longer energetically the highest occupied molecular orbital (HOMO). Recently, we have discovered a brand new class of fully organic SOMO-HOMO converted compounds, and the first such species capable of being manipulated by pH. Using quantum-chemical calculations, validated by gas-phase thermochemistry experiments carried out in the group of Steve Blanksby, we have shown that distonic radical anions

comprising a stabilized radical (such as an aminoxyl, peroxy or aminyl functionality) that is not conjugated (or hyperconjugated) with a remote negatively charged functional group (such as a carboxylate, phosphate, sulphate, alkoxide anion) undergo SOMO-HOMO conversion. When the negatively charged group is protonated the Aufbau orbital configuration is restored (see Fig. 1). Intriguingly, we also found that SOMO-HOMO orbital conversion is associated with a dramatic and unprecedented effect on the stability of the radical, significantly weakening the bonds it forms with hydrogen and with carbon-centred radicals. This long-range substituent effect on radical stability, which is likewise switched off by protonation, persists even in radicals that have no polar resonance contributors, and even remains when the negatively charged groups are deleted altogether and replaced by point charges (i.e. electric fields). This talk will outline the scope, origin and potential applications of the unusual stability and electronic structures of these distonic radical anions.

#### Key Words

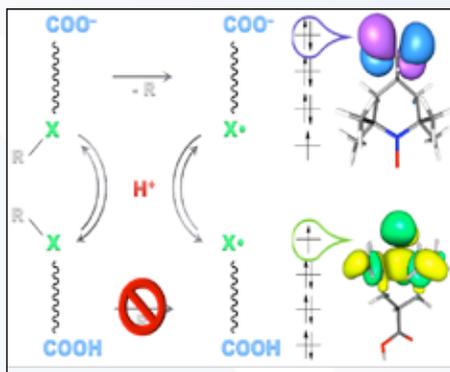
SOMO-HOMO conversion, radical stability, polar effects, distonic radical anions, quantum chemistry

#### References

<sup>1</sup>IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book").

<sup>1</sup>(a) Sugawara, T., Komatsu, H. & Suzuki, K. Chem. Soc. Rev. 40, 3105-3118 (2011). (b) Kusamoto, T., Kume, S. & Nishihara, H. J. Am. Chem. Soc. 130, 13844-13845 (2008). (c) Kobayashi, Y., Yoshioka, M., Saigo, K., Hashizume, D. & Ogura, T. J. Am. Chem. Soc. 131, 9995-10002 (2009).

<sup>1</sup>(a) Gryn'ova, G., Marshall, D.L., Blanksby, S.J., & Coote, M.L. Nature Chem., 5, 474-481 (2013) (b) Gryn'ova, G., & Coote, M.L. submitted.



**Figure 1.** Deprotonation of carboxy-TEMPO results in both SOMO-HOMO orbital conversion and an increase in radical stability by nearly 4 orders of magnitude at room temperature

**12:30pm - 12:45pm**

## Density functional theory calculations of organo-modified silicene

#### Authors

**Dr Michelle Spencer**<sup>1</sup>, Michael Bassett<sup>2</sup>, Dr Tetsuya Morishita<sup>3</sup>, Dr Hideyuki Nakano<sup>4</sup>

1. RMIT University,
2. La Trobe University,
3. Nanosystem Research Institute,
4. Toyota Central

#### Biography

Dr Spencer is a Senior Lecturer in Chemistry at RMIT University, and leader of the Computational Materials Chemistry group.

After completing her Honours and PhD at La Trobe University she held research fellow and senior research fellow positions at RMIT University, followed by an academic appointment at La Trobe University. She also currently holds a Visiting Scientist position at CSIRO and an Honorary Fellow appointment at the University of Melbourne. Her research focuses on using density functional theory and *ab initio* molecular dynamics calculations to investigate a variety of materials and nanomaterials for applications as gas sensors, batteries and electronic devices.

#### Abstract

Two-dimensional (2D) nanomaterials are currently one of the most intensely studied areas of research. 2D nanosheets of silicon are one such example and have been successfully grown via a variety of methods. A single layer Si nanosheet, called silicene, has been synthesised with different surface functionalisations, including the phenyl-modified silicene that has been grown and studied by our group [1,2]. This material has phenyl groups attached to silicene above and below the nanosheet with the under-coordinated Si atoms terminated by H atoms. Using density functional theory (DFT) calculations, we showed that this new nanomaterial is semiconducting, with a direct band gap [3]. From the experimental synthesis, the nanosheets are likely to be stacked on top of each other at a separation distance of  $\sim 10\text{\AA}$  [2], however, no details are known about their stacking geometry and adhesive force, or how the separation distance between the sheets could modify the structural or electronic

properties. As the interaction energy between the sheets is very weak we show that including vdWs forces in the DFT calculations is essential to model the interaction between organo-modified silicene nanosheets, giving a marked improvement in the predicted equilibrium separation distance determined from experimental measurements. As the modified nanosheets are brought closer together, the phenyl groups on the bottom of one nanosheet can fit in between the phenyl groups on the top of the adjacent nanosheet, allowing some interaction between the aromatic rings. The band gap can also be modified by compressing the nanosheets together while retaining a small attraction between them. The unique properties of this nanomaterial could be useful for building stacked structures for optoelectronic applications.

#### References

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- [2] Y. Sugiyama, H. Okamoto, T. Mitsuoka, T. Morikawa, K. Nakanishi, T. Ohta, H. Nakano, *J. Am. Chem. Soc.* 132 (2010) 5946-7.
- [3] M.J.S. Spencer, M. Morishita, M. Mikami, I.K. Snook, Y. Sugiyama, H. Nakano, *Phys. Chem. Chem. Phys.* 13 (2011) 15418-22.

12:45pm - 1:00pm

## Molecular Meccano and Neurodegeneration: The Computational Challenges

### Authors

**Cyril C. Curtain<sup>1</sup>**, Timothy Ryan<sup>1</sup>, Kevin J. Barnham<sup>1</sup>, Colin L. Masters<sup>1</sup>, Roberto Cappai<sup>1</sup>, Robert B. Knott<sup>2</sup>, Agata Rekas<sup>2</sup>

1. The University of Melbourne,  
2. Australian Nuclear Science and Technology Organisation (ANSTO)

### Biography

Cyril Curtain, D.Sc., FRACI is a biophysical chemist. He is currently a Senior Fellow of the Florey Institute of Neuroscience and Mental Health at the University of Melbourne where he studies protein misfolding in neurodegeneration employing small angle X-ray scattering techniques at the Australian Synchrotron and small angle neutron scattering at the Bragg Institute, Lucas Heights. His interest in protein misfolding in neurodegeneration goes back 50 years when he was associated with Dr Carleton Gajdusek in his pioneering study of Kuru in Papua New Guinea.

### Abstract

A significant fraction of every proteome is occupied by biologically active proteins that do not form unique three-dimensional structures. Many of these intrinsically disordered proteins (IDPs) have essential biological functions and possess extensive structural plasticity. This may enable IDPs to perform different functions in different environments. The disadvantage is that many IDPs can also form cross-spine  $\beta$ -structures, creating amyloids and/or cytotoxic oligomers occurring

in a number of diseases. Selection of the initial  $\beta$ -structures from an apparently random pool is poorly understood. Because of side chain steric interference, some structures are frustrated and the pool may not be truly random. Post-translationally modified residues provide an additional complication. This is particularly relevant to the study of the key proteins in the amyloids of neurodegeneration, the A $\beta$  peptide of Alzheimer's and  $\alpha$ -synuclein of Parkinson's diseases. Here, redox processes in the brain can lead to changes such as nitration of tyrosine residues or oxidation of methionine residues. Oxidation of its four methionine residues renders  $\alpha$ -synuclein incapable of forming pre-amyloid fibrils. Using small angle X-ray scattering at the Australian Synchrotron we have shown that oxidation of the methionine residues of  $\alpha$ -synuclein eliminates the extended structures from the ensemble derived from the pool of structures<sup>1</sup>. Understanding how a small change in four residues in 140 can give such a result may lead to insights into how fibril formation might be inhibited by targeting these extended structures in IDPs. This poses substantial computational challenges with a range of solutions, none of which are completely satisfactory. Here, we shall describe some approaches to solving the  $\alpha$ -synuclein ensemble problem that might have general applicability to other pathological IDPs.

### Reference

1. Pham CLL, Kirby N, Wood K, Ryan et al. Guanidine Hydrochloride Denaturation of Dopamine Induced  $\alpha$ -Synuclein Oligomers: A Small Angle X-ray Scattering Study. *Proteins* 2013 Jun 4. doi: 10.1002/prot.24332. [Epub ahead of print]

# Plenary Session

2:00pm - 2:45pm

## Line 'em all up: assembly at complex liquid interfaces

**Prof Geraldine Richmond**

University of Oregon, USA

### Biography

*Geraldine (Ger) Richmond is the Presidential Chair and Professor of Chemistry at the University of Oregon in Eugene, Oregon, USA. Her research using laser spectroscopy and computational methods focusses on understanding the chemistry and physics that occurs at complex interfaces that have relevance to important problems in energy production, environmental remediation and atmospheric chemistry. She is also active in efforts to increase the number and success of women in the sciences around the world through the COACH organization which she founded in 1997. Richmond is a member of the U.S. National Academy of Sciences and the American Academy of Arts.*

### Abstract

Over the past decade we have witnessed many exciting advances in the laboratory towards the development of new materials, in the area of molecular architecture and nanoscience, as well as in the development of new "bio-inspired" materials that seek to emulate materials that have evolved in nature. Many of these new materials are being made in more complex and reactive environments than in the past where vacuum or clean-room

conditions were traditionally used. The assembly of thin films at liquid/solid and liquid/liquid interfaces fall into this category as well the multitude of unique nanostructured materials that assemble in solvents and at surfaces. We have also begun to see advances in moving the synthesis and assembly of these materials to more environmentally benign solvents, such as in aqueous solutions, where complex interactions between the water solvent and the largely hydrophobic material can play a controlling role. This increased complexity of the materials growth environment is usually accompanied by less predictability, often because of our limited knowledge of the fundamental molecular interactions that lead to the assembly and stability of molecules at these interfaces.

This presentation gives an overview of ongoing research in my laboratory that is aimed at obtaining a molecular level picture of the adsorption and assembly of surfactants, nanoparticles and macromolecules from aqueous solution to fluid surfaces. We employ both experimental and computational methods to unravel the complex structural, reactive and bonding interactions present at these interfaces. These fundamental studies have direct relevance to many important areas of technological interest including environmental remediation, waste water treatment, green chemistry, materials growth, surface wetting and hydrophobicity, and macromolecular assembly.

**2:45pm - 3:00pm**

## Conjugated Polymer Films Imaged at High Spatial and Temporal Resolution

### Authors

**A/Prof. Trevor Smith** <sup>1,2</sup>, Dr. Xiaotao Hao <sup>3</sup>, Dr. Clare Henderson <sup>1,2</sup>, Ben Morrison <sup>1,2</sup>

1. The University of Melbourne,
2. ARC Centre of Excellence for Coherent X-Ray Science (CXS),
3. Shandong University,

### Biography

Trevor Smith co-heads the Ultrafast and Microspectroscopy Laboratories in the School of Chemistry at the University of Melbourne. His present research interests include time-resolved fluorescence studies and super-resolution fluorescence imaging techniques applied to a wide range of systems including polymers, biological and botanical samples. He also has strong research interests in evanescent wave-induced fluorescence studies and ultrafast laser spectroscopy. A particular interest is the use of time-resolved and super-resolution fluorescence microscopy techniques to study polymer films for organic photovoltaic devices. He is currently a member of the Australian Research Council Centre of Excellence for Coherent X-Ray Science (CXS) coupling super-resolution optical imaging techniques with coherent X-ray diffractive imaging.

### Abstract

Conjugated polymer-based hybrid nanocomposites have gained worldwide attention in recent years due to their potential application

in efficient and low-cost solar cells. The morphology of thin films of these materials is highly dependent on the conditions under which the film is cast. We have applied super-resolution optical imaging methods and time-resolved emission imaging to study the morphology and photophysics of thin films of various bulk heterojunction materials including poly(3-hexylthiophene) (P3HT) blended with electron acceptors including nanodiamond (ND) particles.

ND particles have been introduced in order to form novel hybrid nanocomposites because of their facile surface functionalisation, biocompatibility, etc.<sup>1</sup> In these composites, the absorption of solar photons by the polymer generates excitons, which may dissociate at the polymer-ND interface, transferring electrons to the ND and leaving positive polarons on the polymer. However, the photoinduced charge separation and recombination processes remain unclear in this novel nanocomposite material. We have investigated photoexcited physical processes in films of P3HT-ND nanocomposite by steady state and time resolved optical spectroscopy and microscopy. Fluorescence decay measurements show a reduction in the emission decay time of the hybrid film compared with the P3HT film, which most likely results from the charge separation between P3HT and ND. Time resolved images allow mapping the dynamics of the photoinduced charge transfer/transport processes as a function of location in the films. Species with longer lifetime (~200ps) are uniformly distributed in P3HT film, while regions exhibiting a shorter emission lifetime (~130ps) in the hybrid film may be

attributed to the charge separation induced by the ND aggregates that are evenly dispersed in the polymer matrix. Femtosecond transient absorption measurements have also been performed on these films. Based on these experimental observations, the photoinduced physical processes and dynamics are analysed and discussed. This study indicates that P3HT-ND bulk heterojunction composites have great potential in photovoltaic application.

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**3:00pm - 3:15pm**

## Molecular Approaches to Next Generation Photovoltaics

### Authors

**A/Prof Timothy Schmidt**<sup>1</sup>, Rowan MacQueen<sup>1</sup>, Dr Yuen Yap Cheng<sup>1</sup>, Dr Tim Schulze<sup>2</sup>, Dr Murad Tayebjee<sup>3</sup>, Dr Andrew Nattestad<sup>4</sup>, Andrew Danos<sup>1</sup>, Dr Angus Gray-Weale<sup>5</sup>, Prof Maxwell Crossley<sup>1</sup>, Prof Klaus Lips<sup>2</sup>,

1. The University of Sydney,
2. Helmholtz Zentrum Berlin,
3. UNSW,
4. University of Wollongong,
5. The University of Melbourne

### Biography

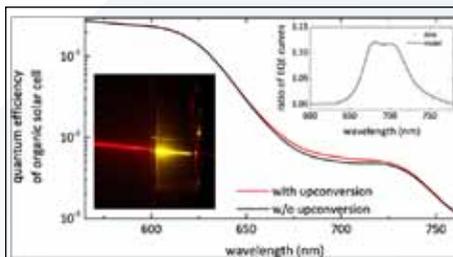
Tim Schmidt gained his BSc (Hons) from this university in 1998 winning the University Medal in theoretical chemistry. He then studied at Churchill College, Cambridge, gaining a PhD in chemistry from the University of Cambridge in 2001 for work on the femtosecond dynamics of molecules in intense laser field under the supervision of Dr Gareth Roberts. Postdoctoral work was performed in the group of Professor John Paul Maier in Basel

on the electronic spectroscopy of highly unsaturated hydrocarbons of astrophysical relevance. Tim returned to Australia in 2003 to work at the CSIRO (CTIP, Lindfield) on modelling of the rubsco enzyme. He commenced as a lecturer in chemistry in April 2004 at The University of Sydney, and was appointed Associate Professor in 2011. Tim is appointed as Professor at The University of New South Wales from 2014. He is the recipient of the 2010 Coblenz Award.

### Abstract

The sun provides more energy to our planet in one hour than our species requires in an entire year. However, harvesting this energy directly as electricity using single-threshold solar cells is fundamentally limited to an upper efficiency of about 33%. This is primarily due to two factors: the inability to absorb sub-bandgap light, and the degradation of energy in excess of the band gap.

Sub band gap absorption may be addressed by upconversion. In our laboratory, we have been investigating sensitized triplet-triplet annihilation as a means to upconvert sub-bandgap photons. In this scheme, sensitizer molecules absorb low energy photons, and rapidly undergo intersystem crossing to a metastable triplet state. This triplet energy is transferred to an emitter molecule, the triplet of which is about half the energy of the lowest singlet. Subsequent annihilation of two emitter triplets brings about one singlet excited emitter, which fluoresces at an energy above that of the initially absorbed photons.



**FIG 1:** Augmentation of solar cell quantum efficiency with upconversion

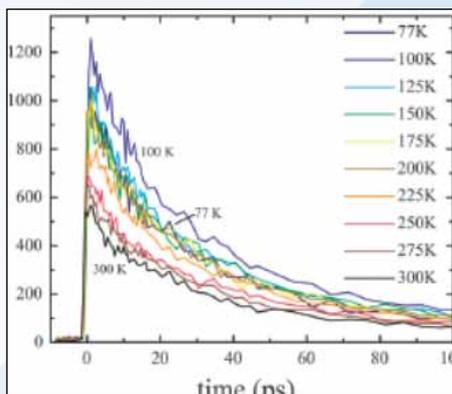
Application of this photochemical upconversion process to amorphous silicon, polymer and dye-sensitized solar cells has resulted in measurable improvements to the sub-band gap photon-to-electron conversion efficiency.[1,2,3] However, the efficiencies are still low, with current augmentations in the 10-30 mA/cm<sup>2</sup> range – about two orders of magnitude below what is required. Work to improve the efficiency using nanostructures is ongoing, and the latest results will be presented.

The opposite process to triplet-triplet annihilation, singlet fission, takes place in organic crystals. In this case, one photon gives rise to multiple excitons which may be individually harvested to boost the current for photons exceeding about twice the band gap. Our theoretical investigations have shown that maximum efficiency at room temperature relies on endothermic singlet fission, with an optimized cell capable of 46%. [4]

We have investigated singlet fission in tetracene films, which display endothermic fission. By varying the temperature, and performing spectroscopy across six orders of magnitude in time-scale (100fs to 100ns), we have arrived at a unified

model for the exciton dynamics in tetracene which touches on a range of phenomena including super-radiance, singlet fission and self-trapping.[5]

Overall, this talk will show the contribution to be made to the photovoltaic area by molecular spectroscopists, and that the detailed understanding and control of energy flow in molecular materials can be harnessed to bring about the solar cells of the future.



**FIG 2:** Initial radiative dynamics of a tetracene thin film

#### References

- [1] Y. Y. Cheng, B. Fückel, R. W. MacQueen, T. Khoury, R. G. C. R. Clady, T. F. Schulze, N. J. Ekins-Daukes, M. J. Crossley, B. Stannowski, K. Lips and T. W. Schmidt, *Energy Environ. Sci.*, 2012, 5, 6953-6959
- [2] A. Nattestad, Y. Cheng, R. W. MacQueen, T. F. Schulze, F. W. Thompson, A. J. Mozer, B. Fückel, T. Khoury, M. J. Crossley, K. Lips, G. G. Wallace, T. W. Schmidt, *J. Phys. Chem. Letters*, 2013, 4 (12), 2073–2078
- [3] T. F. Schulze, J. Czolk, Y. Cheng, B. Fückel, R. W. MacQueen, T. Khoury, M. J. Crossley, B. Stannowski, K. Lips, U. Lemmer, A. Colmann, and T. W. Schmidt, *J. Phys. Chem. C*, 2012 116 (43), 22794-22801

[4] M. J. Y. Tayebjee, A. A. Gray-Weale, and T. W. Schmidt, *J. Phys. Chem. Lett.*, 2012, 3 (19), 2749-2754

[5] M. J. Y. Tayebjee, R. G. C. R. Clady and Timothy W. Schmidt, *Phys. Chem. Chem. Phys.*, 2013, DOI: 10.1039/C3CP52609G

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**3:15pm - 3:30pm**

## Controlling Resonance Energy Transfer between Dyes on a Co-Sensitised Metal-Oxide Surface

### Authors

**Dr Viktoras Dryza**, Prof Evan Bieske  
The University of Melbourne

### Biography

*Viktoras Dryza received his PhD in 2008 from the University of Adelaide, under the supervision of Gregory Metha. He then commenced postdoctoral studies at the University of Melbourne, working with Evan Bieske in the field of gas-phase molecular ion spectroscopy. He is currently an Australian Renewable Energy Agency postdoctoral fellow, conducting research into the light-harvesting properties of organic dye sensitisers for solar cell technologies.*

### Abstract

Dye-sensitised solar cells (DSSCs) are excellent candidates as next-generation solar cells, as they can be constructed from cheap, environmentally friendly materials. Within a DSSC, dye sensitizer molecules anchored to a metal-oxide electrode absorb photons and inject the promoted electrons into the circuit. In order to engineer panchromatic DSSCs, co-sensitisation

of the electrode with two dyes having complementary absorption spectra has been employed. However, resonance energy transfer (RET) between the two dyes usually limits the achievable increase in solar conversion efficiency.

In this presentation, we demonstrate that RET between organic dyes on a co-sensitised metal-oxide surface can be virtually eliminated by deliberately misaligning the excitation transition dipole moments of the two dyes. This is achieved by exploiting the different chemical groups on each dye used to bind to the electrode and which govern the relative orientation of the two dyes on the surface. This maximises the light-harvesting efficiency by insulating the excited state of the short-wavelength absorbing dye against RET, preserving its superior electron injection capacity.

The experiments are conducted in the gas phase by laser probing charged dye-sensitised metal-oxide nanoparticles suspended in an ion trap and recording their time-resolved fluorescence decay curves. The presence of RET is determined by observing a decrease in the donor dye's excited state lifetime upon addition of the acceptor dye. The acceptor dye molecule has a benzoic acid anchoring group, which causes the dye to sit perpendicular to the surface. Detrimental RET interactions occur when the donor dye molecule possesses a cyanoacrylic acid anchoring group, which causes the dye to sit perpendicular to the surface, whereas RET is eliminated when the donor dye molecule possesses a rhodanine acetic acid anchoring group, which causes the dye to lie

parallel to the surface. This concept will help guide the rational design of efficient co-sensitised DSSCs.

## Keynote Session

4:00pm - 4:30pm

### Remote but not disinterested: Measuring the effect of charge on radical stabilisation in distonic radical anions

**Prof Stephen Blanksby**

University of Wollongong

#### Biography

Stephen Blanksby holds a PhD (1999) in gas phase ion chemistry from the University of Adelaide (with Prof J.H. Bowie) and undertook postdoctoral research at the Technical University of Berlin (1999, with Prof H. Schwarz) and at the University of Colorado (with Prof G.B. Ellison). Blanksby was appointed to the School of Chemistry at the University of Wollongong in 2002 and was promoted to Professor in 2012. His research interests are at the interface between fundamental ion chemistry, spectroscopy and analytical mass spectrometry.

#### Authors

David L. Marshall<sup>1,3</sup>, **Stephen J. Blanksby**<sup>1,3</sup>, Ganna Gryn'ova<sup>2,3</sup>, Michelle L. Coote<sup>2,3</sup>

1. School of Chemistry, University of Wollongong, NSW, AUSTRALIA

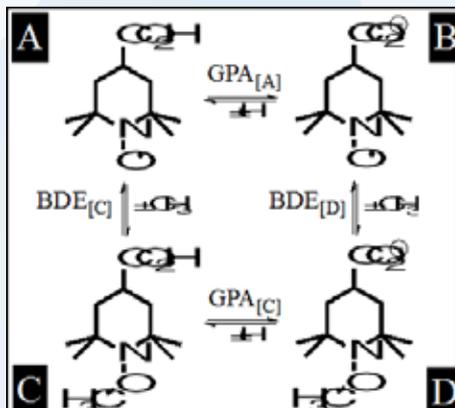
2. Research School of Chemistry, Australian National University, ACT, AUSTRALIA

3. ARC Centre of Excellence for Free Radical Chemistry and Biotechnology

#### Abstract

Distonic radical anions are ionised molecules wherein the radical and anion cannot be formally localised on a common atom. Recent high-level electronic structure calculations have revealed that even remote negative charges in distonic radical anions can afford significant stabilisation to the radical moiety. This effect is apparent where homolytic bond energies remote from an acidic functional group can be lower by up to 35 kJ mol<sup>-1</sup> in the conjugate-base (i.e., anionic) form compared with those in the conjugate-acid (i.e., neutral). These findings demonstrate that simple deprotonation of an acid moiety can flip a "pH-switch", effectively activating remote bonds – some up to 10 Å away – toward homolysis. In an effort to observe this surprising thermochemical phenomenon we measured the gas phase acidity (GPA) of the aminoxyl radical 4-carboxy-TEMPO (A) and its closed-shell, aminoether analogue C (see Figure) using the kinetic method on a tandem mass spectrometer. Consistent with theoretical predictions, these measurements revealed an enhancement in acidity of ca. 20 kJ mol<sup>-1</sup> in the presence of the remote radical moiety (i.e., GPA[C] – GPA[A] = 20 kJ mol<sup>-1</sup>). Analogous experiments conducted across a test set of reference acids established a critical benchmarking tool for the calculations with a mean absolute deviation of just 1.7 kJ mol<sup>-1</sup>. Moreover, by a simple thermochemical cycle the measured difference in gas phase acidity ( $\Delta\text{GPA} = \text{GPA}[\text{C}] - \text{GPA}[\text{A}]$ ) is shown to be equivalent to the difference in NO-CH<sub>3</sub> bond dissociation energies ( $\Delta\text{GPA} = \Delta\text{BDE} = \text{BDE}[\text{C}] - \text{BDE}[\text{D}]$ ), thus providing direct experimental

evidence for this remote radical stabilization is distonic radical ions [1].



[1] Gryn'ova, G., Marshall, D. L., Blanksby, S. J. and Coote, M. L. "Switching Radical Stability By pH-Induced Orbital Conversion" *Nature Chemistry* 2013, 5, 474-481.

**4:30pm - 4:45pm**

## NMR Chemical Shift in molecules with a (quasi)-degenerate Ground State

Authors

**Dr Willem Van Den Heuvel**, Dr Alessandro Soncini  
The University of Melbourne

Biography

*Willem Van den Heuvel obtained a PhD in Chemistry from the University of Leuven, Belgium. He is currently a McKenzie Postdoctoral Fellow at the University of Melbourne, working in the group of Alessandro Soncini.*

Abstract

The chemical shift and other parameters in the nuclear spin Hamiltonian can be calculated ab initio as electronic structure properties of the molecule. The theoretical foundation for this calculation is well-established for closed shell molecules [1]. Here we present a natural extension of Ramsey's theory to molecules with an arbitrary electronic spectrum [2]. This includes paramagnetic systems with a degenerate ground state of spin or spin-orbit character, or systems where this degeneracy is lifted by a small zero-field splitting. In each case the chemical shift depends on the thermal occupation of these electronic states and becomes therefore a thermodynamic quantity. It is also shown that the paramagnetic shift of a degenerate state can be expressed as a contraction of Zeeman and hyperfine coupling tensors, of all ranks required by the size of the degeneracy.

References

[1] N. F. Ramsey, *Phys. Rev.* 78, 699 (1950)

[2] W. Van den Heuvel, A. Soncini, *Phys. Rev. Lett.* 109, 073001 (2012); A. Soncini, W. Van den Heuvel, *J. Chem. Phys.* 138, 021103 (2013); W. Van den Heuvel, A. Soncini, *J. Chem. Phys.* 138, 054113 (2013).

**4:45pm - 5:00pm**

## The THz/Far-IR Beamline at the Australian Synchrotron

### Authors

**Dr Courtney Ennis**<sup>1</sup>, Dr Christopher Medcraft<sup>2</sup>, Andy Wong<sup>3</sup>, Ruth Plathe<sup>1</sup>

1. The Australian Synchrotron,
2. Center for Free-Electron Laser Science,
3. Monash University

### Biography

Courtney is the newest member of the THz/Far-IR Beamline at the Australian Synchrotron; returning home to join the team in November 2013. Courtney earned his PhD at The University of Western Australia (2009); investigating reactive species formed via fast-particle impact of simulated astrophysical ices. A postdoc position at the University of Hawai'i (Ralf Kaiser) followed where Courtney studied the chemical processing of planetary ices and the degradation of aerospace polymers with keV particles. At University College London (Steve Price) he was project leader for the construction of a new apparatus to study the reactions between molecular radicals (formed via laser photo-detachment of pure anion beams) and a target solid; mimicking interstellar dust grain chemistry and also industrial plasma deposition processes. With his new Fellowship at the AS, Courtney will participate in the installation of the new laser systems for gas-phase photolysis and time-resolved spectroscopic studies, and develop the Beamline's surface science infrastructure to carry out astrochemistry experiments for his allocated research.

### Abstract

The Far-IR/THz beamline at the Australian Synchrotron is coupled to a 9-chamber Bruker IFS125HR FT spectrometer equipped with a variety of optical components which can cover the spectral range from 10 to 5000 cm<sup>-1</sup>; this instrument can offer an optimum unapodized resolution of  $\geq 0.00064$  cm<sup>-1</sup>. Experiments from a variety of fields such as atmospheric and astrophysical science, geology, electrochemistry, nano-materials as well as biology have been successfully conducted at the beamline.

There is a range of instruments to accommodate the diverse requirements of the User community. For the gas-phase, room-temperature gas cells with multiple-pass optics, one of which can be coupled to a furnace to study reactive species; there is also a multiple-pass gas cell which can be cooled to liquid nitrogen or helium temperatures in order to study aerosols and cold gases. Condensed-phase Users have access to a cryostat and a grazing incidence angle and a near-normal accessory to study condensed phase systems, thin films and surface interactions.

The synchrotron infrared light offers a S/N advantage over conventional thermal sources, and this advantage varies to a great degree upon the spectral range and the resolution required by the experiment. In this paper, the capabilities and performance of the Far-IR beamline at the Australian Synchrotron will be presented as well as some applications undertaken at the beamline, and future developments such as laser photolysis & pyrolysis, and high-pressure diamond anvil cells.

**5:00pm - 5:15pm**

## Electronic energies, molecular structures and frequencies by systematic molecular fragmentation

### Authors

**Prof Michael Collins**

Australian National University

### Biography

*Michael Collins graduated from the Department of Theoretical Chemistry at Sydney University. After some years postdoctoral experience in the UK and USA, he has been a researcher at the ANU. His main interests in recent years have been in the dynamics of chemical reactions and the molecular potential energy surfaces that govern that dynamics.*

### Abstract

A new version of systematic molecular fragmentation is presented which provides a hierarchy of estimates for the energy, structure, vibrational frequencies and other properties, of large molecules with a computation time that scales linearly with the size of the molecule. This method is combined with an algorithm which ensures that the evaluation of the fragment compositions is efficient for very large molecules. The method is illustrated using a number of examples: Protein structures derived from NMR spectroscopy and evaluation of the binding energies of large water clusters. With this approach, the molecular potential energy surface (PES) of very large systems can be accurately approximated in terms of PESs of relatively small molecular fragments.

**5:15pm - 5:30pm**

## Super-resolution localization microscopy of transfected cells, starved cells and mitochondria

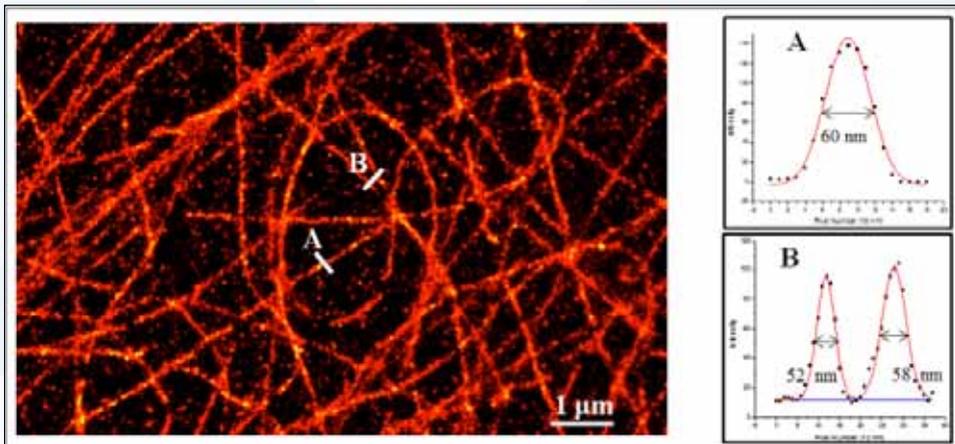
### Authors

**Dr. Toby Bell**, Donna Whelan, Georg Ramm, Markus Bach, Aaron Brice, Dr Greg Moseley  
Monash University

### Abstract

The past decade has seen the development and application of a range of visible light based techniques, known as super-resolution microscopy, capable of generating fluorescence images with resolutions inside the diffraction limit of the imaged light. One widely used approach is based on the detection and 'localisation' of emission from single molecules. Of the many variants of localisation microscopy, direct stochastic optical reconstruction microscopy (dSTORM) is the most straightforward.(1) It takes advantage of fluorescence intermittencies (switching between dark (non-emissive) and light (emissive) states) of single molecules to obtain spatially isolated intensity images of single molecules. Switching between light and dark states is achieved via a balance of laser flux, pH and a reducing buffer.

We have recently implemented a home built dSTORM set-up using off the shelf components for a fraction of the cost of a commercial system. We have developed new as well as optimised existing, fixation and labelling protocols(2) for imaging microtubules, actin filaments and mitochondria in a range of cells.



**Fig.1:** dSTORM image of microtubules labelled with Alexa647 in a fixed HeLa cell. Cross-sections of microtubule filaments clearly show the sub-diffraction resolution achievable.

Our dSTORM set-up and protocols have led to images with resolutions in the tens of nanometre range.

We have now applied our set-up to study a range of biochemical systems. We have imaged microtubules in cells transfected to express proteins associated with Rhabdovirus and show that transfection leads to a dramatic 'bundling' effect of the cell's microtubules. We have imaged starved cells and revealed the presence of sub-diffraction sized autophagosomes. These measurements highlight the ability of localisation super-resolution microscopy, particularly the dSTORM variant, to observe sub-diffraction features in cells and address, in a striking and direct fashion, important biological systems.

#### References

(1) S. van de Linde, S. Wolter, and M. Sauer, *Australian Journal of Chemistry*, 64, (2011) 503-511.

(2) S. van de Linde, A. Loschberger, T. Klein, M. Heidebreder, S. Wolter, M. Heilemann and M. Sauer, *Nature Protocols*, 6, (2011), 991-1009.

**Thursday 5  
December 2013**

## Plenary Session

**9:00am - 9:45am**

### Ultrafast Studies of Single Metal and Semiconductor Nanostructures

**Prof Greg Hartland**

University of Notre Dame, USA

#### Biography

*Prof. Hartland received a B. Sc. (Hons.) from the University of Melbourne in 1985, and a Ph. D. from the University of California, Los Angeles in 1991. He joined the faculty at the University of Notre Dame in 1994, after postdoctoral studies at the University of Pennsylvania. His research interests involve using novel optical techniques to study single nanoparticles, with a goal of understanding how these materials interact with their environment. He is a Senior Editor for the Journal of Physical Chemistry A/B/C, and is on the Editorial Advisory Board of Physical Chemistry Chemical Physics. Prof. Hartland is a Fellow of the American Association for the Advancement of Science (2009), and an American Chemical Society Fellow (2011).*

#### Abstract

Single particle spectroscopy is a powerful tool for studying nanomaterials. It is capable of revealing information about how differences in size, shape and

environment affect properties – which is often hidden in ensemble measurements. In this talk I will present results from transient absorption experiments performed with diffraction limited spatial resolution. These measurements allow us to study single nanostructures, and provide information about their dynamics that is washed out in ensemble experiments. The systems that have been investigated include metal nanowires and nanoparticles, II-VI nanowires and carbon nanostructures. The time scales range from a few hundred fs to a few ns. The results provide detailed information about how these materials interact with their environment, and trapping and recombination of electrons and holes in semiconductor nanowires. Transient absorption images can also be collected, and provide information about the spatial variation of the dynamics, and how the charge carriers move in a nanostructure.

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**9:45am - 10:00am**

### The Photon of Persuasion: Influencing Branching Fractions in the Photodissociation of H<sub>2</sub>CO

#### Authors

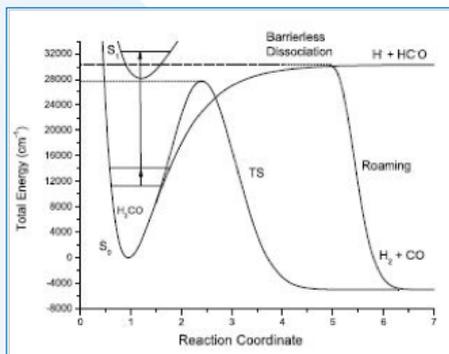
**M. S. Quinn**, B. K. Nauta, S. H. Kable  
The University of Sydney

#### Biography

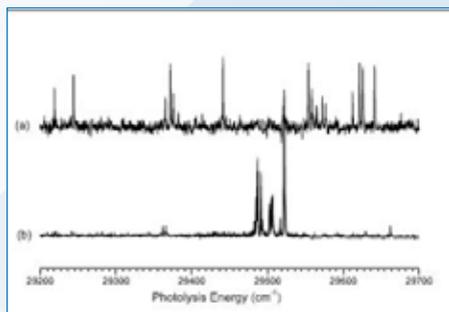
*Mitchell is a second year PhD student with Scott Kable at the University of Sydney working on a variety of Scott's reaction dynamics projects. Today he will be presenting recently obtained data on roaming in formaldehyde.*

## Abstract

By exciting different vibrational modes in a molecule, is it possible to direct a molecule to dissociate via a selected pathway? We are currently investigating the effects of pumping different vibrational modes; specifically the C-H symmetric and anti-symmetric stretches, in the photodissociation of formaldehyde. Formaldehyde has been a very well studied molecule in the study of spectroscopy and reaction mechanisms. Indeed, it was the first molecule where an alternate pathway to molecular products was first discovered and characterised. [1] This alternate pathway, labelled "roaming", is closely coupled to the H + HCO barrierless dissociation pathway. However the molecule has insufficient energy along the C - H bond to fully dissociate and is held together by van der Waals forces until the 'roaming' hydrogen atom abstracts the hydrogen from the formyl co-fragment to form H<sub>2</sub> + CO. Furthermore, roaming reaction pathways have been proposed and/or observed in a number of systems since and it is thought that there may be a roaming pathway for each barrierless dissociation pathway. [2] This talk will examine the effects of exciting different C-H vibrational modes on the branching fraction between the roaming and TS reaction pathways. Velocity map imaging experiments, depicted in Figure 1, will examine the effect of exciting the C-H stretch in both the ground (S<sub>0</sub>) and excited states (S<sub>1</sub>).



**Fig 1:** Schematic of the relevant reaction pathways in formaldehyde. The two arrows depict the two exciting photons, here the formaldehyde C-H stretch is excited in the ground state before a second laser pulse promotes it to S<sub>1</sub>.



**Fig 2:** Photofragmentation spectra of formaldehyde. (a) is the spectrum obtained when the anti-symmetric C-H stretch is pumped in S<sub>0</sub> before excitation to S<sub>1</sub>. (b) is the standard phofex spectrum from ground state S<sub>0</sub> to S<sub>1</sub>.

## References

- [1] Townsend et al. Science, 306 (2004)
- [2] Bowman et al. Ann. Rev. Phys. Chem. 62 (2011) and references therein.

10:00am - 10:15am

## 'Hot' Photo-induced Electron Transfer

Authors

**Prof Ken Ghiggino<sup>1</sup>**, Prof Steven Langford<sup>2</sup>,  
Mr Ben Robotham<sup>1</sup>

1. The University of Melbourne,
2. Monash University

### Biography

Prof Ghiggino is Masson Professor of Chemistry at the University of Melbourne. He is a PhD graduate of the University of NSW and undertook postdoctoral studies at the University of Southampton prior to joining the University of Melbourne. His research covers many aspects of fundamental and applied photochemistry and molecular spectroscopy. He is a past Chair of the RACI Physical Chemistry Division and the recipient of the RACI Physical Chemistry Division Medal and the RACI Australian Polymer Medal.

### Abstract

Photo-induced electron transfer processes are primary events in natural photosynthesis and are the basis for the successful operation of artificial photosynthetic systems, thin film photovoltaic cells and other opto-electronic devices. In the normal course of events photo-excitation of the electron donor-acceptor pair is followed by rapid relaxation to the lowest vibrational levels of the first excited electronic state before the electron transfer process occurs. Much attention has been paid to increasing the subsequent rate of charge separation while retarding the charge recombination process in

order to utilise the electrochemical potential created. However a consequence of the initial non-radiative relaxation process is that excitation energy above the band gap of the absorbing species is wasted as heat. We have been investigating molecular donor-acceptor molecular arrays that have higher electronic excited states that are sufficiently long-lived (picoseconds) to undergo electron transfer to a closely associated acceptor before the initial thermal relaxation process occurs. The rates and mechanisms of such 'hot' electron transfer and subsequent relaxation processes have been resolved by femtosecond transient spectroscopy. The implications of the results for improving the overall light energy conversion efficiency in artificial photosynthetic systems will be discussed.

The second singlet excited ( $S_2$ ) states of some metal centred porphyrins have lifetimes of a few picoseconds that is sufficient for fast electron transfer to compete with intramolecular non-radiative relaxation. For zinc tetraphenylporphyrin complexes with fullerene and with short-bridged covalently linked core-substituted amino naphthalene diimide acceptors,  $S_2$  electron transfer is a dominant process. [1] In the latter case the initial ultrafast electron transfer from  $S_2$  is followed by charge recombination to reform  $S_1$  that subsequently undergoes a further slower electron transfer process to the acceptor. These results have now been extended to supramolecular complexes of the zinc porphyrin with pyridine and isoquinoline functionalised naphthalene diimides where

electron transfer processes are again observed but where the coordinating linker and solvent play major roles in determining the mechanisms operating in each case. The range of energy and electron transfer processes that occur following photo-excitation of arrays consisting of tin tetraphenylporphyrin with covalently attached naphthalene diimides and supramolecular phenolate/BODIPY motifs will also be presented.

[1] B. Robotham, K. A. Lastman, S. J. Langford, K. P. Ghiggino, J. Photochem. Photobiol. A: Chem., 2013, 251, 167-174; S. K. Sugunan, B. Robotham,

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**10:15am - 10:30am**

## Modelling Nano-Scale Structure and Energy Transfer in Conjugated Polymers

### Authors

**Dr David Huang**, Patrick Tapping, Kyra Schwarz, Scott Clifton, Dr Tak Kee  
The University of Adelaide

### Biography

Dr David M Huang is a Lecturer in Chemistry at the University of Adelaide. He received his BSc degree (Hons I and University Medal) in Physical Chemistry from the University of Sydney. He was awarded a Fulbright Scholarship to undertake postgraduate studies in the United States and obtained his PhD in Theoretical Chemistry from the University of California, Berkeley. After a stint as a scientific copy editor for Springer-Verlag, he carried out postdoctoral research at the University of Lyon, then at the University of California, Davis.

He joined the academic staff in the School of Chemistry and Physics at the University of Adelaide in 2010.

### Abstract

The performance of organic electronic devices made from conjugated polymers is sensitive to the nano-scale morphology of the polymers. But modelling the structural and electronic properties of conjugated polymers on length scales that are relevant to device performance – from the molecular level to the 100-nm scale – is challenging. This talk will discuss coarse-grained computational models that we have developed to study the self-assembly of the nano-scale structure of conjugated polymers and the impact of polymer structure on functional properties such as energy transport that are important in devices like organic solar cells. The talk will focus on our studies of the widely used conjugated polymer poly(3-hexylthiophene) (P3HT) and will compare the computational results obtained with ultrafast time-resolved spectroscopic measurements.

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## Keynote Session

**11:00am - 11:30am**

### Shearing nanoconfined fluids

#### Prof Debra Bernhardt

The University of Queensland

### Biography

Debra Bernhardt (nee Searles) is a Group Leader and Professor in the Australian Institute for Bioengineering

and Nanotechnology and School of Chemistry and Molecular Biosciences at The University of Queensland. She is recognised for her contributions to nonequilibrium statistical mechanics and thermodynamics including development of fluctuation theorems and studies of nonequilibrium systems and confined fluids. Her research employs a range of theoretical approaches, nonequilibrium molecular dynamics simulations and quantum chemical calculations. These techniques are used to develop a fundamental understanding of matter and study applications including transport in nanopores, fluctuations, material design, gas separation, and sustainable energy.

#### Authors

Debra J. Searles<sup>a,b</sup>, Stefano Bernardi<sup>a</sup>, Sarah J. Brookes<sup>c</sup>

a. Australian Institute for Bioengineering and Nanotechnology, University of Queensland, Brisbane, Qld 4072, Australia.

b. School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Qld 4072, Australia.

c. Queensland Micro- and Nanotechnology Centre and School of Biomolecular and Physical Sciences, Griffith University, Brisbane, Qld 4111, Australia.

Presenting and Corresponding Author  
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#### Abstract

Fluids in small nanopores have properties that differ from bulk fluids at the same state point due to the restriction of motion and layering effects, especially close to the wall. Of particular interest is their behaviour when they are undergo flow, and this is relevant to a range of phenomena and applications.

Molecule simulations can provide insight into their behaviour that might not be easily assessable using experimental techniques. We show how nonlinear response theory can be applied to these systems and how it can be used to improve the results obtained from simulations, where nonlinearity sets in at relatively low fields.

Study of lubrication is an area where changes in behavior due to flow is important. In many cases lubrication occurs at high strain rates and under high confinement. In this work we use nonlinear response theory and nonequilibrium molecular dynamics techniques to evaluate the response of a fluid in a nanopore to the application of shear. The movement of the boundaries in opposite directions induces the shear. The viscous heat generated inside the pore is removed by a thermostat applied exclusively to the atomic walls, leaving the dynamics of the fluid as realistic as possible.

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**11:30am - 11:45am**

**Adiabatic energy surfaces: the interplay between electronic coupling and electron-vibrational coupling that controls chemical reactivity, spectroscopy, and the development of entanglement**

#### Authors

Noel S. Hush<sup>1</sup>, Jeffrey R. Reimers<sup>2</sup>, Laura K. McKemmish<sup>3</sup>, Ross McKenzie<sup>4</sup>

1. School of Molecular Biosciences, The

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2. School of Chemistry, The University of Sydney, 2006, NSW, Australia.

3. Research School of Chemistry, The Australian National University, Canberra ACT 0200 Australia.

4. School of Mathematics and Physics, The University of Queensland, Brisbane, QLD 4072 Australia

### Biography

Noel Hush graduated from the University of Sydney with B.Sc. (Hons) and M.Sc degrees in 1945 and 1948. In 1949, he accepted an invitation as Lecturer in Physical Chemistry at the University of Manchester, in the Department restructured by Michael Polanyi. He moved to the University of Bristol in 1955, also holding numerous visiting appointments in the US, and in 1971 returned to Sydney as Professor of Theoretical Chemistry, the first such appointment providing undergraduate to postdoctoral teaching in the subject in Australia. As Emeritus Professor since 1989, he has continued to work in the area of quantum chemistry on problems of structure and dynamics. He is a Fellow of the Australian Academy of Science and the Royal Society of London and is a Foreign Member of the American Academy of Arts and Sciences and the US Academy of Sciences. His most recent award is the biennial Ahmed Zewail Prize for Molecular Science in 2013.

### Abstract

Initial and final states of electron transfer systems can be represented by two-site diabatic energy surfaces generated through electron-vibrational interaction of strength  $\lambda$ . These are coupled by the resonance

interaction  $J$  to yield upper and lower adiabatic potential-energy surfaces. For  $2J < \lambda$ , the lower surface is symmetry-broken (double wellled), and a general picture of thermal and optical (intervalence) transfer emerges. Building on the insights of Michel Polanyi, this approach links in with general theories of chemical reaction dynamics– for example from proton transfer to inversion (e.g. ammonia, for which the resonance energy is ten times that of benzene), and understanding of ground state geometries (c.f. Walsh “rules”). This is illustrated by application to the ground states of a series of molecules ranging from BNB and the Creutz-Taube ion to the ionized bacterial photosynthetic reaction centre to the molecular conductor  $\text{Alq}_3$  used in OLED and other devices. The quantum-mechanical entanglement, i.e., the non-intuitive intrinsic aspect of quantum phenomena (which manifest, e.g., the EPR paradox), resulting from adiabatic coupling is calculated. Thus a remarkable unification of very diverse chemical phenomena can be achieved in terms of the fundamental quantities  $J$ ,  $\lambda$ , and a possible reaction energy change  $E_0$ .

### Key Words

*Vibronic coupling, electron transfer, isomerization, aromaticity, entanglement, Born-Oppenheimer breakdown, potential-energy surfaces*

11:45am - 12:00pm

## Spin-system crossing points in reaction mechanisms

### Authors

**Brian F Yates**<sup>1</sup>, Miranda F Shaw<sup>2</sup>, Alireza Ariafard<sup>3</sup>, David S McGuinness<sup>4</sup>, Robert Robinson<sup>5</sup>

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5. University of Tasmania, Private Bag 75 Hobart, TAS 7001, [Robert.Robinson@utas.edu.au](mailto:Robert.Robinson@utas.edu.au)

### Biography

Professor Brian Yates is currently seconded to the Australian Research Council as an Executive Director. He spends one day a week at the University of Tasmania where he continues to head up an active research program in computational chemistry with particular applications to organometallic, inorganic and organic chemistry.

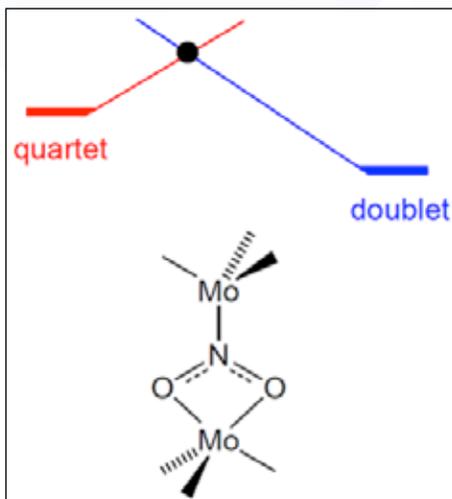
### Abstract

Low-lying energy levels with different spin states are ubiquitous in transition metal systems and they can play a role in many organometallic reactions. For example, in some cases the reagent might exist in a doublet ground state, but it is the quartet state which is the more reactive or which has a lower activation energy for the

reaction in question. In many cases it is assumed that inter-system crossing can occur readily and does not hinder the reaction. We have carried out a number of studies in which we have determined the location and energy of these inter-system crossing points. In this presentation I will discuss the importance (or otherwise) of the spin-system crossing points for reaction mechanisms, provide examples from our recent work on catalytic polymerisation reactions and small molecule activation, and discuss different methods for their evaluation and validation.

### Key Words

Minimum energy crossing points, spin system crossing



## Keynote Session

12:00pm – 12:30pm

### Are bond critical points really critical for hydrogen bonding?

**Dr Joseph Lane**

The University of  
Waikato, New Zealand

#### Biography

*Jo obtained his BSc(Hons) and PhD from the University of Otago in 2005 and 2008 respectively. His PhD and postdoctoral supervisor was Prof. Henrik Kjaergaard, now at Copenhagen University. In 2009, Jo was appointed as a Lecturer in Physical and Theoretical Chemistry at the University of Waikato and was subsequently promoted to Senior Lecturer in 2012. Jo has won several awards including an Early Career Research Excellence Award and an Emergent Teaching Excellence Award.*

#### Abstract

Hydrogen bonding interactions are of importance in a diverse range of applications. Consequently, the exact definition of what actually constitutes a hydrogen bond arouses passionate discourse amongst even the most mild-mannered chemists. One of the most popular theoretical approaches used to identify hydrogen bonding involves a topological analysis of the electron density: where chemical bonds, just like atoms, are assumed to be physical entities that can be located in three-dimensional space. Within this theoretical framework, the presence of a bond critical point between the donor and acceptor groups is considered evidence of hydrogen bond formation. However,

this criterion controversially excludes some otherwise apparent hydrogen bonds whilst also identifying some unphysical hydrogen bonds. Our recent work highlights some of these controversial examples and shows that a regional analysis of the reduced electron density gradient provides a more chemically intuitive description of hydrogen bonding. This regional definition of interactions overcomes the known caveat of only analyzing electron density critical points, which raises the title question. Namely, is it the presence of an electron density bond critical point that defines a hydrogen bond or the general topology in the region surrounding it?

**Friday 6  
December 2013**

## **Plenary Session**

**9:00am - 9:45am**

### **Probing Actinide Bonding using Multiphoton Excitation and Photoelectron Spectroscopy**

**Prof Michael Heaven**  
Emory University, USA

#### *Biography*

*Michael C. Heaven received his B. Sc. in Chemistry in 1975 and his Ph. D. in Physical Chemistry in 1979, both from the Queen Mary College, University of London. After postdoctoral studies at University of London, England and Bell Laboratories, Murray Hill, NJ from 1979–1982, he became an Assistant Professor at the Department of Chemistry, Illinois Institute of Technology, Chicago. In 1986, he joined the Department of Chemistry, Emory University as Associate Professor and was promoted to Professor in 1992. From 1996–1998, he was Director of Graduate Studies and from 2003–2009 Associate Chair of the Department of Chemistry, Emory University. His research interests include the electronic spectroscopy of transient intermediates, energy transfer kinetics, intermolecular forces, and unimolecular decay dynamics.*

#### *Abstract*

Understanding the influence of electrons in partially filled f- and d-orbitals on bonding and reactivity is a key issue for actinide chemistry. This subtle question can be investigated using a combination of well-defined experimental measurements and high-level theoretical calculations. Gas phase spectroscopic data are particularly valuable for the evaluation of theoretical models. Consequently, the primary objectives of our research program are to obtain gas phase spectra for small actinide and lanthanide compounds. Development of the tools for recording such spectra is also a component of this endeavor. To complement the experimental effort we are investigating the potential for using relativistic ab initio calculations and semi-empirical models to predict and interpret the electronic energy level patterns for f-element compounds.

Multiple resonance spectroscopy and jet cooling techniques are being used to unravel the complex electronic spectra of Th and U compounds. Recent results for the oxides, sulfide and halides will be discussed. Systematic errors in the accepted values for the ionization energies have been discovered, and the patterns of electronic states for these molecules provide information concerning the occupation of the 5f orbitals and their participation in bond formation.

**9:45am - 10:00am**

## Assignment of the Q-Bands of the Chlorophylls: Coherence Loss via Qx-Qy Mixing

### Authors

**Prof Jeffrey Reimers**<sup>1</sup>, Dr Zheng-Li Cai<sup>1</sup>, Dr Rika Kobayashi<sup>2</sup>, Dr Margus Ratsep<sup>3</sup>, Prof Arvi Freiberg<sup>3</sup>, Prof Elmars Krausz<sup>4</sup>

1. The University of Sydney,
2. Australian National University,
3. University of Tartu,
4. The Australian National University

### Biography

Professor Reimers learned spectroscopy under the direction of Ian Ross and Gad Fischer at ANU before modelling the thermodynamics and spectroscopy of water under Bob Watts. He learned semiclassical simulation methods at UC San Diego under the direction of Kent Wilson and Rick Heller before moving to the University of Sydney in 1985. He has received the HG Smith Medal of the RACI and been elected as a Fellow of the Australian Academy of Science for his analyses of the operation of bacterial photosynthesis and of synthetic molecular electronic devices. He is currently Chair of the Physical Chemistry Division of the RACI.

### Abstract

We provide a new and definitive spectral assignment for the absorption, emission, high-resolution fluorescence excitation, linear dichroism, and/or magnetic circular dichroism spectra of 32 chlorophyllides in various environments. This encompasses all data used to justify previous assignments and provides a simple

interpretation of unexplained complex decoherence phenomena associated with Qx → Qy relaxation. Whilst most chlorophylls conform to the Gouterman model and display two independent transitions Qx (S2) and Qy (S1), strong vibronic coupling inseparably mixes these states in chlorophyll-a. This spreads x-polarized absorption intensity over the entire Q-band system to influence all exciton-transport, relaxation and coherence properties of chlorophyll-based photosystems. The fraction of the total absorption intensity attributed to Qx ranges between 7% and 33%, depending on chlorophyllide and coordination, and is between 10% and 25% for chlorophyll-a. CAM-B3LYP density-functional-theory calculations of the band origins, relative intensities, vibrational Huang-Rhys factors, and vibronic coupling strengths fully support this new assignment.

**10:00am - 10:15am**

## Quantum enhancement of steady-state light harvesting in sunlight

**Dr Ivan Kassal**

The University of Queensland

### Biography

*Dr Kassal graduated from Stanford University in 2006 with degrees in chemistry and philosophy. In 2010, he received his Ph.D. in chemical physics from Harvard University, for a thesis exploring the applications of quantum computing to problems in chemistry. Since 2011 he has been at the University of Queensland as a holder of a UQ Postdoctoral Research Fellowship, focusing on quantum effects in biological systems and the dynamics of energy transport in light harvesting complexes.*

### Abstract

Photosynthetic organisms harvest light through large antenna complexes composed of many chlorophyll molecules supported by protein backbones. Recent experimental studies have found that energy is transported through antenna complexes, and onward to the reaction centre, in a coherent, wavelike manner [1]. Not only was this surprising—quantum effects were thought unable to survive for so long in biological systems at room temperature—but it also led to speculation that evolution optimised photosynthesis to take advantage of some sort of quantum enhancement.

I'll describe some of the quantum effects in light harvesting, with a special focus on the role played

by the coherence of the incident light [2–5]. Indeed, energy transport is quite different in spectroscopic experiments driven by femtosecond laser pulses than it is in natural sunlight. In particular, sunlight is stationary and incoherent for all practical purposes, meaning that any molecular system excited by it will be in a time-independent steady state, with a density matrix almost completely diagonal in the energy basis [2]. I'll discuss how continuous transport proceeds through this steady state, and how to calculate it efficiently. In particular, finding the steady state—and all associated observables such as the efficiency—is dramatically simpler than calculating the complete time-evolution followed by ensemble averaging. Instead, the problem reduces to finding the nullspace of a simple, Markovian Liouvillian. In other words, neither wavelike transport nor non-Markovian effects—which are important to understanding ultrafast experiments—have an influence on steady-state transport.

However, even though there is no wavelike transport in sunlight and the process might therefore appear completely incoherent, the underlying quantum dynamics can nevertheless influence the overall (incoherent) rates [4]. I will give several examples both of model systems and of natural light-harvesting complexes where the underlying coherence enhances the transport efficiency. From these examples, we can infer principles of quantum enhancement that can guide the design of more efficient artificial light harvesting in sunlight.

## References

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## Keynote Session

**10:45am - 11:15am**

### **Harnessing the Power of the Sun – Self-Assembled Porphyrin-fullerene Complexes as Functional Components**

#### **A/Prof Cather Simpson**

The University of Auckland, New Zealand

#### **Biography**

*Cather joined The University of Auckland in 2007 to establish and direct the Photon Factory, a new multi-user ultrafast laser and microfabrication facility. Her appointment is held jointly in Physics and Chemistry, and she is a member of the MacDiarmid Institute for Advanced Materials and Nanotechnology. She earned her Ph.D. in the USA as a Howard*

*Hughes Predoctoral Fellow. After a Department of Energy Distinguished Postdoctoral Fellowship, she joined Case Western Reserve University to pursue the research in ultrafast energy conversion by molecular systems that she has continued at Auckland. Recent awards include a National Tertiary Teaching Excellence Award (2013).*

#### **Abstract**

Solar energy is the key source of renewable energy that will meet our current and future global energy demands. Research is advancing on many fronts to make collecting, storing and using energy in the form of light a reliable, efficient, inexpensive and clean technology. In our lab, we are using laser spectroscopy techniques to explore the potential of self-assembled, porphyrin-fullerene complexes as the active light harvesting and initial charge-separation components for devices that convert light to a quasi-stable charge-separated state. Advantages of these complexes include simpler synthesis, wide absorption across the visible spectrum, and the relatively low reorganization energy of fullerenes. Multi-step electron transfer steps can be designed into these compounds to extend their charge-separated state lifetimes into practical timescales. Here we report the photodynamics of several sets of calix[4]arene-linked bisporphyrin-fullerene complexes intended to test hypotheses about structure-function relationships. Our primary tool is ultrafast transient absorption spectroscopy in the visible and near-IR spectral regions. Following photoexcitation of the porphyrin, the initial charge separation step occurs within the first few tens of

picoseconds. In these mechanistic studies, charge recombination is in the nanosecond range. The use of a secondary donor as a porphyrin ligand extends the charge-separated state lifetime, but not in through the anticipated mechanism. Initial studies of novel solid-state porphyrin-fullerene constructs show the effects crystal packing on the electron transfer process. The results are discussed with reference to the development of similar self-assembled architectures as useful solar energy harvesting complexes.

**11:15am - 11:30am**

## Reactivity of Gallium Nanoclusters

**Dr David Henry**  
Murdoch University

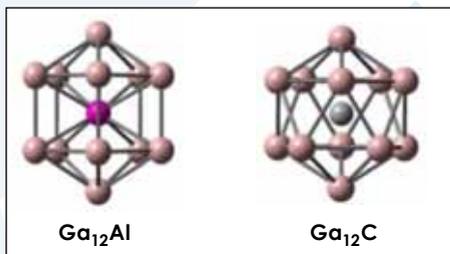
### Biography

Dr Henry obtained his PhD in Physical Organic Chemistry from Deakin University in 1998 studying the kinetics of hydrogen atom transfer from organotin hydrides to carbon centred radicals using both theoretical and experimental methods. He then had a 3 year post-doctoral fellowship at ANU in the group of Prof. Leo Radom (ANU) studying radical thermochemistry and reactivity. Following this he then spent 7 years with the group of Prof. Irene Yarovsky at RMIT University working on a range of projects including, polymer coatings, Langmuir monolayers and nanoparticles. He is currently a lecturer in Chemical and Analytical Sciences at Murdoch University (Western Australia,) with research interests in Physical and Analytical

Chemistry including nanoparticles, bioinorganic chemistry and soil chemistry.

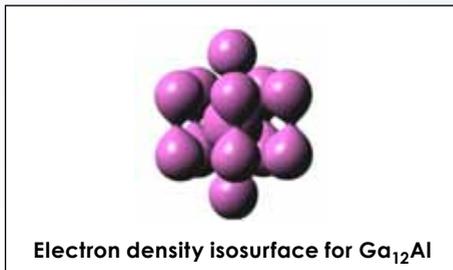
### Abstract

The properties of metal clusters can differ significantly from that of bulk materials and are often dependant on not only the composition but also the size of the cluster.[1] As a result, cluster based materials are increasingly being investigated for their reactivity and catalytic activity which may be enhanced due to their high surface-to-bulk ratio.

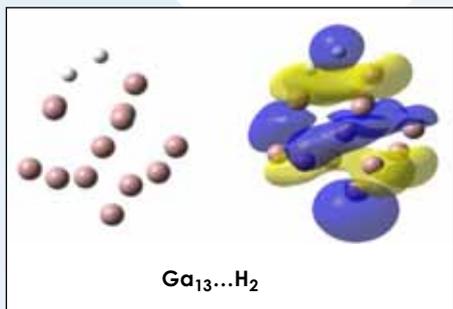


Density functional theory is used in this study to investigate the structures, stabilities and reactivity of doped gallium nanoclusters,  $\text{Ga}_{12}\text{X}$  ( $\text{X} = \text{B}, \text{C}, \text{N}, \text{Al}, \text{Si}, \text{P}, \text{Ga}, \text{Ge}, \text{and As}$ ). Gallium exhibits a strong preference for formation of  $\text{Ga}_2$  subunits within both the bulk structure and in the structure of small clusters.[2] This tendency significantly contributes to the general preference for decahedral symmetry in  $\text{Ga}_{12}\text{X}$  clusters because it facilitates the formation of five  $\text{Ga}_2$  subunits in the equatorial inter-ring region. Furthermore, in all of the studied cases, doping of the  $\text{Ga}_{13}$  cluster leads to increased stability. Generally the endohedrally doped isomers are either lower in energy or close in energy to the isomers with the dopant at the surface of the cluster. Endohedral  $\text{Ga}_{12}\text{C}$  is the most stable cluster and exhibits the most

Jellium-like orbital structure. Trends in vertical ionization potentials and electron affinities can be explained in terms of the interactions in frontier orbitals and generally adhere to the predictions of the Jellium model.



Covalency in the surface bonds of  $\text{Al}_{12}\text{X}$  clusters has previously been shown to be an important factor in determining the reactivity of clusters and the regioselectivity of surface interactions.[3] The  $\text{Ga}_2$  subunits of  $\text{Ga}_{12}\text{X}$  clusters exhibit considerable covalency which can be tuned by the addition of dopants thereby offering considerable potential to utilise these species as cluster based catalysts.[4]



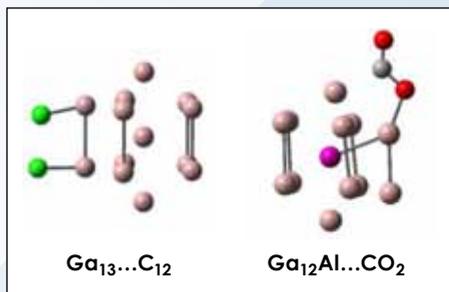
So far a number of favourable interactions between  $\text{Ga}_{12}\text{X}$  species and small molecules have been identified and characterised including dissociation of diatomic molecules and chemisorption of  $\text{CO}_2$ .

#### References

- [1] Clusters and Nano-Assemblies, 2005, (Eds. P. Jena, S. N. Khanna, B. K. Rao) (World Scientific: Singapore).
- [2] Gaston, N.; Parker, A. J. Chem. Phys. Lett. 2011, 501, 375-378.
- [3] Henry, D.J.; Szarek, P.; Hirai, K.; Ichikawa, K.; Tachibana, A.; Yarovsky, I. J. Phys. Chem. C 2011, 115, 1714-1723.
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#### Key Words

*Cluster reactivity, regioselectivity, chemisorption, covalency*



11:30am - 11:45am

## Metal Clusters on Oxide Surfaces for Catalysis

### Authors

**Gunther Andersson** <sup>1</sup>, Gregory Metha <sup>2</sup>, Vladimir Golovko <sup>3</sup>

1. Flinders University,
2. University of Adelaide,
3. University of Canterbury

### Biography

*Gunther Andersson is Assoc. Prof for Physics and Nanotechnology at Flinders University and strategic leader of the Flinders Centre for NanoScale Science and Technology. He obtained his PhD from the University of Witten-Herdecke (Germany) in 1998. After a Postdoc at the Eindhoven University of Technology (The Netherlands) in the field of organic light emitting diodes he obtained his Habilitation in Physical Chemistry at Leipzig University (Germany) in 2006. In 2007 he moved to Flinders University. His current research activities are in the field of catalysis with nano-clusters, renewable energies and liquid surfaces.*

### Abstract

Gold particles with a size reduced below 5 nanometres are known to be catalytically active [1-3]. Moreover, it has been demonstrated that the onset of catalytic activity of gold often coincides with the loss of metallic properties of Au nanoparticles at around 1.5-2 nm. This size-threshold is established for both naked clusters prepared under UHV conditions [4] and chemically-synthesised well-defined metal

nanoparticles immobilized onto inert supports [5]. Metal clusters can be deposited from the gas phase as size selected clusters or by the evaporation of metals or from the liquid phase when using chemically synthesised nanoparticles [6, 7]. The latter route offers the huge benefit of easy scale-up. Removal of ligands is often postulated as a necessary step for making the adsorption sites at the surface of the clusters catalytically active.

The chemically made clusters are deposited from solution onto oxide surfaces by dip coating after application of various surface pre-treatments. We have found that the pre-treatment of the oxide surface plays a crucial role in the agglomeration during the deposition process.

After the deposition of the clusters, the surfaces are characterised with electron spectroscopy (metastable induced electron spectroscopy (MIES), X-ray and UV photoelectron spectroscopy (XPS and UPS)) as well as X-ray absorption spectroscopy. These data are analysed with assistance from detailed modelling that provides information about likely geometry and electronic structure. The characterisation allows determining whether or not clusters agglomerate during deposition and post-deposition treatment and what the electronic structure of the deposited clusters is. It is assumed that the electronic structure plays a crucial role in the catalytic activity.

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## Keynote Session

11:45am - 12:15pm

### Photodissociation of small aromatic species in the gas-phase and liquid-phase microdroplets

**Dr Adam Trevitt**

University of Wollongong

#### Biography

*Adam completed undergraduate and Honours at the University of Adelaide then a PhD at University of Melbourne. Next was a postdoc at University of California Berkeley/ Lawrence Berkeley National Labs. He commenced his independent career at the University of Wollongong in 2008 where he runs the Laser Chemistry Laboratory and teaches chemistry. His research focuses on understanding chemistry in combustion environments, liquid microdroplets and in the gas-phase using lasers, mass spectrometry and synchrotron techniques.*

#### Authors

*Christopher S. Hansen, Phillip J. Tracey<sup>1</sup>, Bartholomew S. Vaughn<sup>1</sup>, Brendon J. Roberts<sup>1</sup>, Berwyck L. J. Poad<sup>1</sup>, Stephen J. Blanksby<sup>1</sup> and **Adam J. Trevitt<sup>1</sup>***

*1. Laser Chemistry Laboratory, School of Chemistry, University of Wollongong, NSW, 2522*

#### Abstract

Photons initiate chemical action by exciting molecules to more active bound states or by breaking bonds to create reactive products.

Fundamental insights into these processes has, for example:

- led to a useful understanding of atmospheric photochemistry (like haze formation and ozone depletion/creation)
- aided the mitigation of inefficiencies in organic-sensitized solar cells
- directed targeted photodynamic therapies in biological systems.

To make further inroads and master the photochemistry underpinning these applications, fundamental questions remain to be answered – the particular directions of our research group are the wavelength dependent photodissociation channels and photoproduct characterisation of molecules both in the gas and liquid phase.

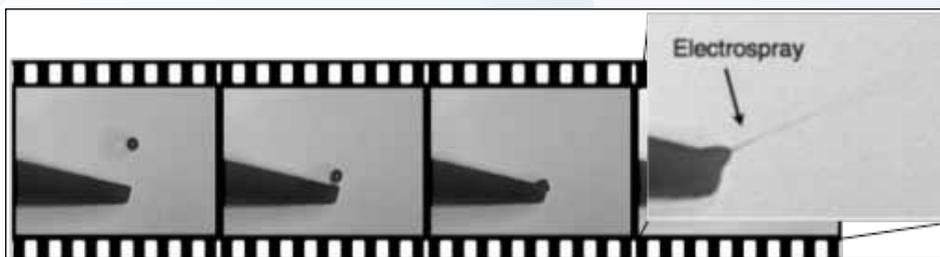
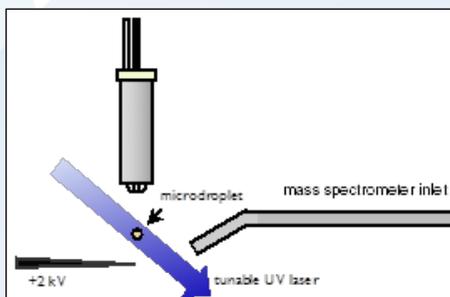
Two techniques will be described in this presentation – one that couples tunable UV-vis laser radiation to a linear ion trap for gas-phase action spectroscopy of ions and the second instrument unites single microdroplet generation techniques, laser photolysis and mass spectrometry for rapid-acquisition of liquid-phase action spectroscopy. Our new single-droplet desorption strategy is shown in the figure below where a single droplet impinges on a thin needle held at 2 kV. The subsequent

electrospray is sampled by a mass spectrometer. This is done one droplet at a time: one droplet, one laser pulse, one spectrum.

The gas-phase and liquid-phase photodissociation spectra of small aromatics are compared to probe the effect of the solvent. Dissociation in these systems can be facilitated by ground state unimolecular rearrangement following rapid interconversion from excited state(s) and this process is studied in both phases. Also, using the microdroplet apparatus, the fate of photogenerated phenyl and benzyl-type aromatic radicals is explored in various solvents. The droplet photodissociation apparatus allows rapid surveys of liquid-phase chemistry in seconds using only picolitres (pL) of sample.

#### Key Words

*Laser, radical chemistry, mass spectrometry, photodissociation, spectroscopy.*



**12:15 pm - 12:30 pm**

## Ligand-mediated control of the surface plasmon resonance in metal nanoparticles generated by laser ablation

### Authors

**Prof Mark Buntine**, Ashley Mulder, Rhys Tilbury, Michael Wolter, Melissa Werrett, Phillip Wright, Dr Max Massi, Dr Paolo Raiteri  
Curtin University

### Biography

Mark Buntine, FRACI C Chem, is President of the RACI. He is the Immediate Past Chair of the Physical Chemistry Division and a former President of the South Australian Branch and a member of the Executive Committee of the Australian and New Zealand Society for Mass Spectrometry. He is the Head of the Chemistry Department at Curtin University. Mark's research interests include the use of lasers to explore a variety of chemical phenomena, augmented by *ab initio* computational chemistry studies. He is a recipient of the RACI's Rennie Memorial medal. Mark is a foundation Director of the Advancing Science by Enhancing Learning in the Laboratory (ASELL) project. He has been awarded numerous university, state and national awards for his learning and teaching activities.

### Abstract

We report on the production and characterisation (spectroscopic and microscopic) of metal nanoparticles generated by the Laser Ablation Synthesis in Solution (LASiS) approach. In particular, we generate the metal nanoparticles encapsulated and

stabilised by a variety of ligands in solution. The encapsulation ligands mediate the nanoparticle surface electron density and thus influence the optical properties of the surface plasmon resonance transition. This manipulation of the electronic structure of the nanoparticle surface has implications for a variety of possible applications. However, the ability to fully exploit potential end-use applications requires a detailed understanding of the metal-ligand binding preferences. We make use of Molecular Dynamic simulations to explore these binding preferences and report on the synergistic interplay of experiment and theory in aiding our understanding of the ligand-mediated optical properties of the metal nanoparticles.

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**12:30pm -12:45pm**

## Roaming, roaming everywhere

### Authors

**Prof Scott Kable**, A/Prof Meredith Jordan, Dr Klaas Nauta, Mr Mitchell Quinn, Mr Kelvin Lee  
The University of Sydney

### Biography

Scott Kable is a professor of chemistry at the University of Sydney. He earned his PhD at Griffith University and did 3 years post-doctoral research at Cornell University before returning to Australia at the University of Sydney in 1992. His research has been recognised by the Le Fevre Award of the Australian Academy of Science, a JILA Fellowship, and a Fulbright Senior Fellowship in 2010. He is currently a member of the ARC College. Scott has been awarded

several University and National Teaching Awards.

#### Abstract

Reactions that occur near the energetic threshold can be very different to those where energy is in excess. The rate of a dominant reaction mechanism can be slowed, which allows other processes to be observed. These "near threshold" processes are always present, but often obscured by the dominant mechanism, and can explain unusual kinetic behaviour, and the presence of unexpected reaction products. One such near threshold mechanism in photodissociation is "roaming", in which two departing fragments orbit each other and re-collide in a different configuration. This gives rise to unexpected photochemical products, with an unusual distribution of energy.

Roaming in acetaldehyde has been somewhat controversial in recent years. Some time ago we published the first observation of roaming in acetaldehyde photodissociation. [1] Experimentally, the CO fragments were observed to be much colder than the same products formed via the traditional transition state mechanism. 15% of the CO yield was estimated to be due to roaming. More recent experiments probing the CH<sub>4</sub> photofragment attributed roaming to be 85% of the CO yield. [2] Even more recently, a third group measured the product state distribution of the CO by the technique of ion imaging and inferred 10-20% roaming yield. [3]

In this talk, I shall demonstrate that all three previous experiments are valid, but that all three have misinterpreted the data. There are actually

two different roaming pathways in CH<sub>3</sub>CHO photodissociation, giving rise to two different energy distributions in the roaming CH<sub>4</sub> + CO products. These two distributions had been misinterpreted previously as evidence for roaming and transition state mechanisms instead of two roaming mechanisms. While there is evidence for a third pathway via the conventional transition state, our experiments demonstrate that it is a minor pathway.

This is the first demonstration that multiple roaming pathways exist in the same molecule. It adds to the growing belief that roaming mechanisms are ubiquitous and that they may provide explanations for many reactions with unexplained kinetic behaviour.

#### References

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- [3] Rubio-Lago et al, PCCP, 14, 6067 (2012).

## Plenary Session

1:45pm - 2:30pm

### Probing molecular ions with laser-cooled atomic ions

**A/Prof Kenneth Brown**

Georgia Institute of Technology, USA

#### Biography

*Kenneth Brown is an Associate Professor in the Schools of Chemistry and Biochemistry; Computational Science and Engineering; and Physics at the Georgia Institute of Technology. He received his PhD from University of California, Berkeley studying theoretical issues in quantum information in the group of Birgitta Whaley. As a postdoctoral fellow at MIT, he worked on trapped ion and NMR quantum information experiments in the group of Isaac Chuang. His current research interests are cold molecular ions and quantum information.*

#### Abstract

Laser-cooled atomic ions can be exquisitely controlled at the quantum level. As a result, trapped atomic ions have been used to build extremely precise atomic clocks, quantum simulators of magnetic materials, and prototype quantum computers. This control can also be used to sympathetically cool and probe co-trapped molecular ions. Current experiments with mixtures of molecular ions and laser-cooled atomic ions include the measurement of chemical rates at temperatures of a few Kelvin and precision spectroscopy of vibrational transitions.

My group is studying the limit of performing molecular spectroscopy with a single molecular ion and a single atomic ion. Precise measurement of molecular ion transitions has applications in both astrochemistry and the measurement of possible time variations in fundamental constants. I will present our work on determining the molecular ion mass by resolved atomic sideband spectroscopy and our progress towards measuring the vibrational overtones metal hydride ions.

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2:30pm - 2:45pm

### Resonance and Photoisomerization in Fluorescent Protein Chromophores: Reversible Photobleaching Rate and Proximity to the Cyanine Limit

#### Authors

**Dr Seth Olsen**

The University of Queensland

#### Biography

*Dr. Olsen was born and educated in the USA. He received a Bachelor's of Science with Honours in physics at the College of William and Mary in Virginia in 1997 and a PhD in Biophysics and Computational Biology by the University of Illinois at Urbana-Champaign in 2004. His research interests lie at the boundary of physics, chemistry and molecular biology and revolve around the transduction of energy by self-organizing molecular machines.*

## Abstract

The green fluorescent protein (GFP) and its natural and engineered variants represent some of the most powerful tools of modern molecular and cellular biophysics. Reversible photobleaching in GFP variants is a two-edged sword; on the one hand it can complicate the acquisition and interpretation of fluorescence images collected using these markers, on the other hand it has been exploited as a platform for new sensing and imaging technology development. Understanding the reversible photobleaching process of GFP variants is of interest for the development of new technologies, and also as an important model system for understanding general photobiological yield and control problems. Structural data suggest that, in many cases, reversible photobleaching is associated with photoisomerization and/or phototitration of the chromophore of the protein.[1] Recently, new data have suggested that the rate of reversible photobleaching in some GFP variants is correlated the charge-transfer dipole magnitude associated with excitation of the chromophore.[2] In this talk, I will show how these correlations can be simply explained once it is recognized that the chromophore of these proteins belongs to a well-known and very important class of organic chromophores: the cyanine dyes. The mechanism has profound implications for engineering the properties of fluorescent proteins, which I will discuss.

[1]. P. Dedecker et al. J. Am. Chem. Soc. 135 (2013) 2387.

[2]. M. Drobizhev et al. Scientific Reports. 2 (2012) 688.

**2:45pm - 3:00pm**

## Reactive Simulations of Carbonates in Water

### Authors

**Dr Paolo Raiteri**<sup>1</sup>, *Dr Chris Knight*<sup>2</sup>, *Prof Greg Voth*<sup>2,3</sup>, *Prof Julian Gale*<sup>1</sup>

1. Curtin University,
2. Argonne National Laboratory,
3. James Franck Institute, and Computation Institute

### Biography

*Dr Raiteri obtained his PhD from the University of Milano-Bicocca in 2003. He successively moved to the group of Prof Parrinello at ETH Zurich, where he worked for 4 years as a research assistant. In 2008 Dr Raiteri joined Curtin University as a Early Career research fellow and he is currently a senior research fellow holding an ARC fellowship.*

### Abstract

Carbonates are ubiquitous materials that can commonly be encountered in everyday life in the form of anything from scale in domestic and industrial appliances through to as constituents of the exoskeleton of marine organisms. Despite its abundance and importance a detailed understanding of the mechanisms controlling the dissolution and growth of carbonate materials is still out of reach. This has in fact proven to be particularly challenging, both for experimentalists and theoreticians, and only in recent years have atomistic pictures of the early stages of nucleation of calcium carbonate started to emerge<sup>1,2</sup>. In particular pH, which is known to play a key role in controlling the delicate balance between growth and

dissolution of these materials, has been the main obstacle to performing realistic simulations of carbonate materials and it has often been neglected or treated in approximate ways.

In this presentation we show a first application of reactive classical molecular dynamics simulations to the case of calcium carbonate dissolution and growth. Here the reactivity is added through the MS-EVB formalism<sup>3</sup> on top of carefully calibrated empirical forcefields, which are known to reproduce the thermodynamic properties of the unreactive species<sup>4</sup>. This approach allows the advantages of quantum simulations (reactivity) to be combined with those of empirical simulations (speed) at the small cost of adding only few extra parameters to reproduce the reaction barrier. The reported results demonstrate how to the thermodynamic properties of the system can be accurately reproduced and how the introduction of reactivity affects the early stages of nucleation and dissolution of calcium carbonate.

## References

[1] Gebauer D., Voelkel A., and Coelfen H., 2008, "Stable Prenucleation Calcium Carbonate Clusters", *Science*, 322(5909), pp. 1819–1822.

[2] Wallace A. F., Hedges L. O., Fernandez-Martinez A., Raiteri P., Gale J. D., Waychunas G. A., Whitlam S., Banfield J. F., De Yoreo J. J., "Microscopic Evidence for Liquid-Liquid Separation in Supersaturated CaCO<sub>3</sub> Solutions", *Science*, accepted 24/06/13.

[3] Knight C., Lindberg G. E., and Voth G. A., 2012, "Multiscale reactive molecular dynamics", *Journal of Chemical Physics*, 137(22), p. 22A525.

[4] Demichelis R., Raiteri P., Gale J. D., Quigley D., and Gebauer D., 2011, "Stable prenucleation mineral clusters are liquid-like ionic polymers", *Nature Communications*, 2, p. 590.

**3:00pm - 3:15pm**

## **Effective and ineffective transition metal catalysis in reversible hydrogen storage**

**Dr Terry Frankcombe**

*Australian National University*

### **Biography**

*Terry Frankcombe completed his PhD under the supervision of Prof Sean Smith at the University of Queensland in 2002. He was a postdoc first at UQ, then with Geert-Jan Kroes at the University of Leiden. He held a Marie Curie Fellowship at the University of Gothenburg with Gunnar Nyman in 2007 before returning to Australia to work with Michael Collins at ANU. He was awarded an ARC Future Fellowship in 2010.*

### **Abstract**

One of the barriers to transitioning to a hydrogen-mediated energy economy is the lack of appropriate hydrogen storage technologies. One of the most popular potential storage systems is storing hydrogen as a complex metal hydride that decomposes on heating, but reconstitutes under hydrogen pressure (known as reversible hydrogen storage). Thermodynamic and gravimetric considerations point to using sodium alanate,  $\text{NaAlH}_4$ , as the storage material. Doping with transition metal catalysts improves dehydrogenation kinetics and is essential for reversible hydrogen storage. Titanium was the first active catalyst discovered and remains one of the best. Light transition metal elements near titanium in the periodic table are also effective. What are not effective are the

heavy, high d transition metals such as platinum and palladium that are usually active in hydrogen catalysis in other contexts. This work examines an oft-neglected aspect of the role of the transition metal catalysts, namely rehydrogenation of the decomposition products. The effect of catalyst atoms embedded in the surface of sodium hydride has been investigated using DFT methods, along with how the interaction with hydrogen molecules changes. Dramatic and simply rationalisable differences are seen between the behaviour of dopants that are effective (Sc, Ti and V) and those that are not (Pt and Rh). The results suggest that a "hydrogen pump" mechanism is active in the rehydrogenating system. This is one of the first studies to effectively rationalise the difference in activity of different transition metal dopants.

## Keynote Session

3:45pm - 4:15pm

### Ultrafast Probes of Free Charge Photogeneration in Organic Photovoltaics

**Dr Justin Hodgkiss**

Victoria University of Wellington,  
New Zealand

#### Biography

*Dr Justin Hodgkiss is a senior lecturer in Physical Chemistry at Victoria University of Wellington, a Rutherford Discovery Fellow and a Principal Investigator in the MacDiarmid Institute for Advanced Materials and Nanotechnology. Justin completed his Ph.D. at Massachusetts Institute of Technology in 2006 with Daniel Nocera, followed by post-doctoral research at the University of Cambridge with Sir Richard Friend before returning to New Zealand in 2009. His research program exploits ultrafast optical spectroscopy to probe the optoelectronic functionality organic semiconductors. His work on organic photovoltaics was recently recognized with the Young Scientist Prize from the Asian and Oceanian Photochemical Association.*

#### Authors

**Justin Hodgkiss<sup>1</sup>**, Kai Chen<sup>2</sup>, Alex Barke<sup>2</sup>,  
Shyamal Prasad<sup>2</sup>

1. School of Chemical and Physical Sciences, Victoria University of Wellington and MacDiarmid Institute for Advanced Materials and Nanotechnology, PO Box 600, Wellington 6140, New Zealand.  
[Justin.Hodgkiss@vuw.ac.nz](mailto:Justin.Hodgkiss@vuw.ac.nz)

2. School of Chemical and Physical Sciences, Victoria University of Wellington

and MacDiarmid Institute for Advanced Materials and Nanotechnology, PO Box 600, Wellington 6140, New Zealand.

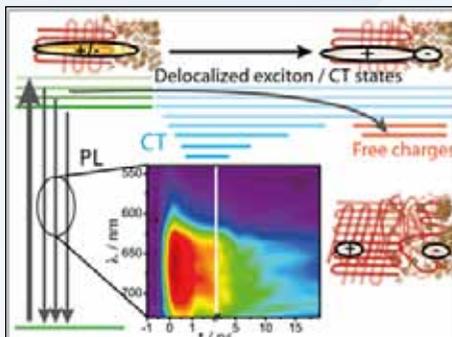
#### Abstract

Several characteristic lengths are central to free charge photogeneration in polymer-fullerene organic photovoltaics. Recent measurements suggest that the observed ultrafast branching between tightly bound charge pairs and separated charges is linked to the spatial extent of excitons and polarons. We have developed a series of time-resolved optical spectroscopy experiments that resolve different properties of bound and free charges, including the characteristic length scales associated with the key branching step. An underpinning capability of all of our measurements is the sensitivity to carry out measurements at low enough laser excitation intensity to mimic solar excitation conditions.

Using an ultrafast Kerr gate photoluminescence spectrometer, we resolve substantial high-energy emission from hot excitons prior to energetic relaxation, which occurs predominantly on a sub-ps timescale. Consistent with quantum chemical calculations, ultrafast annihilation measurements show that excitons initially extend along a substantial chain length with a volume approaching 20 nm<sup>3</sup>, prior to localization induced by structural relaxation. Moreover, we see that hot excitons are initially highly mobile and the subsequent rapid decay in mobility is correlated with energetic relaxation. The relevance of these measurements to charge photogeneration is confirmed by our measurements in blends. We find

that charge photogeneration occurs predominately via these delocalized hot exciton states in competition with relaxation and independently of temperature.

By resolving the effect of temperature and excitation density on charge recombination via transient absorption spectroscopy in polymer-fullerene blends, we are able to access a regime where all photogenerated charge pairs are frozen out following the primary charge transfer step and recombine via tunneling. The exponential distance dependence of electron tunneling provides a sensitive probe of the distance distribution of initial charge pairs. We show that the most efficient blends are associated with substantially longer initial electron-hole pair distances, which may be linked to the delocalization of the primary excitation.



#### Key Words

Organic photovoltaics, ultrafast fluorescence spectroscopy, ultrafast transient absorption spectroscopy.

## 4:15pm - 4:30pm

### Aerosol icing on the cake: IR spectroscopy of nanoscale particles

#### Authors

**Dr Evan Robertson<sup>1</sup>**, Dr Chris Medcraft<sup>2</sup>, Mr Andy Wong<sup>2</sup>, Dr Chris Thompson<sup>2</sup>, Prof Don McNaughton<sup>2</sup>, Dr Dominique Appadoo<sup>3</sup>, Dr Sigurd Bauerecker<sup>4</sup>

1. La Trobe University,
2. Monash University,
3. Australian Synchrotron,
4. Technische Universität Braunschweig,

#### Biography

Dr Evan Robertson qualified for his PhD at Monash University, then worked as a post-doctoral researcher in laser spectroscopy with Prof. John Simons at the University of Oxford. In 2001, he returned to the School of Chemistry at Monash University to take up Logan and ARC research fellowships, followed by a lectureship. In 2009, he moved to La Trobe University where he leads a research group in optical spectroscopy manifested in two major areas: (1) laser-based spectroscopy directed towards understanding gas phase conformation and clusters of biomolecules; and (2) FTIR spectroscopy relevant to planetary atmospheric and interstellar chemistry.

#### Abstract

Atmospheric aerosols scatter and absorb radiation, influence cloud formation and play a role in heterogeneous chemical reactions in the atmosphere, affecting the concentration and distribution of atmospheric trace gases.

IR spectroscopy, with its acute sensitivity to the chemical bonding environment, has been widely used to study clusters and aerosols. Recently, a new generation of collisional cooling cell designed by one of our collaborators has created new possibilities for systematically studying aerosols generated by pulsed sequences of injections. We have used one of these cells, coupled to the Bruker IFS125HR spectrometer on the High Resolution Infrared Beamline at the Australian Synchrotron, for both high resolution gas phase studies and for aerosol studies. Development work on the cooling cell has made it possible for the first time to extend these types of aerosol measurements to the crucial but hitherto unexplored far IR region. IR Spectra have been measured for aerosols comprised of small organic and inorganic molecules, and aerosols of water ice provide a case study of how much may be learned from such spectra.

Crystalline water ice particles in the nanoscale size regime were generated by rapid collisional cooling at temperatures ranging from 4-209 K. Their spectra have been measured in the far-IR region for the first time, using synchrotron radiation, and also in the mid-IR region. Spectral diagnostics, such as the ratio of surface related dangling OH to interior H-bonded OH stretch bands, reveal the manner in which particle size depends on bath gas temperature and density, and on water molecule concentration. Notably, the aerosol spectra show significant differences compared to previous thin film spectra. The particle size regime (3-150 nm) is such that scattering effects are negligible, and the onset of less crystalline behaviour may be observed for particles

smaller than around 5nm. These measurements provide a means to assess optical constants required for radiative forcing calculations in many contexts, including earth's energy balance.

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## 4:30pm -4:45pm

### Helium Nanodroplet Isolation Spectroscopy of Hydridotrioxigen and of its Complexes with Dioxygen

#### Authors

**Paul Raston**<sup>1</sup>, Tao Liang <sup>2</sup>, Gary Douberly<sup>2</sup>  
1. The University of Adelaide,  
2. University of Georgia

#### Biography

*Paul Raston completed his undergraduate studies at Griffith University, after which he moved to the Cowboy State to pursue his graduate studies at the University of Wyoming. During this time in the group of David Anderson he focused on the isolation and spectroscopy of radicals in solid hydrogen. He has been a Postdoc in the group of Wolfgang JÄager at the University of Alberta where he explored microscopic superfluidity in helium and hydrogen clusters. More recently Paul was a Postdoc in the group of Gary Douberly at the University of Georgia where he investigated highly reactive species in helium nanodroplets, which he will talk about today. He is currently at The University of Adelaide where he has just begun a four year Ramsay Fellowship.*

## Abstract

The hydridotrioxygen (HOOO) radical and its deuterated analogue (DOOO) have been isolated in helium nanodroplets following the in-situ association reaction between OH and O<sub>2</sub>. The infrared spectrum in the 3500-3700 cm<sup>-1</sup> region reveals bands that are assigned to the  $\nu_1$  (OH stretch) fundamental and  $\nu_1+\nu_6$  (OH stretch plus torsion) combination band of the trans-HOOO isomer. The helium droplet spectrum is assigned on the basis of a detailed comparison to the infrared spectrum of HOOO produced in the gas phase [E. L. Derro, T. D. Sechler, C. Murray, and M. I. Lester, J. Chem. Phys. 128, 244313 (2008)]. Despite the characteristic low temperature and rapid cooling of helium nanodroplets, there is no evidence for the formation of a weakly bound OH-O<sub>2</sub> van der Waals complex, which implies the absence of a kinetically significant barrier in the entrance channel of the reaction. There is also no spectroscopic evidence for the formation of cis-HOOO, which is predicted by theory to be nearly isoenergetic with the trans isomer. Stark spectroscopy of the trans-HOOO species provides vibrationally averaged dipole moment components that qualitatively disagree with predictions obtained from CCSD(T) computations at the equilibrium, planar geometry, indicating a floppy complex undergoing large-amplitude motion about the torsional coordinate. Under conditions that favour the introduction of multiple O<sub>2</sub> molecules to the droplets, bands associated with larger H/DOOO-(O<sub>2</sub>)<sub>n</sub> clusters are observed shifted ~1-10 cm<sup>-1</sup> to the red of the trans-H/DOOO  $\nu_1$  bands. Detailed ab initio calculations were carried out for

multiple isomers of cis - and trans-HO<sub>3</sub>-O<sub>2</sub>, corresponding to either hydrogen or oxygen bonded van der Waals complexes. Comparisons to theory suggest that the structure of the HO<sub>3</sub>-O<sub>2</sub> complex formed in helium droplets is a hydrogen-bonded 4A' species consisting of a trans-HO<sub>3</sub> core. The computed binding energy of the complex is approximately 240 cm<sup>-1</sup>. Despite the weak interaction between trans-HO<sub>3</sub> and O<sub>2</sub>, non-additive red shifts of the OH stretch frequency are observed upon successive solvation by O<sub>2</sub> to form the larger clusters with  $n > 1$ .

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**4:45pm - 5:00pm**

## Can dianions make strong gas phase bases?

### Authors

**Dr Berwyck Poad**, Nicholas Reed, Dr Adam Trevitt, Prof Stephen Blanksby  
University of Wollongong

### Biography

Dr Berwyck Poad is an ARC DECRA fellow at the University of Wollongong, focusing most of his attention on multiply charged anions. Berwyck completed his PhD with Prof. Evan Bieske at the University of Melbourne in 2009, before undertaking post doctoral work at The University of Wollongong and then the University of California, San Diego.

### Abstract

Multiply charged anions have been proposed as a route to create gas phase bases, potentially even stronger than the current strongest

reported gas phase base, LiO<sup>-</sup> [1]. The additional charge(s) present on a doubly (or multiply) charged system leads to an increased proton affinity, but at the same time a reduced electron affinity. Computational studies probing the limits of gas-phase basicity concluded that to create multiply charged anions that are both highly basic, but have a positive electron binding energy "will be a challenge... even if multiply charged anions are considered [and] lithium hydroxide will be hard to replace at the top of the gas-phase acidity scale" [1].

In this contribution, we present experimental evidence for deprotonation of per-deuterated methane and deuterium by a dianion "superbase," demonstrating that it is possible to generate dianions that behave as particularly strong gas phase bases. Using electrospray ionisation mass spectrometry, a series of dianions originating from para phenylenedipropionic acid have been generated in the gas phase and isolated within a linear quadrupole ion trap. Subsequent ion-molecule reactions between the doubly deprotonated species and neutral reagents of known gas phase acidity have allowed the relative basicity of the dianion species to be bracketed, providing evidence that one of the dianions generated possesses a proton affinity in excess of the methanide anion (416.7 kcal/mol) and is a good candidate for the strongest known gas phase base.

#### Reference

[1] Tian, Chan, Sullivan, Radom, Kass, PNAS 105 (22), 7647 – 7651

**5:00pm – 5:15pm**

## Rotational spectroscopy of PANH and cyano substituted PAH species

#### Authors

**Prof Donald McNaughton**<sup>1</sup>, Dr Peter Godfrey<sup>1</sup>, Prof Jens Uwe-Grabow<sup>2</sup>, Dr Michael Travers<sup>2</sup>, Michaela Jahn<sup>2</sup>, David Dewald<sup>2</sup>

1. Monash University,
2. Gottfried-Wilhelm-Leibniz-Universität

#### Biography

*Don did his PhD at Monash University in the last century and after a post doc at Sussex Uni in microwave and high resolution infrared spectroscopy returned to Monash. Over his career he has branched out and is director of the centre for biospectroscopy at Monash where the focus is the use of FTIR and Raman microspectroscopy and imaging for investigating the biochemistry of biological systems. Since 2006 he has renewed his interest in interstellar chemistry and microwave spectroscopy, which is the subject of this talk*

#### Abstract

It has been postulated that polycyclic aromatic heterocycle (PAH) variants containing one or more nitrogen substituents, the polycyclic aromatic nitrogen heterocycles (PANHs), may be responsible for variations in peak positions in IR interstellar emission features<sup>1</sup>. In order to provide data that could eventually unambiguously confirm the presence of such species in the ISM we have measured and assigned the pure rotational spectra of the 2 and 3 ring PANHs<sub>2,3</sub> employing Stark modulated millimetre wave

absorption free jet spectroscopy and FTMW spectroscopy of a supersonic rotationally cold molecular beam. Given that some 40 cyano containing species have been identified in the interstellar medium the spectra of the cyano-naphthalenes and cyano-phenanthrenes have also been recorded and assigned. Unlike the PAHs themselves these species have large dipole moments and quadrupole nuclei, leading to intrinsically strong lines and fine structure that assists in any identification in spectra obtained from the ISM. For all species quadrupole coupling constants, essential for full prediction of interstellar lines have been determined.

Given that no aromatic species have been identified in the interstellar medium the spectra of these molecules present an excellent opportunity for eventual identification of aromatic species and further insights into interstellar chemistry.

#### References

- [1] D. M. Hudgins, C. W. Bauschlicher, L. J. Allamandola, *Astrophys. J.*, **632**, 316 (2005)
- [2] D McNaughton, P. D. Godfrey, R. D. Brown, S. Thorwirth, J.-Uwe Grabow, *Astrophys. J.*, **678**, 309 (2008)
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**5:15pm - 5:30pm**

## Understanding electronic structures of molecules from gamma-ray spectroscopy

Author

**Feng Wang**

Swineburne University of Technology

Biography

*Professor Feng Wang is a leading theoretical chemist in molecular electronic structures through molecular spectroscopy. She has been elected as Fellow of RACI and Fellow of AIP, working at the interface of chemistry and physics. For more details please see her staff website at*

Abstract

Positrons are antimatter of electrons. Annihilation gamma ray spectra are used in a variety of fields including medicine and drug design, where positron emission tomography (PET) is used to monitor metabolic and other biological processes, and in materials science, where positron annihilation is used to characterize materials and material surfaces. It may provide an innovative way for the breakthrough in the study of electron-electron interactions and ionization processes of molecules. In this presentation, the quantum mechanically study of spectra of annihilation gamma rays for molecules will be briefly reviewed. The low-energy plane-wave-positron approximation (LEPWP) [1] was developed to calculate the Doppler-shift of gamma-ray for molecules quantum mechanically. It was soon discovered that the calculated Doppler-shift of molecules were approximately 70-80% of the measurements [2-4], leading to the

question: do all valence electrons of a molecule contribute equally to the Doppler-shift of gamma-ray? Follow this direction, we studies alkanes and their derivatives, which leading to the development of a number of concepts such as positrophilic electrons [5], the lowest occupied valence orbital (LOVO) [6], the mechanism for the determination of the positrophilic electrons of the molecules [7] and the concept of quality of profile (QP) to quantify the agreement between calculated and measured gamma-ray profiles in the entire region rather than at a particular point [8].

#### References

- [1] F. Wang, L. Selvam, G. F. Gribakin and C. M. Surko, *J. Phys. B*: 43, 165207(2010).
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- [6] X. G. Ma and F. Wang, *Radiat. Phys. Chem.*, 89(2013)14-19.
- [7] X. G. Ma and F. Wang, *J Phys. Soc. (Jpn)* (accepted, 2013).
- [8] X. G. Ma and F. Wang, (submitted, 2013).

## Keynote Session

5:30pm- 6:00pm

### Ab initio molecular dynamics of molecules in strong laser fields

**Professor H. Bernhard Schlegel**

Wayne State University, USA

#### Biography

H. Bernhard Schlegel is Distinguished Professor of Chemistry at Wayne State University. After earning a BSc from the University of Waterloo, Ont. (1972) & a PhD in Theoretical Organic Chemistry at Queen's University, Kingston, Ont. Canada (1975), he was a post-doctoral fellow with Kurt Mislow & Lee C. Allen at Princeton U. (1976) & with John A. Pople at Cargenie-Mellon U. (1977). He spent two years in industry as a computational chemist at Merck & Co. before accepting a faculty position at Wayne State University in 1980. Schlegel's research explores potential energy surfaces for chemical reactions through the use of molecular orbital calculations, & includes both method development & applications. The development of new algorithms addresses topics such as geometry optimization, searching for transition states, reaction path following and ab initio molecular dynamics. Schlegel is a Fellow of the American Chemical Society, the American Association for the Advancement of Science & the Royal Society of Chemistry, & is a member of the International Academy of Quantum Molecular Science. Schlegel is an associate editor for the *Journal of Chemical Theory & Computation*. In 2013, he received the ACS Award for Computers in Chemical & Pharmaceutical Research.

## Abstract

Short, intense laser pulses can deposit a substantial amount of energy in a molecule. Such highly energized molecules can undergo rapid rearrangements and dissociation. The effect of a strong electric field on the motion of a molecule can be simulated by *ab initio* classical trajectory calculations in the time-varying field. Our calculations show that if the molecule can be aligned in the field, very short and intense mid-IR pulses can cause the selective dissociation of stronger bonds in  $\text{CF}_3\text{Br}^+$  and  $\text{C}_6\text{H}_5\text{I}_2^+$ , and can enhance the yield of higher energy  $\text{HCl}^+$  products in the fragmentation of formyl chloride cation,  $\text{ClCHO}^+$ . A new, more accurate Hessian-based predictor-corrector algorithm for simulating classical trajectories of molecules in intense laser fields will also be discussed.

## Key Words

*Ab initio molecular dynamics, strong field chemistry*



**Poster  
Presentations**

## Poster Session One

- 1 **In silico investigation of inhibiting signaling molecules for bacterial quorum sensing using molecular modelling**  
*Marawan Ahmed, Stefanie Bird, Enzo Palombo, Kevin Prince, Feng Wang*
- 2 **Far-Infrared Absorption Spectra of Synthetically-Prepared Ligated Metal Clusters with Au<sub>6</sub>, Au<sub>8</sub>, Au<sub>9</sub> and Au<sub>6</sub>Pd Metal Cores**  
*Jason Alvino, Trystan Bennett, A/Prof Greg Metha*
- 3 **Catalysis by design: H<sub>2</sub>-selective formic acid decomposition by zeolites**  
*Ruth Amos*
- 4 **A Phase Space Theory for Roaming Reactions**  
*Duncan Andrews, A/Prof Meredith Jordan, Prof Scott Kable*
- 5 **Femtosecond Laser Parameters Required for Optimal Laser Ablation of Bone**  
*Simon Ashforth, A/Prof Cather Simpson, Dr Jessica Costa*
- 6 **Twisted Aromatics as Potential Chromophores for Luminescent Solar Concentrators**  
*James Banal, Kenneth Ghiggino, Wallace Wong*
- 7 **Size consistency in Fragment Molecular Orbital Approach Coupled with Second Order Perturbation Theory (FMO-MP2)**  
*Dr Santiago Barrera Acevedo, Dr Ekaterina Izgorodina*
- 8 **Spatial imaging of fluorescence and photocurrent in thin film photovoltaics**  
*Ognjen Belic, Prof Ken Ghiggino, A/Prof Trevor Smith*
- 9 **Far-Infrared Absorption Spectra of Synthetically-Prepared, Ligated Metal Clusters with Ru<sub>3</sub>, Ru<sub>4</sub>, and AuRu<sub>3</sub> cores**  
*Trystan Bennett, Jason Alvino, A/Prof Greg Metha*
- 10 **Thermodynamics of Alcohol and Water Binary Mixtures**  
*Quinn Besford, Dr Angus Gray-Weale*
- 11 **A Molecular Understanding of Photochemical Upconverters for Highly Efficient Solar Cells**  
*Simon Blacket, Dr David Huang*

- 12 **High-Throughput, Microfluidic Synthesis of Janus Particles**  
*Siobhan Bradley, Prof Thomas Nann, Dr Marta Krasowska*
- 13 **A Mechanistic Study into the Destabilization of DNA Triplexes**  
*Alex Button*
- 14 **Advances and Challenges in High-Level Quantum Chemistry Protocols**  
*Dr Bun Chan*
- 15 **Incoherent Photon Upconversion and its Applications**  
*Yuen Yap Cheng, Andrew Nattestad, Tim F. Schulze, Rowan W. MacQueen, Jens Czolk, Tony Khoury, Maxwell J. Crossley, Alexander Colsmann, Klaus Lips, Timothy W. Schmidt*
- 16 **Isomer Specific Action Spectra of Retinal Chromophores in the Gas Phase**  
*Neville Coughlan, Brian Adamson, Dr Evan Bieske*
- 17 **New crown ether core-substituted naphthalene diimide cation sensors**  
*Rosalind Cox, Saman Sandanayake, David Scarborough, Ekaterina Izgorodina, Prof Steven Langford, Dr Toby Bell*
- 18 **The Role of Spin in Triplet-Triplet Upconversion**  
*A. Danos, T. Keevers, Y. Y. Cheng, D. R. McCamey, T. W. Schmidt*
- 19 **The Quantum Nature of H<sub>2</sub> Bound to Li<sup>+</sup>-benzene**  
*Jordan D'Arcy, Stephen Kolmann, A/Prof Meredith Jordan*
- 20 **The multiple structures of vaterite**  
*Dr Raffaella Demichelis, Dr Paolo Raiteri, Prof Julian Gale*
- 21 **Excited State Localization and Excitation Energy Migration in Multichromophoric Aminoarenes**  
*Dr Miroslav Dvorak, Dr Martin Michl, Dr Numan Almonasy, Prof Milos Nepras*
- 22 **Alzheimer's Disease Amyloid-Beta Peptide Interaction with Platinum-based Inhibitors**  
*Dr Vidana Epa, Dr Victor Streltsov, Dr Simon James, Dr Vijaya Kenche*
- 23 **Does SOMO-HOMO conversion enhance catalysis in radical enzymes?**  
*Sarah Faulkner, Michelle Coote, Colin Jackson*
- 24 **New Gaussian wave packet methods for chemical dynamics**  
*Dr Terry Frankcombe*

- 25 **A Single Molecule Spectroscopic Evaluation of a Tetra Core-Substituted Naphthalene Diimide**  
*Brenton Graystone* , *Dr Subashani Maniam* , *Prof Steven Langford* , *Dr Toby Bell*
- 26 **Circularly Polarised Luminescence Spectroscopy of Photosystem II**  
*Jeremy Hall* , *Dr Paul Smith* , *Dr Rafael Picorel* , *Prof Elmars Krausz*
- 27 **Gas phase photodissociation of N-substituted pyridinium derivatives: electronic spectroscopy and product characterisation**  
*Christopher Hansen* , *Dr Benjamin Kirk* , *Prof Stephen Blanksby* , *Dr Adam Trevitt*
- 28 **Ultrafast Spectroscopy of Curcumin in Diamide Linked  $\gamma$ -Cyclodextrin Dimers**  
*Takaaki Harada* , *Hamish McTernan* , *Dr Duc-Truc Pham* , *Prof Lincoln Stephen* , *Dr Tak Kee*
- 29 **Density Functional Theory and Photo-Ionisation Studies of Gold-Cerium Oxide Clusters**  
*Robert A Hardy* , *Aidan M Karayilan* , *Gregory F Metha*
- 30 **Identification of TCNQF4 Oxidation States via Experimental and Theoretical Vibrational Spectra**  
*Dr Naomi Haworth* , *Dr Chris Thompson* , *Dr Jinzhen Lu* , *Nguyen Vo* , *A/Prof Lisa Martin* , *Thanh Le* , *Alan Bond*
- 31 **Analysis of conformations and vibrational frequencies of AMP, ADP, and ATP: A combined computational and experimental study**  
*Alireza Heidari* , *Pravindya Haputhanthri* , *Dr Ekaterina Izgorodina* , *A/Prof Bayden Wood*
- 32 **Imaging Chemical Extraction by Polymer Inclusion Membranes Using Fluorescence Microscopy**  
*Dr Clare Henderson* , *Edward Nagul* , *A/Prof Trevor Smith* , *Prof Spas Kolev*
- 33 **Investigation of the optical and emission properties of CdSe nanocrystals using defocused widefield microscopy**  
*Heather Higginbotham* , *Dr Tich Lam Nguyen* , *Dr Alison Funston* , *Prof Paul Mulvaney* , *Dr Toby Bell*
- 34 **Barriers for Proton Transport in Hydrogen-bound Systems Including Protic Ionic Liquids**  
*Dr Jennifer Hodgson* , *Ahmed Halima* , *Dr Ekaterina Izgorodina* , *Prof Douglas MacFarlane*

- 35 **Experimental and Computational Studies on Bimetallic Clusters of Platinum and Cerium**  
*Aidan Karayilan, A/Prof. Gregory Metha*
- 36 **Mapping Charge Generation in an Organic Semiconductor using Two-Dimensional Photon Echo Spectroscopy**  
*Dr Tak Kee, Yin Song, Dr Yoichi Kobayashi, Dr Ryan Pensack, Prof Gregory Scholes*
- 37 **Probing Spin-Dependent Transport and Recombination in Organic Light-Emitting Diodes through Magnetic Resonance**  
*Thomas Keevers, Andrew Danos, Dr Karl Weber, Dr Scott Watkins, Dr Dane McCamey*
- 38 **Photochemical Studies of Self-Assembled Porphyrin-fullerene Complexes through Transient Absorption Spectroscopy**  
*Julie Kho, A/Prof Peter Boyd, Dr Ali Hosseini, A/Prof Cather Simpson*
- 39 **How do Bond Dissociation Enthalpies Depend on Protonation State?**  
*Michael Morris, Dr Bun Chan, Prof Leo Radom*
- 40 **DFT Studies of N<sub>2</sub>O Reactivity with Vanadium and N-Heterocyclic Carbenes**  
*Miranda Shaw, Brian Yates*
- 41 **Fourier Transform Infrared Spectroscopic Detection of DNA in Cells**  
*Donna Whelan, Dr Keith Bambery, Dr Ljiljana Puskar, Prof Don McNaughton, Ass/Prof Bayden Wood*

## Poster Session Two

- 42 **An Impulsive Phase Space Theory for Triple Fragmentation**  
**Duncan Andrews**, Nicholas Hobday, Mitchell Quinn, Dr Klaas Nauta, A/Prof Meredith Jordan, Prof Scott Kable
- 43 **Calculating the energetics and dynamics of the interaction of molecules with semiconductor surfaces using fragmentation and ab initio calculations: hydrogen atoms and hydrogen-terminated silicon (111)**  
**Dr Terry Frankcombe**
- 44 **A new way to add hydrogen to aromatics: REMPI studies of benzene+H, toluene+H, naphthalene+H**  
**Dr Olha Krechkivska**, Dr Klaas Nauta, Prof Scott Kable, Prof Timothy Schmidt
- 45 **Molecular dynamics simulations of the glass transition of water using different intermolecular potentials**  
**Cara Kreck**, Prof Ricardo Mancera
- 46 **Quasi-Classical Trajectories on a Zero-Point Energy Corrected Potential Energy Surface**  
**Kelvin Lee**, Stephen Kolmann, Mitchell Quinn, Dr Klaas Nauta, Prof Scott Kable, A/Prof Meredith Jordan
- 47 **New Insights into 1,2,4-trioxolane Stability and the Crucial Role of Ozone in Promoting Polymer Degradation**  
**Richmond Lee**, Michelle Coote
- 48 **A Kinetic Study of Keto-Enol Tautomerisation of the Medicinal Agent Curcumin with NMR Spectroscopy**  
**Mandy Leung**, Prof Stephen Lincoln, DrTak Kee
- 49 **Flexible or Rigid? Investigating the Effect of Surface hardness on Anti-Fouling performance**  
**Kamron Ley**, Dr George Yiapanis, Dr Dave Winkler, Dr Shane Maclaughlin, Dr Evan Evans, Prof Irene Yarovsky
- 50 **Free Energy of Solvation for a Uranium ion in the LiCl-KCl Eutectic**  
**Cassandra Lutzko**, Maoyan Liu, Angus Gray-Weale
- 51 **Nanostructured Upconverters for Solar Energy Applications**  
**Rowan MacQueen**, Yuen Yap Cheng, Timothy Schmidt

- 52 **In situ High-Resolution Raman Imaging of Erythrocytes from Whole Blood**  
**K.M. Marzec**, M. De Veij, D. Pérez Guaita, B. R. Wood, S. Chlopicki, M. Baranska
- 53 **Ramps: A new type of basis function for faster quantum chemistry calculations**  
**Laura K. McKemmish**, Dr Andrew T. Gilbert, Prof Peter M. W. Gill
- 54 **Using 2-Aminopurine to Study Excitation Energy Transfer in DNA**  
**Grant McKenzie**, Anita C. Jones
- 55 **A new semi-confocal high-resolution FTMW spectrometer**  
**Dr Chris Medcraft**, Dr Thomas Betz, Dr Melanie Schnell
- 56 **Building Dipole Moment Surfaces with Modified Shepard Interpolation**  
**Michael Morris**, A/Prof Meredith Jordan
- 57 **Triple-fragmentation of Formaldehyde: using Velocity Map Imaging and 2D REMPI to determine complete photochemical quantum yields**  
**Dr Klaas Nauta**, Nicholas Hobday, Mitchell Quinn, Gaby de Wit, Duncan Andrews, A/Prof Meredith Jordan, Prof Scott Kable
- 58 **Spectroscopic investigation of boron porphyrin/porphyrinoid complexes**  
**Nina Novikova**, A/Prof Cather Simpson, Prof Penelope Brothers
- 59 **Jet-Cooled Excitation Spectra of Large Benzannulated Benzyl Radicals: 9- anthracenylmethyl (C15H11) and 1-pyrenylmethyl (C17H11)**  
**Gerard O'Connor**, Dr George Bacskay, Gabrielle Woodhouse, Dr Tyler Troy, Dr Klaas Nauta, Prof Scott Kable, A/Prof Timothy Schmidt
- 60 **Self-Assembled Nanostructures for High Resolution Characterisation**  
**Adabelle Ong**, Benjamin Morrison, Clare Henderson, Trevor Smith
- 61 **Product Branching Studies of ortho-Substituted Phenyl + O<sub>2</sub> Reactions: Experimental and Theory**  
**Matthew B. Prendergast**, Benjamin B. Kirk, Stephen J. Blanksby, Gabriel da Silva, Adam J. Trevitt
- 62 **Helium Nanodroplet Isolation Spectroscopy of the Hydroxyl Radical and of its Complexes with Carbon Monoxide and Methane**  
**Paul Raston**, Tao Liang, Emmanuel Obi, Gary Douberly

- 63 **New spin-component scaled MP2 coefficients to approximate CCSD(T) for charged systems**  
*Jason Rigby, Dr Ekaterina Izgorodina*
- 64 **Permanent Dipole Correlations Drive Self-Assembly in Various Solvents**  
*Cameron Ritchie, Dr Angus Gray-Weale*
- 65 **Conformational analysis of biomolecules in the gas-phase by optical spectroscopy? Don't amide if I do**  
*Patrick Robertson, Isabella Lobo, Dr Evan Robertson, Dr David Wilson*
- 66 **Near-IR Femtosecond Transient Absorption Spectroscopy of Poly(3-hexylthiophene) Nanofibres**  
*Charu Rohatgi*
- 67 **Electronic Spectroscopy of Cyclic Hydrocarbon Cations in the Gas Phase using Resonance-Enhanced Photodissociation**  
*Julian Sanelli, Dr Nahid Chalyavi, Dr Viktoras Dryza, Prof Evan Bieske*
- 68 **MCSCF models and competing mechanisms of  $[4\pi + 2\pi]$  cycloadditions**  
*David Scarborough, Christopher Thompson, Ekaterina Izgorodina*
- 69 **Photocatalysis of CO<sub>2</sub> and H<sub>2</sub>O using Aun cluster doped TiO<sub>2</sub> nanoparticles**  
*Kathryn Schroeder, Jason Alvino, Trystan Bennett, Gregory Meth*
- 70 **Transient Absorption Spectroscopy of Novel Semiconducting Block Copolymers for Organic Solar Cells**  
*Kyra Schwarz, Prof Ken Ghiggino, A/Prof Trevor Smit*
- 71 **Phototautomerisation of Carbonyls to Enols at Atmospheric Pressure of N<sub>2</sub>**  
*Miranda Shaw, Alexander Clubb, Balint Sztaray, David Osborn, Meredith Jordan, Scott Kable*
- 72 **Vortex magnetic states in frustrated molecular metal rings: towards single-molecule spin torque effects despite the weak spin-orbit coupling**  
*Dr Alessandro Soncini*
- 73 **Predicting the outcomes of oxidising processes: The development of a QM/MM hybrid simulation method**  
*Dr Matthew Stewart, Prof Harry Ridgway, Prof Stephen Gray, A/Prof Todor Vasiljevic, Prof John Orbell*

- 74 **Simulation of Energy Transport in Conjugated Polymer Systems**  
*Patrick Tapping, Dr Tak Kee, Dr David Huang*
- 75 **Distance dependent parallel interactions of graphene with a variety of aromatic molecules**  
*Asya Tawfiq, Dr Graham E. Ball, A/Prof John A. Stride*
- 76 **Seeing Red: Using Femtosecond Transient Absorption Spectroscopy to Investigate Photodegradation in Anthraquinone Dyes and Pigments**  
*Sarah Thompson, Dr Charles Rohde, Dr Erin Griffey, A/Professor Cather Simpson*
- 77 **Ligand-mediated control of the surface plasmon resonance in metal nanoparticles generated by laser ablation**  
*Rhys Tilbury, Ashley Mulder, Michael Wolter, Dr Massiliano Massi, Prof Mark Buntine  
Curtin University*
- 78 **Measuring photo-initiated radical chemistry in single microdroplets**  
*Bartholomew Vaughn, Phillip Tracey, Dr Adam Trevitt*
- 79 **Origin of visible-light activity of fluorinated titanium dioxides: A DFT study**  
*Dr Yun Wang, Dr Haimin Zhang, Dr Porun Liu, Prof Huijun Zhao*
- 80 **Time-resolved resonance Raman spectroscopy of aryl-diphosphenes**  
*Xindi Wang, Jennifer Stott, A/Prof M Cather Simpson*
- 81 **Super-Resolution Fluorescence Microscopy for Imaging Virally Induced Changes to the Cell Cytoskeleton**  
*Donna Whelan, Aaron Brice, Dr Gregory Moseley, Dr Toby Bell*
- 82 **Infrared Spectroscopy of Ethylene Aerosols using Synchrotron Radiation**  
*Andy Wong, Prof Don McNaughton, Dr Dominique Appadoo, Ruth Plathe, Dr Evan Robertson, A/Prof Sigurd Bauerecker*

## Poster I

**Marawan Ahmed, Stefanie Bird, Enzo Palombo, Kevin Prince, Feng Wang**  
Swinburne University

### In silico investigation of inhibiting signaling molecules for bacterial quorum sensing using molecular modelling

#### Abstract

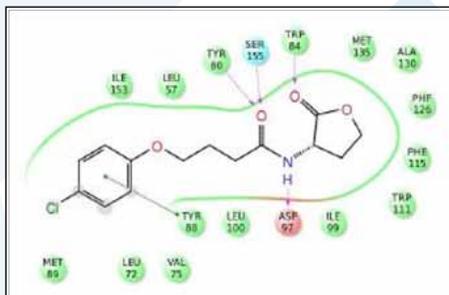
Treatment of bacterial infections is a major global challenge. It is estimated that bacterial resistance can increase mortality and morbidity by a factor of two [1]. Bacteria continue to develop resistance to current anti-bacterial agents and the problem is becoming more wide-spread [2,3]. The challenge to stop bacterial growing is to inhibit bacterial quorum sensing (QS) through the use of small signal molecule inhibitors.

In the present study, the origin of the anti-quorum sensing (QS) activities of several members of a two recently synthesized and in vitro tested classes of lactone (Figure 1) and thiolactone based inhibitors were computationally investigated. Docking and molecular dynamic (MD) simulations and binding free energy calculations of the inhibitors against CviR protein (Figure 2) were carried out to reveal their exact binding and inhibitory profiles. The higher in vitro inhibitory activity of the lactone based inhibitors relative to their thiolactone isosteres was verified based on estimating the

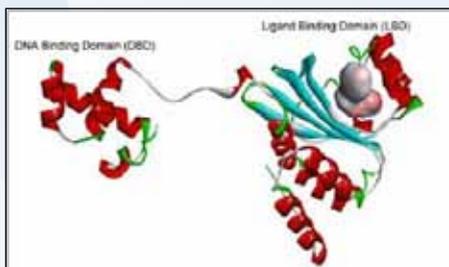
binding energies, the docking scores and monitoring the stability of the complexes produced during the MD simulations [4]. The strong electrostatic contribution to the binding energies may be responsible for the higher inhibitory activity of the lactone with respect to the thiolactone series. Preliminary results from this project will be presented at the conference.

#### Keywords

Quorum Sensing; lactone inhibitors; Docking; Molecular dynamics



**Figure 1:** Interaction diagrams for a potential CviR antagonist from the lactone series of inhibitors (PDB code: 3QP5).1: 2D ligand



**Figure 2:** Three dimensional (3D) ribbon representation for the CviR monomer. Solid surface in the LBD represent the exact binding location of the inhibitors.

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## Poster 2

**Jason Alvino**, *Trystan Bennett*,  
*A/Prof Greg Metha*  
*The University of Adelaide*

### Far-Infrared Absorption Spectra of Synthetically-Prepared Ligated Metal Clusters with Au<sub>6</sub>, Au<sub>8</sub>, Au<sub>9</sub> and Au<sub>6</sub>Pd Metal Cores

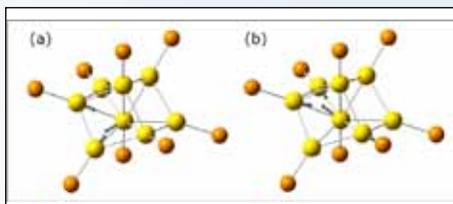
#### Abstract

For many years it has been known that semiconductor surfaces or particles such as TiO<sub>2</sub> can absorb light in order to directly drive the processes behind industrially relevant chemical reactions including water splitting, CO<sub>2</sub> reduction, and many others. It has been shown in recent years that doping TiO<sub>2</sub> with various noble metal nanoparticles

and clusters made up of elements such as Au or Pt can promote such reactions by acting as a 'reservoir' for photo-generated electrons. An important step in understanding the basis for such dramatic increases in catalytic potential is the characterisation of these species. Given the difficulty associated with acquiring experimental data due to the incredibly small size regime of clusters, theoretical chemistry can provide an invaluable tool to complement and enhance experimental techniques.

The far infra-red absorption spectra of a series of chemically synthesised, atomically precise phosphine-stabilised gold cluster compounds have been recorded using Synchrotron light for the first time. Far-IR spectra of the Au<sub>6</sub>(Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>, Au<sub>8</sub>(PPh<sub>3</sub>)<sub>8</sub>(NO<sub>3</sub>)<sub>2</sub>, Au<sub>9</sub>(PPh<sub>3</sub>)<sub>8</sub>(NO<sub>3</sub>)<sub>3</sub>, and Pd(PPh<sub>3</sub>)Au<sub>6</sub>(PPh<sub>3</sub>)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub> clusters reveal a complex series of peaks between 80 and 475 cm<sup>-1</sup>, for which all significant peaks can be unambiguously assigned by comparison with DFT geometry optimisations and frequencies calculations. Strong absorptions in all spectra near 420 cm<sup>-1</sup> are assigned to the P-Ph<sub>3</sub> stretching vibrations. Distinct peaks within the spectrum of each specific cluster are assigned to the cluster core vibrations: 80.4 and 84.1 cm<sup>-1</sup> (Au<sub>6</sub>) 165.1 and 166.4 cm<sup>-1</sup> (Au<sub>8</sub>), 170.1 and 185.2 cm<sup>-1</sup> (Au<sub>9</sub>), and 158.9, 195.2, and 206.7 cm<sup>-1</sup> (Au<sub>6</sub>Pd).

The positions of these peaks are similar to those earlier observed to occur for the neutral Au<sub>7</sub> cluster in the gas phase (Science, 2008, 321, 674-676). Au-P stretching vibrations only occur for Au<sub>6</sub> near 420 cm<sup>-1</sup>, although they appear near 180 cm<sup>-1</sup> for Au<sub>6</sub>Pd and involve gold core vibrations.



**Figure 1:** Calculated normal mode displacements associated with the cluster core vibrations for Au<sub>8</sub> at (a) 165.1 cm<sup>-1</sup> and (b) 166.4 cm<sup>-1</sup>. Phenyl groups are omitted for clarity.

## Poster 3

**Ruth Amos**

Australian National University

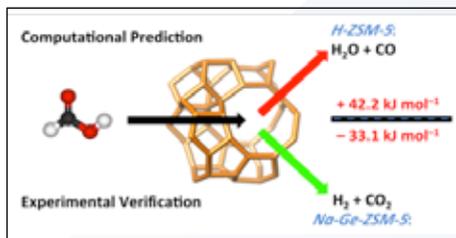
### Catalysis by design: H<sub>2</sub>-selective formic acid decomposition by zeolites

#### Abstract

One of the major questions of the twenty-first century is how to ensure a sufficient and sustainable supply of energy. Hydrogen fuel cells have been proposed as a clean energy alternative. However, one major difficulty that needs to be overcome is finding a viable way to transport H<sub>2</sub>. Formic acid is a possible medium for H<sub>2</sub> storage and transport as it is not flammable, non-toxic, easily stored and handled, and has a useful

energy density. A catalyst promoting the selective dehydrogenation of formic acid would permit the use of formic acid in the transport and storage of hydrogen.

We have been investigating modifications to zeolites that would enable their use as robust and selective catalysts for the decomposition of formic acid to hydrogen and carbon dioxide. Modified zeolites were designed using ab initio calculations, then synthesized and tested to confirm the predictions of the calculations. The results show that a germanium catalyst with a sodium counterion will selectively dehydrogenate formic acid whereas the protonated zeolite will be selective for dehydration. These results show how computational approaches can be elegant and powerful tools in the design of the new catalysts required to answer important and urgent scientific and technological problems.



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## Poster 4

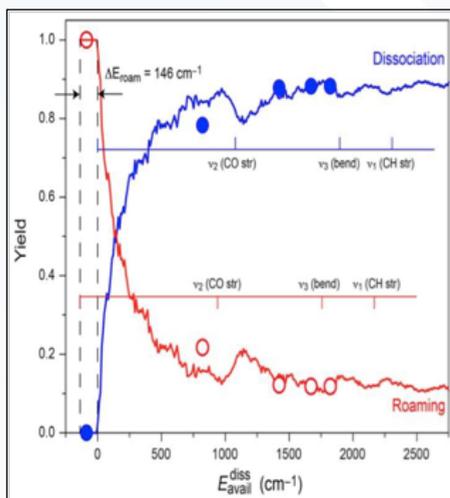
**Duncan Andrews**, A/Prof Meredith Jordan,  
Prof Scott Kable  
The University of Sydney

### A Phase Space Theory for Roaming Reactions

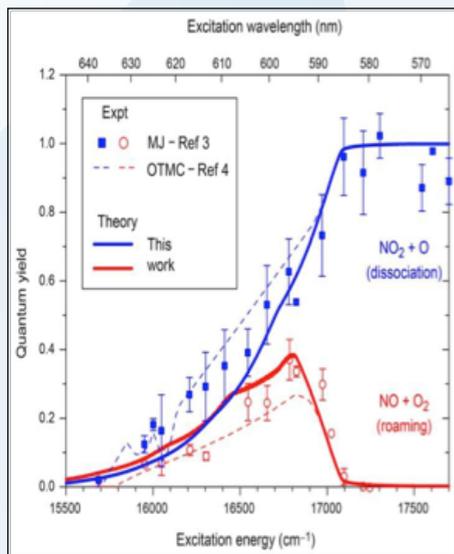
#### Abstract

We describe a new, simple theory for predicting the branching fraction of products in roaming reactions, compared to the analogous barrierless bond dissociation products. The theory assumes that roaming branches from a barrierless bond dissociation channel at large inter-fragment separations, where the system is not ergodic. The theory uses a phase space theory (PST) formalism to divide reactive states in the bond dissociation channel into states with enough translational energy to dissociate and states that may roam. Two parameters are required:  $\Delta E_{\text{roam}}$ , the energy difference between the bond dissociation threshold and the roaming threshold, and the roaming probability,  $\text{Proam}$ , the probability that states that may roam do roam rather than recombine to form reactants. We treat  $\text{Proam}$ , which is somewhat analogous to the Arrhenius A-factor, as the only adjustable parameter in the PST-roaming theory. The PST-roaming theory is tested against experimental and theoretical data on the dissociation dynamics of  $\text{H}_2\text{CO}$ ,  $\text{NO}_3$  and  $\text{CH}_3\text{CHO}$ . The theory accurately models the relative roaming to bond dissociation branching fraction over the experimental or theoretical energy range available in the literature for each species.  $\Delta E_{\text{roam}}$  is initially fixed to an experimental or theoretical value and  $\text{Proam}$  is fit

to the relevant branching ratios. The best studied system is  $\text{H}_2\text{CO}$  and the results of our PST-roaming theory are compared to experiment in figure 1. [1, 2] For  $\text{NO}_3$ , the best fit to the experimental data is obtained for  $\text{Proam} = 0.0075$ , which is consistent with the known geometric constraints to formation of  $\text{NO} + \text{O}_2$ . Using this value and the experimental rotational and vibrational temperatures, we can accurately model low temperature experimental branching fractions, a low temperature  $\text{NO}$  yield spectrum and quantum yield data for room temperature  $\text{NO}_3$  photolysis, see figure 2. [3, 4] The combination of other kinetic theories and the PST-roaming theory will provide rate coefficients for roaming reactions.



**Figure 1.** Branching fractions for roaming and dissociation predicted by the PST-roaming theory (lines) and experimental values (circles). [1, 2]



**Figure 2.** Quantum yields for room-temperature  $\text{NO}_3$  photolysis predicted by the PST-roaming theory (bold lines) and experimental values (symbols and dashed lines). [3, 4]

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## Poster 5

**Simon Ashforth**, A/Prof Cather Simpson,  
Dr Jessica Costa  
University of Auckland

### Femtosecond Laser Parameters Required for Optimal Laser Ablation of Bone

#### Abstract

Femtosecond lasers, which emit high peak intensity laser pulses in the femtosecond range, are currently utilised in industries from cataract surgery to optical technologies. The first investigations of hard biological tissue ablation were conducted in the field of dentistry [1, 2]. However, laser surgery has yet to show wide-scale success in the field of orthopaedics. Our research investigates the optimum laser parameters required for laser ablation of bone.

Using a femtosecond laser (pulse width = 100fs, repetition rate = 1kHz,  $\lambda = 800\text{nm}$ ), a series of linear cuts and craters were machined in freshly harvested bone. By changing the peak pulse power applied to the bone sample, we determined the single pulse ablation threshold and relating the diameter of an ablated spot to the Gaussian spatial distribution of energy [3]. The ablation threshold was found to be  $11.21 \pm 0.11 \text{ Jcm}^{-2}$  in both ovine and bovine bone tissue indicating that laser ablation of bone tissue is independent of target species.

Further experiments were conducted to determine the relationship between cortical bone removal and the number of incident pulses applied. By altering the laser spot translation rate, we varied the

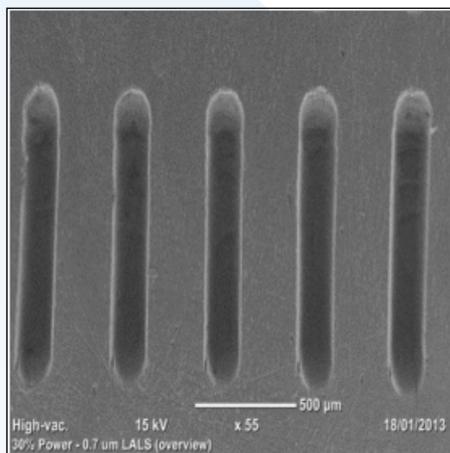
number of pulses at each point along the scribed linear cut. Optical coherence tomography (OCT) and image analysis showed that feature depth is linearly related to the number of pulses applied, irrespective of donor species. Through analysis of these trends, determined that the current minimum cut depth of a single pulse is  $0.54\mu\text{m}$  at a peak pulse fluence of  $7.81\text{ Jcm}^{-2}$ , reaching a maximum cut depth of a single pulse of  $3.47\mu\text{m}$  at a peak pulse fluence of  $59.79\text{ Jcm}^{-2}$ .

We also investigated the effects of focal depth on ablation rate and found that the optimum depth of focus for maximum ablation occurs when the laser spot is focused below the surface of the bone. OCT and image analysis showed that the optimum depth of focus for maximum ablation occurs when the laser spot is focused a  $2300 \pm 100\mu\text{m}$  below the target surface. Comparisons to femtosecond ablation of PMMA and stainless steel showed that maximum ablation occurs when the laser spot is focussed between  $2000$  and  $3000\mu\text{m}$  below the target surface.

Structural analysis of the ablation features using environmental scanning electron microscopy was performed to assess damage to the surrounding structure. Femtosecond laser irradiation of bone tissue under our experimental conditions leads to no signs of thermal shockwave cracking, molten debris deposition or charring of the osseous tissue whilst leaving hydroxyapatite crystal structure intact [4].

Finally, preliminary results will be presented to assess the cellular viability and healing ability of live

animal test subjects over a 12 week time period following femtosecond laser bone surgery.



**Figure 1.** Five lines inscribed in bovine cortical bone. The sample was translated past the focal spot at  $0.70\mu\text{m}/\text{step}$ , corresponding to 77 overlapped pulses at each position, in this example. The incident laser pulse parameters:  $1\text{ kHz}$ ,  $800\text{ nm}$ ,  $100\text{ fs}$ ,  $23.91\text{ J cm}^{-2}$  pulse fluence. Spot beam waist radius =  $26.8\mu\text{m}$  and is not varied.

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## Poster 6

**James Banal, Kenneth Ghiggino,  
Wallace Wong**  
The University of Melbourne

### Twisted Aromatics as Potential Chromophores for Luminescent Solar Concentrators

#### Abstract

Fluorescence quenching due to aggregation and small Stokes shift akin to conventional luminescent solar concentrator (LSC) dyes – perylenes, coumarins, and rhodamines – limits the observed concentration efficiency of LSC devices from reaching theoretical efficiencies. To solve these problems, we propose the use of twisted aromatic chromophores as active materials for LSC devices. These chromophores have atypical properties such as quantum yield enhancement upon aggregation and large Stokes shift, which are ideal LSC chromophore properties. We examined the photophysical properties of different twisted aromatic chromophores for LSC applications. Both experimental and computational results suggest that LSCs with pristine twisted aromatic chromophore films have comparable efficiencies to LSCs containing chromophores dispersed in polymer matrices or based on other state-of-the-art strategies, such as fluorescence resonance energy transfer or chromophore alignment that are designed to circumvent concentration quenching and parasitic reabsorption problems.

## Poster 7

**Dr Santiago Barrera Acevedo,  
Dr Ekaterina Izgorodina**  
Monash University

### Size consistency in Fragment Molecular Orbital Approach Coupled with Second Order Perturbation Theory (FMO-MP2)

#### Abstract

The Fragment Molecular Orbital (FMO) approach is a computational method that can produce accurate ab initio energy calculations of large molecular systems with thousands of atoms. The FMO approach divides a system into small fragments and performs calculations of all individual fragments, as well as, combinations of two fragments (two-body effect or FMO2) and three fragments (three-body effect or FMO3). The FMO approach can be combined with different levels of ab initio theory such as a second order of perturbation theory, MP2. The energetic contributions of all the fragments approximate the calculation of the whole system at such level of theory. Previously in our group, it was shown that the three-body effect was necessary to accurately reproduce the MP2 energies of ionic liquid clusters, consisting of 48 and 16 ions. The aim of this investigation is to reduce the number of combinations of two and three-body fragments in the FMO calculation, so that computational time and cost are minimised. Therefore, much larger clusters of ionic liquids (which require more computational time and cost) can also be studied. This hypothesis is based on the fact that in large systems of ionic liquids, the dispersion

interaction between distant ion pairs ( $\geq 10 \text{ \AA}$ ) can be neglected. Any quantum chemical method needs to satisfy the size-consistency property to ensure reliable results with increasing number of molecules in the simulation. A size-consistent method requires that the total energy of two non-interacting systems, calculated directly as a molecular-system, should be the sum of the energies of the two sub-systems calculated separately. To carry out this investigation, clusters of ionic liquids of 16, 32 and 64 ion pairs are considered. The ionic liquids are chosen from routinely used combinations of cations, such as C2mim, C2mpyr, N-pyrid and P2222, and anions, such as BF<sub>4</sub>, Br, Cl, DCA and NTF<sub>2</sub>. The comparison of the results is done with respect to the FMO3 calculations including all possible combinations of two and three-body effects. Calculations are performed using the program GAMESS-US in our group cluster GAIA, linked to the Monash Campus Cluster.

## Poster 8

**Ognjen Belic**, Prof Ken Ghiggino,  
A/Prof Trevor Smith  
The University of Melbourne

### Spatial imaging of fluorescence and photocurrent in thin film photovoltaics

#### Abstract

Photovoltaic cells are an integral part in converting nations to carbon-free electricity generation. They allow for zero-emission energy conversion from a natural, and an essentially endless, source – the Sun. Thin-film polymer photovoltaic cells, an emerging alternative for conventional silicon cells, show particular promise in contributing to energy demand due to their ease of processing and relatively lower manufacturing costs. However, efficiency issues including optimising active layer morphology currently hinder widespread introduction of this type of solar cell. In this work we describe the development of an instrument for simultaneously monitoring the photocurrent and fluorescence of thin film photovoltaic materials on a microscopic scale. This allows spatial mapping of these important photovoltaic parameters and correlations with blend morphology of the materials can be deduced. The conjugated polymers MEH-PPV, MDMO-PPV and P3HT were blended with PCBM to create photovoltaic devices that were imaged for photocurrent and fluorescence with micron spatial resolution. Our results indicate the impact of film formation conditions on morphology and device characteristics.

## Poster 9

**Trystan Bennett**, Jason Alvino,  
A/Prof Greg Metha  
The University of Adelaide

### Far-Infrared Absorption Spectra of Synthetically-Prepared, Ligated Metal Clusters with Ru<sub>3</sub>, Ru<sub>4</sub>, and AuRu<sub>3</sub> cores

#### Abstract

Over the past decade there has been great interest shown in the size-dependent chemical properties of metal clusters deposited onto active surfaces, particularly with a focus on catalysis. Most of this work has involved the study of size-selected clusters produced in the gas phase and subsequently deposited, or soft-landed, onto appropriately prepared surfaces. Less common are studies that involve the preparation of ligand-stabilised metal clusters via chemical synthesis, immobilisation of these onto a support, and the subsequent activation of the cluster cores by removal of some, or all, of the ligands.<sup>1</sup>

Infra-red spectroscopy is commonly used to observe the vibrational frequencies of key functional groups to monitor changes in chemical bonding during chemical synthesis. Despite this, there have been few studies on ruthenium-based systems which have published detailed infra-red and Raman spectra,<sup>2,3</sup> and none that have attempted to computationally identify individual atomic contributions to each spectral feature. This could be due to significant difficulties associated with acquisition of high-quality data

across a wide range of frequencies necessary for detailed investigation, in conjunction with the significant and unique computational challenges presented by these systems.<sup>4</sup> In our work we have taken far-IR spectra at the IR beamline of the Australian Synchrotron, which are presented and elucidated with the assistance of computational Density Functional Theory based calculations. Comparisons are made to previous literature for the Ru<sub>3</sub> system,<sup>2,3</sup> with both the low-wavelength Raman and IR data discussed. Key metal core vibrations are identified for all species, and a novel theory for the unexpectedly intensity of these key features is presented, wherein it is proposed that the experimental intensity of a given feature depends on the atomic motion contribution of the metal core to that transition.

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## Poster 10

**Quinn Besford**, *Dr Angus Gray-Weale*  
*The University of Melbourne*

### Thermodynamics of Alcohol and Water Binary Mixtures

#### Abstract

Alcohol and water mixtures have long been known to have unusual mixing thermodynamics, where the entropy of the system increases far less than expected for an ideal solution of randomly mixed molecules<sup>1</sup>. Many have argued that this is due to alcohol and water forming clathrate-like structures in the surrounding water. However, experiments and simulations have failed to convincingly show these structures<sup>2</sup>.

We investigate these anomalous thermodynamics with respect to dipole correlation forces in alcohol and water mixtures. Permanent dipole moments in a polar liquid rotate thermally, and their rotations become correlated, giving rise to an attractive dispersion interaction.

A polar correlating liquid, such as water, has a dispersion interaction arising from orientational correlations between the molecules electric dipole moments. This results in a mean force called the *g*-force. The significance of the *g*-force has been investigated for single component liquids, such as its role in the water's hydrophobic effect, but not for binary liquid mixtures. We develop a model for predicting the *g*-force contribution to the thermodynamics of mixing for binary systems. Our model largely encompasses the static dielectric constant of the mixtures and the related Kirkwood *g*-factor

(a measure of average alignment of dipoles within the liquid). The Kirkwood *g*-factor is a leading term in our model for the *g*-force.

Our model suggests the strength of dipole correlation is not linear with composition of each polar correlating species. Upon mixing, a clear correlation is seen between the loss of dipole correlation and the size of the alcohol. We see that a larger alcohol, such as tert-butanol, destabilises a greater amount of dipole correlations between water molecules than a smaller alcohol such as methanol.

The predicted free energy cost from the loss of *g*-force correlation agrees well with experimental thermodynamic data on binary mixing with water across a range of alcohols and compositions.

We show the *g*-force resulting from dipole correlations in a polar liquid can account for the anomalous mixing thermodynamics of these polar systems. The *g*-force contribution shows strong agreement with the excess free energy of these systems, and the entropic component of the *g*-force shows the same abnormalities as the excess entropy data for these systems, and thus also agrees with the excess enthalpy. The *g*-force has a strong dependence on the molecular dipole moment, which has shown to be significantly different in the liquid-phase to the gas-phase<sup>3</sup>. We choose appropriate dipole moments, but point out that accurate calculations of the liquid-phase dipole moments will serve as a good test of our theory. Our model involves no other adjustable parameter, and the results suggest the *g*-force is the dominant force for these mixtures.

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## Poster II

**Simon Brackett**, *Dr David Huang*  
*The University of Adelaide*

### A Molecular Understanding of Photochemical Upconverters for Highly Efficient Solar Cells

#### Abstract

Single-junction solar cells are fundamentally limited by their inability to absorb photons with energies below the band-gap. However, through the process of photochemical upconversion by triple-triplet annihilation (TTA-UC), sub-band-gap photons can be converted into higher-energy photons that can potentially be absorbed by the cell.

In TTA-UC, a sensitizer molecule absorbing a low-energy photon undergoes a transition to its first excited singlet state and subsequently crosses to the excited triplet state. When this sensitizer encounters an emitter molecule in the ground state it may transfer its energy to the emitter, promoting the emitter to a long-lived triplet state. Subsequent collision of two emitters, each in the triplet state, can result in triplet-triplet annihilation (TTA) and potentially

yield an emitter in an excited singlet state with approximately twice the triplet energy. The return of the excited emitter to the ground state is accompanied by the emission of a high-energy photon.

The process of TTA-UC in solution is in part controlled by the diffusion of both emitters and sensitizers in solution. This diffusion influences the time scales and frequency of sensitizer-emitter and emitter-emitter collisions. The relative orientation of emitters during a collision affects their electronic coupling, which in turn impacts TTA efficiency. Furthermore, the efficiency of annihilation has been shown experimentally to be affected by the presence of an external magnetic field.

We use classical molecular dynamics (MD) simulations to investigate the collisions between emitter molecules. The relative orientation of rubrene and perylene molecules (both shown to be effective emitters) during a collision and the influence of temperature on the time scales of these collisions are investigated. Results from the MD studies are combined with quantum theory to determine the probability of the formation of an emitter in the excited singlet state following TTA to give a molecular understanding on the efficiency of this process. The results are also compared with experiments of analogous systems.

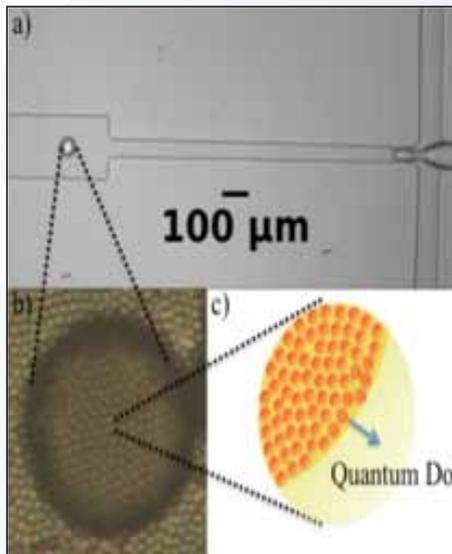
## Poster I2

**Siobhan Bradley**, Prof Thomas Nann,  
Dr Marta Krasowska  
University of South Australia

### High-Throughput, Microfluidic Synthesis of Janus Particles

#### Abstract

The synthesis of asymmetric structural units is essential for the bottom up assembly of nanomaterials into superstructures in order to mimic nature. Janus particles – particles with two “faces” - can be considered as one such structural unit. Synthetic methods for creating Janus particles in bulk conditions exist but result in low yields, varied composition or particles that are not uniform in size or geometry. Microfluidics offers much more controlled reaction conditions that can be exploited to produce high volumes of uniform particles.<sup>1,2</sup> This work involves the simple synthesis of Janus particles using a droplet-based microfluidic device. A flow-focusing geometry is integrated into the device to form monodisperse droplets of an immiscible liquid containing homogeneous particles of controlled wettability. The particles are trapped at the droplet interface and the surface of the outer hemisphere in contact with the continuous phase is modified. Finally, quantum dots are attached to this same hemisphere to create the final, partially fluorescent Janus particles. Such asymmetric particles are characterised using fluorescence spectroscopy, atomic force microscopy (AFM), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and transmission electron microscopy (TEM).



**Figure 2:** a) Droplet generation in the microfluidic device. b) Optical micrograph of a pickering emulsion c) Schematic of the produced Janus particle where quantum dots are attached to one hemisphere.

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#### Acknowledgements

Australian National Fabrication Facility (ANFF)

## Poster 13

**Alex Buffon**

*The University of Adelaide*

### A Mechanistic Study into the Destabilization of DNA Triplexes

#### Abstract

Friedreich's ataxia (FRDA) is a neurodegenerative disorder and the most common of the ataxia's (affecting 1 in 50,000). The disorder is caused by the formation of a triple-stranded DNA triplex about an expanded GAA repeat tract sequence in the genome. The presence of this DNA triplex causes an inhibition of the neighbouring FXN gene, which results in the symptoms of FRDA. Recent in vivo studies have shown that destabilization of the DNA triplex causes an increased activity of the FXN gene and thus it is hypothesised that therapeutic destabilization of the DNA triplex could provide an effective treatment for FRDA. Short polyamides provide an attractive candidate for therapeutic destabilization due to their low toxicity and high relative cell permeability.

DNA triplexes containing a 5 GAA repeat tract were produced from free oligomers. These triplex structures were simulated using an atomistic model and were compared to experimental results obtained by ion-mobility mass spectrometry. The theoretical and experimental collisional cross-sections were compared as a means of confirming the accuracy of the simulations. The DNA triplexes were characterised by ion-mobility mass spectrometry as well as by UV-Vis melting spectra fluorescent gel electrophoresis

experiments. The destabilisation of DNA triplexes by two known polyamide triplex destabilisers, Netropsin & Diminazene, as well as a series of N-methyl pyrrole analogues of Netropsin, was investigated experimentally & by simulation to elucidate the molecular-level mechanism of triplex destabilisation.

## Poster 14

**Dr Bun Chan**

*The University of Sydney*

### Advances and Challenges in High- Level Quantum Chemistry Protocols

#### Abstract

Computational chemistry is nowadays an indispensable tool to chemists. In particular, the emergence of quantum chemistry composite protocols has enabled highly accurate prediction of thermochemical properties for a wide range of small to medium-sized species. These methods generally provide excellent approximations to a high-level procedure by a combination of lower-level methods, at a substantially reduced computational cost. Further development of these procedures will enable accurate computations for larger systems that are beyond the reach of current methodologies, and improve the accuracy for systems that represent significant difficulties even for the latest protocols. In this presentation, a synopsis on our development of composite methods will be given, together with an overview on challenges that remain to be overcome.

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## Poster 15

**Yuen Yap Cheng<sup>1</sup>**, Andrew Nattestad<sup>2</sup>, Tim F. Schulze<sup>3</sup>, Rowan W. MacQueen<sup>1</sup>, Jens Czolk<sup>4</sup>, Tony Khoury<sup>1</sup>, Maxwell J. Crossley<sup>1</sup>, Alexander Colsmann<sup>4</sup>, Klaus Lips<sup>3</sup>, Timothy W. Schmidt<sup>1</sup>

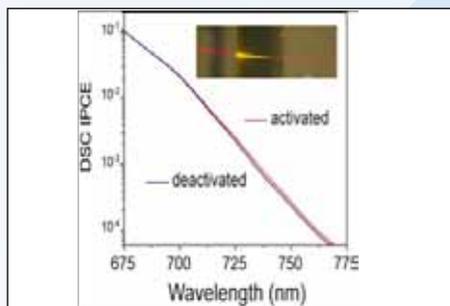
1. The University of Sydney, 2. The University of Wollongong, 3. Institute for Silicon Photovoltaics, Helmholtz-Zentrum Berlin, Germany, 4. Karlsruhe Institute of Technology, Germany

### Incoherent Photon Upconversion and its Applications

#### Abstract

Incoherent photon upconversion (UC) via triplet-triplet annihilation (TTA) is a potential photochemical process to assist semi-conductors towards efficient use of the solar spectrum for photoelectric conversion and water splitting. This system comprises of a sensitizer-emitter mixture: the sensitizer molecules absorb low energy photons ( $h\nu_1$ ) and store the energy in their long-lived first excited triplet state (T1). Each emitter molecule quenches the energy from one T1 sensitizer, followed by TTA among T1 emitters to generate one excited singlet emitter (S1) and one ground state emitter (S0). The S1 emitter then fluoresces a higher energy photon ( $h\nu_2$ ) to return to its ground state. We have shown upconversion from red to yellow

light, red to green, red to blue and from green to blue light. The red to yellow upconversion achieved a TTA efficiency of 33% with a theoretical limit of 60%; the highest reported yield and surpasses the previously assumed 11.1% limit. This red to yellow UC system has been shown capable of assisting the sub-bandgap light harvesting of amorphous silicon solar cells<sup>3</sup>, organic cells<sup>4</sup> and dye-sensitized solar cells (DSC)<sup>5</sup>.



**Figure 1:** Enhanced DSC incident photon-to-current conversion efficiency (IPCE) has been observed with activated UC system under sub-bandgap illumination.

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## Poster 16

**Neville Coughlan**, Brian Adamson,  
Dr Evan Bieske  
The University of Melbourne

### Isomer Specific Action Spectra of Retinal Chromophores in the Gas Phase

#### Abstract

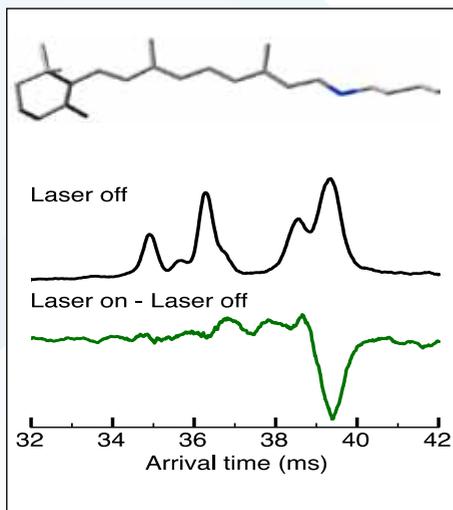
This poster describes the behaviour of gas-phase molecular ions undergoing photo-isomerization and photo-dissociation in a custom-built ion mobility spectrometer. The target molecules are protonated Schiff bases of retinal. Retinal is the light-sensitive molecule that triggers the chemical cascade underpinning human vision. Photo-isomerization is the fundamental event that alters the quaternary conformation of Rhodopsin, signalling absorption of light. Lysine and butylamine Schiff bases of retinal have been prepared to model the immediate biological environment of the chromophore. We aim to collect photo-isomerization action spectra of these species by measuring the photo-response as a function of laser wavelength. The experimental approach is based on an ion mobility spectrometer, with the provision for optical access to drifting ions. Electrosprayed ions are periodically injected into the drift region, and travel under the influence of an electric field through nitrogen buffer gas towards a detector. The drift speed of the charged molecules depends on their collision cross section and therefore, their conformation. Because the ions are mass selected, isomers of each species with the same  $m/z$  are resolved. To measure a photo-isomerization action spectrum the

ion packets are irradiated with tuneable laser light at the entrance of the drift region. Absorption of a photon induces photo-isomerization or photo-dissociation of the ions, altering their conformation and consequently their drift speed. These processes are observed by comparing ions' arrival time distributions (ATD) with the laser off and with the laser on. It is evident several isomers of retinal and the Schiff bases exist in the gas state as indicated by their ATDs (Fig. 1). Density functional theory (DFT) calculations are implemented to complement the experimental data. Geometries and vibrational frequencies are calculated at the M062X/6-311G(2d,2p) level to map the ground state potential energy surface. TD-DFT calculations are used to model the first excited state potential energy surface. Ion mobilities are predicted using MOBCAL, using the calculated geometries and charge distributions.

[N-retinylidene-n-butylamine + H]<sup>+</sup>  
[N-retinylidene-n-butylamine + H]<sup>+</sup>  
[N-retinylidene-n-butylamine + H]<sup>+</sup>

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**Fig. 1:** ATDs of electro sprayed ions (left, grey = C, blue = N, hydrogens omitted for clarity) drifting in nitrogen buffer gas: laser off (right, top); difference between laser on (532 nm Nd/YAG) and laser off ATDs (right, bottom)

## Poster 17

**Rosalind Cox, Saman Sandanayake, David Scarborough, Ekaterina Izgorodina, Prof Steven Langford, Dr Toby Bell**  
Monash University

### New crown ether core-substituted naphthalene diimide cation sensors

#### Abstract

Chemosensors are compounds which give a strong optical readout, such as a colour change in the UV-visible region or in fluorescence output, on binding with a target analyte. This allows for real-time and real-space sensing of the analyte as well as providing high sensitivity and a rapid response time, particularly

through fluorescence readouts.<sup>1</sup> Chemosensors for targeting cations have been of interest over many years due to their importance in biological processes.<sup>2</sup> Crown ethers are well established as effective binding sites for cations. They have the advantage of being selective towards different cation targets by altering the size and nature of the crown. Core substituted naphthalene diimides (cNDIs) are a new class of chromophore with attractive optical properties such as tunable absorption and emission properties depending on the nature and number of the core substituents and are ideally suited for forming the basis of new chemosensing molecular systems.<sup>3</sup>

We recently developed two cNDI systems capable of sensing protons via optical and fluorescent readouts.<sup>4,5</sup> The ease of functionalising cNDIs has led to the exploration of cNDIs as other potential sensors. By changing the nature of the substituent to different sized crown ethers, specific cations can be targeted. Two new cNDI based chemosensors 1 and 2, that incorporate a crown ether binding site directly have now been synthesised and their physical properties investigated. Here we show that altering the size of the crown ether not only changed the target analyte, but also affected the sensing mechanism of the chemosensor.

Compound 2 showed selective binding towards K<sup>+</sup> and Na<sup>+</sup>, giving a response in the UV-Visible absorption spectra. Within 1 equivalent of the target cation, the absorbance blue shifted 75 nm (Fig 1b) providing a clear optical readout of the presence of K<sup>+</sup> or Na<sup>+</sup>. Compound 1, which

incorporates a slightly smaller crown, was shown to be selective to  $\text{Ca}^{2+}$ , showed an increase in fluorescence output, but only minimal changes in its UV-Visible spectrum. Furthermore, 1 requires many times excess to fully restore fluorescence.

Computational studies were performed on 1 and 2 to investigate the binding mechanisms involved. For 2, insertion of the cation is directly into the crown ether, where it coordinates to the oxygen atoms in the crown. This causes the crown to twist out of plane relative to the rest of the molecule, inhibiting electron donation from the lone pair from the tertiary nitrogen to the NDI core. This creates the significant colour change observed in the UV-Vis absorption spectra. For 1, however, the target analyte,  $\text{Ca}^{2+}$ , does not sit in the crown, but rather coordinates to both the crown ether oxygens and the oxygen of the imide.

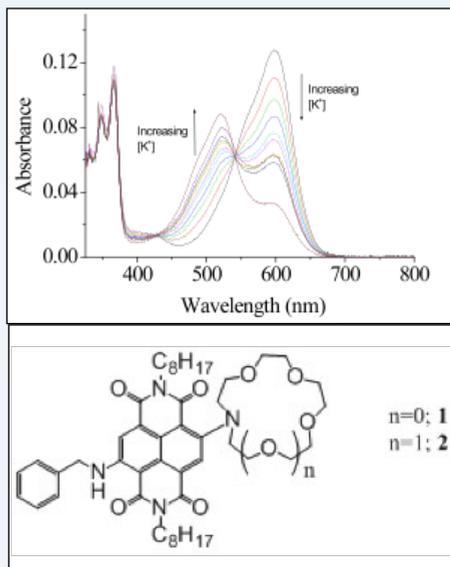
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**Figure 1.** a) Structure of crown ether based SANDIs. b) UV-Vis absorption spectra of 2 in EtOH, and with successive additions of 0.125 equivalents of KCl up to 1.0 equivalents.

## Poster 18

**A. Danos, T. Keevers, Y. Y. Cheng, D. R. McCamey, T. W. Schmid**  
The University of Sydney

### The Role of Spin in Triplet-Triplet Upconversion

#### Abstract

Triplet-Triplet Annihilation (TTA) Upconversion is a class of photochemical reactions that combine the energies of two incoherent photons into one of higher energy. Liquid upconverting mixtures are being investigated as a way to enhance solar electricity generation: using these devices, wavelengths of sunlight with

energy below the bandgap of a semiconductor photovoltaic device, which are normally not absorbed, can be reclaimed and converted into electricity. Peak enhancements of the external quantum efficiency of over 2% have been reported and work continues to increase this enhancement further.

The upconversion process begins when sensitizer molecules absorb low energy photons and generate triplet excited states in other emitter molecules. An annihilation event allows two excited emitter molecules to disproportionate their energy, producing one higher energy excited singlet and one ground state singlet. Fluorescence from the highly excited singlet produces the upconverted photon.

Fundamental aspects of the spin mixing process that controls annihilation remain poorly understood. Our aim is to develop a quantum mechanical description of the annihilation event, which can predict the formation probabilities of the different multiplicity products, and improve upon kinetic models which currently dominate this field.

Electron Paramagnetic Resonance (EPR) is an ideal tool for examining the role of triplet spin in TTA upconversion. Following Zeeman splitting by a magnetic field, microwave or radiofrequency radiation can be used to manipulate the populations of the triplet spin states. Simultaneous measurement of the upconversion intensity reveals changes in the formation rate of the singlet product. Of particular interest to us are: the low field spin populations of molecules in solution, identifying which triplet pair configurations

contribute to the singlet product or quench triplet energy, whether spin orientations are preserved in non-annihilating collisions, and explaining reported non-uniform effects of static magnetic fields on upconversion intensity.

In the absence of applied magnetic fields, we expect nuclear coupling to align electron spin with an axis of the excited molecules. In this case, the formation probabilities of the different multiplicity annihilation products depend on the relative orientations of the colliding molecules. Molecular dynamics simulations of our upconverting mixtures are used to determine average collision rates and orientations, which can then be compared to experimental upconversion rate constants.

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## Poster 19

*Jordan D'Arcy, Stephen Kolmann,  
A/Prof Meredith Jordan  
The University of Sydney*

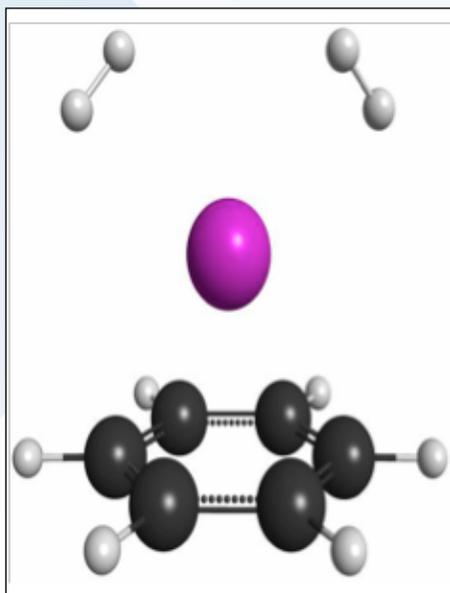
### The Quantum Nature of H<sub>2</sub> Bound to Li<sup>+</sup>-benzene

#### Abstract

Microporous materials such as metal-organic frameworks (MOFs) are under investigation as potential H<sub>2</sub> storage materials. As the lightest molecule, H<sub>2</sub> exhibits quantum-mechanical behaviours at low temperatures, such as the delocalisation of its nuclear wave function. The effect of this behaviour on the interaction between H<sub>2</sub> and microporous storage materials remains largely unexplored, and computational simulations of H<sub>2</sub> uptake typically

treat H<sub>2</sub> as a classical point particle. (H<sub>2</sub>)<sub>n</sub>-Li<sup>+</sup>-benzene ( $n = 1-3$ ) [1] is a model system for H<sub>2</sub> adsorbed to a Li-doped MOF or similar material. The small size of the system facilitates the fully coupled, anharmonic quantum treatment of H<sub>2</sub>, using the rigid-body approximation. In previous work, we performed rigid-body quantum diffusion Monte Carlo (RB-DMC) simulations on H<sub>2</sub>-Li<sup>+</sup>-benzene, and found that zero-point energy accounted for 35% of the 19.0 kJ mol<sup>-1</sup> binding energy, resulting in the delocalisation of H<sub>2</sub> above the Li<sup>+</sup>-benzene system. [2] Here, we extend the study to (H<sub>2</sub>)<sub>2</sub>-Li<sup>+</sup>-benzene. RB-DMC simulations were performed on a potential-energy surface interpolated from M05-2X/6-311+G(2df,p) electronic structure calculations. We found that the addition of a second H<sub>2</sub> to Li<sup>+</sup>-benzene was insufficient to localise the H<sub>2</sub> nuclear wave function, and both H<sub>2</sub> remained delocalised above the system. Zero-point energy was almost 45% of the 13.3 kJ mol<sup>-1</sup> electronic binding energy, indicating that the quantum nature of H<sub>2</sub> cannot be ignored in these weakly bound systems. Furthermore, we performed RB-DMC simulations on a fragment potential for (H<sub>2</sub>)<sub>2</sub>-Li<sup>+</sup>-benzene, reducing computational expense with no loss in accuracy. The fragment potential-energy surface will be applied to (H<sub>2</sub>)<sub>3</sub>-Li<sup>+</sup>-benzene, as well as larger RB-DMC and path-integral simulations with periodic boundary conditions. With periodic boundary conditions, the (H<sub>2</sub>)<sub>n</sub>-Li<sup>+</sup>-benzene system is extended in three dimensions, forming a more realistic representation of a microporous H<sub>2</sub> storage material. Bulk H<sub>2</sub> uptake characteristics will be predicted over a range of temperatures, without neglecting quantum behaviour.

Through a better understanding of the way H<sub>2</sub> interacts with microporous frameworks, materials with improved H<sub>2</sub> storage capacities can be designed.



**Figure 1.** The (H<sub>2</sub>)<sub>2</sub>-Li<sup>+</sup>-benzene model system. Hydrogen atoms are white, carbon atoms black and Li<sup>+</sup> pink.

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## Poster 20

**Dr Raffaella Demichelis**, *Dr Paolo Raiteri*,  
*Prof Julian Gale*  
*Curtin University*

### The multiple structures of vaterite

#### Abstract

Vaterite ( $\text{CaCO}_3$ ) is a metastable polymorph that plays a fundamental role in the nucleation and crystal growth of calcium carbonate under biogenic conditions. In particular, the nucleation of vaterite is often observed from amorphous calcium carbonate precursors, with biomolecules acting as structural stabilisers.

Despite the role of vaterite in biomineralization, the nature of its disordered structure has been object of intense debated for a long time, with various authors suggesting apparently conflicting models. Through first principle simulation, a link between the most recent models proposed in the literature has been established.

The new model, consisting of multiple structures, is supported by recent experimental evidences showing that vaterite crystallises with “at least” two different structures. The disorder of vaterite is here interpreted in terms of different orientations of the carbonate anions, different stacking sequences of the carbonate layers, and possible chiral forms. Hence, vaterite should be considered as a combination of different forms exhibiting similar average properties, rather than a single “disordered” structure. Furthermore, chirality represents a new and important

direction for future investigation that may influence which of the possible vaterite structure is obtained.

More generally, a wide variety of structures exhibiting minor structural and energetic differences might exist in nature, as a result of nucleation in different environments and at different conditions, which might promote the formation of a particular stacking sequence or chirality.

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## Poster 21

**Dr Miroslav Dvorak**<sup>1</sup>, *Dr Martin Michl*<sup>2</sup>,  
*Dr Numan Almonasy*<sup>3</sup>, *Prof Milos Nepras*<sup>3</sup>

1. *The University of Sydney*,
2. *Czech Technical University in Prague*,
3. *University of Pardubice*

### Excited State Localization and Excitation Energy Migration in Multichromophoric Aminoarenes

#### Abstract

Aminoaryl derivatives connected to 1,3,5- triazine ring have been used as molecular building blocks for preparation of a manifold of multichromophoric compounds. Specifically, dyads with 1-aminopyrene as a donor and 3-aminobenzanthrone or 3-aminoperylene as an acceptor of electronic excitation energy and multichromophoric compounds with different number of aminopyrene or aminoanthracene moieties were prepared in order to study electronic excitation energy transfer and localization of excited states [1, 2].

The fluorescence anisotropy measurements of two sets of molecules containing different number (one, two or three) of 1-aminopyrene or 2-aminoanthracene chromophores attached to the central triazine ring were used to investigate excitation energy migration. The fluorescence anisotropy has similar features for both sets of compounds: In the case of single 1-aminopyrene chromophore, it has almost constant value near 0.3 over the lowest absorption band. On the other hand, the anisotropy increases with wavelength from much lower value  $\sim 0.1$  at the blue edge and approaches the value of  $\sim 0.3$  at the red edge of the peak in the case of molecules containing two or three chromophores [3]. Similar holds for 2-aminoanthracene derivatives. The presence of additional aminoanthracene chromophores results into decrease of the fluorescence anisotropy value across the region 320-400 nm compared to the molecule bearing only the single aminoanthracene. This decrease is pronounced with the increasing number of the chromophores. But, at the very red edge of the spectra, the fluorescence anisotropy reaches almost the same value of about 0.3 for all three compounds.

Quantum chemical methods were used for calculation of excited states properties of the above mentioned compounds. The calculations indicate the presence of pairs or triplets of excited singlet states in compounds with two or three identical aryl-amino substituents, respectively. The excited states in these pairs and triplets have similar nature as two lowest excited states of the compounds with only single

aminoaryl substituent and are predominantly localized on the individual chromophores.

We interpret the photophysical behavior of these types of multichromophores in terms of excitation energy migration, which causes depolarization of fluorescence in the case of higher energy excitation, and direct population of localized excited state in the case of excitation to the red edge of the absorption band.

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## Poster 22

**Dr Vidana Epa**<sup>1</sup>, *Dr Victor Streltsov*<sup>1</sup>,  
*Dr Simon James*<sup>1</sup>, *Dr Vijaya Kenche*<sup>2</sup>

1. CSIRO Materials Science & Engineering,  
2. Florey Institute of Mental Health

### Alzheimer's Disease Amyloid-Beta Peptide Interaction with Platinum-based Inhibitors

#### Abstract

Alzheimer's disease (AD) is a progressive neurodegenerative disorder causing the most common form of dementia in humans. The pathology of AD is characterised by large extracellular plaques in the brain. The major component of these plaques is the 39-43 amino acid residue amyloid beta (A $\beta$ ) peptide. Binding of metal ions such as Cu, Fe, and Zn to A $\beta$  not only enhances its

aggregation, but also, in the case of Cu and Fe, leads to the production of reactive oxygen species (ROS) in the presence of reducing agents such as ascorbate. Anti-AD therapeutic design has focussed both on the inhibition of production of A $\beta$  as well as on the inhibition of aggregation of A $\beta$ . Recently it has been shown that Pt(II)-1,10-phenanthroline compounds bind to A $\beta$ , inhibit the A $\beta$  aggregation and generation of ROS, and ablate the A $\beta$ -induced neurotoxicity. Knowledge of the atomic structure of the complexes made by these Pt compounds with A $\beta$  would greatly facilitate therapeutic development. In this work, we combined density functional theory modelling with X-ray absorption spectroscopy and mass spectrometry experiments to derive structural models of the interaction of these Pt compounds with A.

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## Poster 23

**Sarah Faulkner**<sup>1</sup>, **Michelle Coote**<sup>2</sup>,  
**Colin Jackson**<sup>1</sup>

1. Australian National University, 2. ARC Centre of Excellence for Free-Radical Chemistry and Biotechnology, Research,

### Does SOMO-HOMO conversion enhance catalysis in radical enzymes?

#### Abstract

In the absence of direct conjugation, remote substituent effects on radical stability are generally thought to decay rapidly with distance and become insignificant beyond a few Angstroms' separation. However, recently it has been shown that

neutral delocalised radicals can be stabilized significantly by remote negative charges, even in the absence of permanent dipoles. This electrostatic stabilizing effect occurs because the delocalised electrons of the radical interact less strongly with the negative charge than the radical's positive nuclei, resulting in a net lowering in the system's energy and in particular, the energy of the SOMO. This SOMO stabilization is so pronounced that it drops lower in energy than some of the radical's fully occupied orbitals, in direct violation of the Aufbau principle; an effect known as 'SOMO-HOMO conversion'. The stabilization is more pronounced with a more delocalised radical and a more localised negative charge, the latter corresponding to an unstable anion in real systems. This effect has currently been observed only in the gas phase and non-polar solvents, where the anion is free from the stabilizing effects that are provided by a polar solvent. However, the active site of an enzyme is a highly controlled environment which is often isolated from the solvent; this is particularly true of enzymes which generate radicals during catalysis, as they must protect the radical long enough for the desired reaction to occur. SOMO-HOMO conversion could enhance enzyme catalysis in two ways; by stabilizing the transition state of a reaction more than the enzyme-reactant complex, or by stabilizing a product radical, making the overall reaction more thermodynamically favourable. Following investigation of a wide range of radical enzymes, a member of the radical SAM superfamily has been found which appears to

provide an excellent environment for SOMO-HOMO conversion. Its active site is largely hydrophobic and becomes sealed from solvent when its substrate binds. In this hydrophobic site are several aspartate residues which are predicted to have unusually high pK<sub>A</sub>'s, a feature that is unexplained by the current literature. It also forms a highly stable protein radical during its catalysis. In order to test whether this enzyme uses SOMO-HOMO conversion to assist radical formation, these unusually unstable aspartates are being mutated to asparagine; a residue with similar hydrogen bonding properties and shape, but unable to form an anion. The reaction rates of these mutant enzymes, along with predictions from QM/MM modelling and DFT calculations on small model systems of the wild type and mutant active sites, will be used to determine whether SOMO-HOMO conversion in the transition state or product enhances the enzyme's catalysis.

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## Poster 24

**Dr Terry Frankcombe**

*Australian National University*

### New Gaussian wave packet methods for chemical dynamics

#### Abstract

Quantum dynamics calculations in molecular scattering are demanding. Even after 40 years of development, the state of the art for accurate scattering simulations is simulating reactions in five atom systems. Grid-based methods dominate the field, despite requiring computational

effort that scales exponentially with the system size. Methods based on Gaussian wave packets (GWPs) present an alternative to the grid-based approaches, offering advantages such as better scaling to large numbers of degrees of freedom and much more achievable requirements for potential energy surface evaluation. However, contemporary GWP-based approaches such as full multiple spawning and the variational multiconfigurational Gaussian method are not effective when applied to many types of reactions.

We have recently developed a new GWP-based method incorporating several key innovations. The Basis Expansion Leap multiconfigurational Gaussian (BEL-MCG) method uses Gaussian functions simply as a flexible, redundant basis set. Basis function motion is completely removed from the physics of the system, dramatically reducing the number of equations of motion required. This method allows accurate propagation of the quantum wave packet describing molecular nuclei, giving accurate reaction probabilities on any reasonable molecular potential energy surface. The Schrödinger equation is solved to a pre-specified level of accuracy, meaning all quantum effects are reproduced. Similar methodology can be used to calculate the rovibrational ground state wave function of a system, allowing the rapid calculation of zero point energies without reference to presumed functional forms or harmonic/anharmonic character. In this talk the BEL-MCG approach shall be described and demonstrated with simple and multi-dimensional examples.

## Poster 25

**Brenton Graystone**, Dr Subashani Maniam,  
Prof Steven Langford, Dr Toby Bell  
Monash University

### A Single Molecule Spectroscopic Evaluation of a Tetra Core-Substituted Naphthalene Diimide

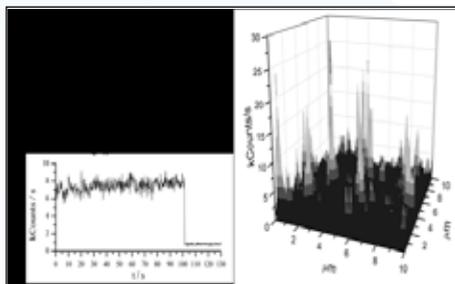
#### Abstract

Since the first reported observation of single molecules at room temperature using fluorescence microscopy, the use of single molecule fluorescence microscopy (SMFM) techniques, particularly in biophysics, has rapidly expanded.<sup>1,2</sup> With this expansion, dyes that absorb and emit in the red region of the electromagnetic spectrum have become highly sought after. This is due to the decreased background absorption and emission observed when imaging biological materials in this region, the so-called biological 'window of transparency'.<sup>2</sup> The advantage of SMFM techniques is that detailed information, often lost to ensemble averaging, is revealed.<sup>2</sup> As a result a better understanding of the various behaviours that make up the properties of the bulk sample are obtained.

A chromophore for use in SMFM techniques must meet specific requirements: large molar absorption coefficients,  $\epsilon$ , high fluorescence quantum yields,  $\Phi_f$ , and high photostability - being capable of at least  $10^6$  absorption-emission cycles prior to irreversible photobleaching. Long fluorescence lifetimes in the nanosecond range are also useful. There are few red emitting dyes that meet these requirements and the

search for more is ongoing.

Substituted amino naphthalene diimides (SANDIs) show promise in SMFM applications, as they generally possess high quantum yields ( $\Phi_f \sim 0.5$ ), long fluorescence lifetimes ( $\tau_f \sim 10$  ns) and are photostable under SMFM conditions.<sup>2,3,4</sup> However, a drawback of these fluorophores is their low molar absorptivity ( $\epsilon \sim 8$ -20000 mol<sup>-1</sup>cm<sup>-1</sup>L).<sup>2,3,4</sup> We have recently developed a deep red-emitting SANDI 1 ( $\lambda_{max} = 666$  nm) which shows promise in addressing this drawback (Fig. 1). The molar absorptivity is greatly improved ( $\epsilon \sim 72000$  mol<sup>-1</sup>cm<sup>-1</sup>L), and although there is some trade off in quantum yield ( $\Phi_f \sim 0.17$ ), 1 is ca. 3 times brighter than simple mono- and di-substituted SANDIs in the literature.<sup>4</sup>



**Figure 1:** a) Structure of 1; b) Photon trajectory; c) intensity map of single molecules of 1.

Single molecules of 1 in PMMA films show that the intensity of emission, fluorescence lifetime and emission maxima did not vary significantly over time, or from molecule to molecule. Many molecules were exceptionally long-lived, undergoing hundreds of millions of excitation-emission cycles before photobleaching. Thus 1 appears ideally suited to single molecule labelling applications.

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## Poster 26

**Jeremy Hall**<sup>1</sup>, **Dr Paul Smith**<sup>1</sup>, **Dr Rafael Picorel**<sup>2</sup>, **Prof Elmars Krausz**<sup>1</sup>

1. Australian National University,  
2. CSIC, Zaragoza, Spain

### Circularly Polarised Luminescence Spectroscopy of Photosystem II

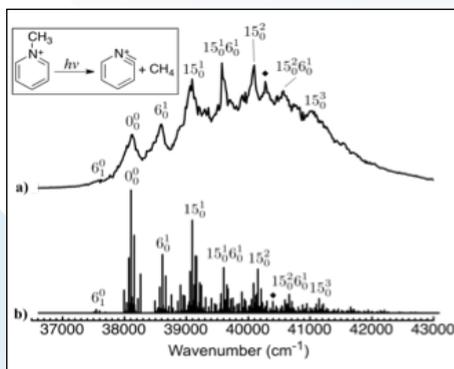
#### Abstract

Photosystem II (PSII) is the enzyme that performs the initial reactions of oxygenic photosynthesis, including water splitting and formation of oxygen gas. This multi-protein complex contains two light-harvesting antenna proteins, CP43 and CP47, connected on either side to the reaction centre (RC). Chlorophyll molecules bound at specific locations in the antennas absorb light energy and transfer it to chlorophylls in the RC. Excitation of the RC initiates a series of electron-transfer reactions whose final result is the reduction of a plastoquinone molecule using electrons extracted from H<sub>2</sub>O, with oxygen gas

generated as a waste product. The main electron-transfer cofactors of PSII are known from various spectroscopies, confirmed by x-ray crystallography. However unresolved questions remain regarding kinetics and mechanisms in the enzyme.<sup>1</sup> The antenna chlorophylls are well separated from the reaction centre, and the question of whether the rate-limiting step is excitation energy transfer or electron transfer remains a controversial topic. One key method in understanding the dynamics of PSII is the use of multi-dimensional computational analysis to model spectroscopic results such as absorption, circular dichroism, fluorescence, and others in terms of the crystal structure, in parallel. So far, different studies have successfully accounted for different sets of spectroscopies but strong disagreement between these studies suggests that the true solution is some way off.<sup>2</sup>

Circularly polarised luminescence (CPL, the difference between left- and right-circularly polarised light in emission) is one technique that has not yet been brought to bear on this challenging problem. Optical activity in light harvesting proteins arises from exciton coupling between chlorophyll molecules that are packed in chiral arrangements. This coupling is relatively easily determined by the distances and orientation of the chlorophyll transition dipoles involved. The CPL of exciton states matches their circular dichroism. Rather than making CPL redundant, this fact is useful for identifying the fluorescing exciton states in PSII, as fast excitation energy transfer to the lowest excited state cannot be taken for granted. CPL results can therefore provide an additional constraint for structure-

based calculations of PSII dynamics. Many challenges arose in measuring the polarisation of emission from fragile protein complexes at temperatures down to 5 K. With accuracy of circular polarisation of 1 part in 104 required, polarisation artifacts were particularly troublesome. Artifact-free circular polarisation of luminescence from PSII core complexes and the isolated proximal antennas CP43 and CP47 have now been obtained providing further insights into this important enzyme.



**Figure 1.** (a) PD action spectrum monitoring the methane ( $\text{CH}_4$ ) loss channel from the UV photolysis of *N*-methylpyridinium. (b) Simulated *N*-methylpyridinium UV absorption spectrum.

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## Poster 28

**Takaaki Harada**, Hamish McTernan, Dr Duc-Truc Pham, Prof Lincoln Stephen, Dr Tak Kee  
The University of Adelaide

### Ultrafast Spectroscopy of Curcumin in Diamide Linked $\gamma$ -Cyclodextrin Dimers

#### Abstract

Curcumin is a biologically active polyphenol extracted from turmeric. Poor aqueous stability and solubility of curcumin have thus far hindered the development of curcumin as a drug. Cyclodextrins (CDs) have been suggested as drug delivery agents for curcumin owing to their non-toxic nature. Our previous study showed that diamide linked  $\gamma$ -CD dimers, namely 66 $\gamma$ CD2su or 66 $\gamma$ CD2ur, are able to stabilize curcumin at a greater extent than single CDs through a cooperative 1:1 host guest complexation. We have proposed that the high stability of curcumin may be attributed to exclusion of water molecules in 66 $\gamma$ CD2su and 66 $\gamma$ CD2ur. However, fluorescence spectroscopic results suggest that there are still some interactions between curcumin and water in 66 $\gamma$ CD2su and 66 $\gamma$ CD2ur. In this study, we aim to use ultrafast spectroscopy to understand the water-curcumin interactions on the time scales of 100 femtoseconds (fs, 10<sup>-15</sup> s) and picoseconds (ps, 10<sup>-12</sup> s). Ultrafast excited state dynamics of curcumin in 66 $\gamma$ CD2su and 66 $\gamma$ CD2ur will be presented in comparison to curcumin in methanol. When free curcumin is present in methanol, the excited state is deactivated through fluorescence, solvation, solvent-mediated excited state intramolecular hydrogen

transfer (ESIHT), giving rise to an excited lifetime of  $\sim 200$  ps. The solvent-mediated ESIHT is an efficient relaxation pathway due to a hydrogen bond network. In contrast, the excited states of curcumin in 66 $\gamma$ CD2su and 66 $\gamma$ CD2ur show an incomplete recovery, even at  $t > 2.5$  ns. We propose that 66 $\gamma$ CD2su and 66 $\gamma$ CD2ur restricts the hydrogen bond network between curcumin and water molecules, leading to ineffective solvent-mediated ESIHT. Therefore, deactivation of the excited state curcumin relies on other slow pathways including vibrational relaxation, resulting in observed a long decay time constant.

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## Poster 29

**Robert A Hardy**, Aidan M Karayilan,  
Gregory F Metha  
The University of Adelaide

### Density Functional Theory and Photo-Ionisation Studies of Gold-Cerium Oxide Clusters

#### Abstract

The potential for transition metal clusters deposited on metal oxide surfaces to catalyse industrially and environmentally relevant heterogeneous processes such as the water gas shift reaction and CO oxidation/NO<sub>x</sub> reduction has sparked intense research within the nanocatalysis industry. Particular interest has been directed toward gold clusters chemisorbed to cerium oxide surfaces which have been shown to catalyse low temperature oxidation reactions. The catalytic propensity of these systems has been attributed to the low oxidation

potential of cerium oxide which allows surface oxygen atoms to be readily abstracted by adsorbed gas phase reactants. The adsorption of small gold clusters to the cerium oxide surface has been proposed to facilitate this process.

We use DFT to calculate small Ce<sub>3</sub>O<sub>n</sub> and AuCe<sub>3</sub>O<sub>n</sub> ( $n=1, \dots, 6$ ) clusters as model surface analogues to study the effects of gold adsorption on the cerium oxide surface. Our calculations of the Ce<sub>3</sub>O<sub>n</sub> cluster show a decrease in the oxygen binding energy coupled with an increase in ionisation energy as the cluster species become more highly oxidised. Furthermore, the Ce<sub>3</sub>O<sub>5</sub> and Ce<sub>3</sub>O<sub>6</sub> clusters are calculated to photo-dissociate in preference of photo-ionisation; this is consistent with our photo-ionisation produced mass spectra in which we are unable to detect these species. Similar trends for ionisation and oxygen binding energy are observed for the AuCe<sub>3</sub>O<sub>n</sub> cluster series, albeit with a ca. 2eV weakening in the oxygen binding energy for the AuCe<sub>3</sub>O<sub>6</sub> cluster compared to Ce<sub>3</sub>O<sub>6</sub>. We propose that gold facilitates the initial abstraction of oxygen atoms from the ceria surface by adsorbed reactants but does not increase the amount of oxygen available for reaction.

## Poster 30

**Dr Naomi Haworth<sup>1,2</sup>**, Dr Chris Thompson<sup>1</sup>,  
Dr Jinzhen Lu<sup>1</sup>, Nguyen Vo<sup>1</sup>,  
A/Prof Lisa Martin<sup>1</sup>, Thanh Le<sup>1</sup>, Alan Bond<sup>1</sup>

1. Monash University,  
2. Deakin University

### Identification of TCNQF4 Oxidation States via Experimental and Theoretical Vibrational Spectra

#### Abstract

2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, TCNQF<sub>4</sub>, is an intriguing molecule which has extensive  $\pi$ -bonding throughout its structure. Upon reduction, either mono- or dianionic molecular ions can be formed, both of which show delocalisation of the  $\pi$  electrons. These systems have therefore been of great interest for the synthesis of coordination polymers with useful magnetic and electronic properties. However, characterisation of the TCNQF<sub>4</sub> oxidation state(s) present in these materials has often been challenging. Infrared and Raman spectroscopy provide valuable tools for this purpose; however their usefulness has been hampered by confusion over peak assignments and lack of understanding of the impact of reduction on the vibrational spectra.

We have used density functional theory (B3LYP/6-31(2df,p)) to probe the changes in molecular and electronic structure as well as variations in (and mixing of) the TCNQF<sub>4</sub> vibrational modes as the molecule is reduced. This has allowed us to clarify the peak assignments and identify spectral characteristics

which are diagnostic of the different TCNQF<sub>4</sub> oxidation states. Some vibrational frequencies, particularly the nitrile stretching modes, are extremely sensitive to the crystalline environment of the molecule. We have also explored the effects of nearby charged species within crystal lattices on the molecular and electronic properties of TCNQF<sub>4</sub> species.

One particularly interesting characteristic of experimental TCNQF<sub>4</sub>- and TCNQF<sub>4</sub><sup>2-</sup> infrared spectra is that bands are often observed corresponding to symmetric modes which would normally be expected to be infrared silent. We probe the nature of these transitions and explain the spectroscopic phenomena which allow them to absorb infrared light.

## Poster 31

**Alireza Heidari**, Pravindya Haputhanthri,  
Dr Ekaterina Izgorodina,  
A/Prof Bayden Wood  
Monash University

### Analysis of conformations and vibrational frequencies of AMP, ADP, and ATP: A combined computational and experimental study

#### Abstract

In the previous ground breaking work by our group it was reported that the conformation of DNA is strongly dependent on hydration in cells and isolated nuclei.<sup>1</sup> While this phenomena is well known for isolated DNA it had not be previously

reported in cells and isolated nuclei. The A-DNA form is prevalent when the humidity drops below 75%, while above this level the B-DNA form dominates. The main spectral differences observed going from the hydrated B-DNA form to the dehydrated A-DNA form include: (1) a shift in the  $\nu_{\text{asym}}(\text{PO}_2^-)$  from  $\sim 1225$   $\text{cm}^{-1}$  to  $\sim 1240$   $\text{cm}^{-1}$  band, (2) a reduction in intensity of the  $\nu_{\text{sym}}(\text{PO}_2^-)$ , and (3) a shift in the base stacking mode at  $\sim 1715$   $\text{cm}^{-1}$  to  $\sim 1710$   $\text{cm}^{-1}$ . In order to gain an understanding into the origin of these spectral changes we have applied a range of computational chemistry methods to model single nucleotides such as AMP, ADP, and ATP to predict their vibrational frequencies and infrared intensities with the aim to establish a computational methodology for studying more complex oligonucleotides and ultimately DNA itself. The goal of the study was two-fold: (1) investigate the influence of explicit and implicit solvents on the stretching and bending vibrations associated with the phosphodiester bonds and the nucleic bases including AMP, ADP, and ATP and (2) compare the performance of various quantum chemical methods for the prediction of vibrational frequencies and intensities of simple nucleotides. The implicit solvent was treated through a Conductor-like Polarizable Continuum Model (CPCM) using water as solvent, whereas for the explicit solvent water molecules were placed around the nucleotide. A wide range of density functional theory (DFT) methods such as B3LYP, M06L, M06, M062X, B97D, PBE, PBE1, TPSS, TPSSH, LC-BLYP, LC-wPBE, B2PLYP, and mPW2PLYP were selected. Among ab initio methods a second order perturbation theory method, MP2, was the only feasible method to

perform geometry optimisations with subsequent frequency calculations. Both MP2 and DFT-based methods were combined with a series of basis sets ranging from traditional Pople's basis sets to correlation-consistent Dunning's basis sets. The computer-generated spectra are compared with experimental spectra recorded using Attenuated Total Reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. In this presentation a detailed comparison between the calculated and experimental results will be presented.

#### Key Words

AMP, ADP, ATP, Nucleotides, MP2, DFT, Basis sets, Gas phase, Explicit solvent, Implicit solvent, Conformations, ATR-FTIR spectroscopy

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#### Acknowledgments

*The authors would like to acknowledge and sincerely thank the Monash e-Research Centre, the National Facility of the National Computational Infrastructure, and Multi-modal Australian ScienceS Imaging and Visualisation Environment for a generous allocation of computational resources.*

## Poster 32

**Dr Clare Henderson**<sup>1,3</sup>, Edward Nagul<sup>2,3</sup>,  
A/Prof Trevor Smith<sup>1,3</sup>, Prof Spas Kolev<sup>2,3</sup>

1. ARC Centre of Excellence for Coherent X-ray Science, 2. Centre for Aquatic Pollution Identification and Management, 3. The University of Melbourne

### Imaging Chemical Extraction by Polymer Inclusion Membranes Using Fluorescence Microscopy

#### Abstract

Polymer inclusion membranes (PIMs) extract chemical species from solution<sup>1</sup> and show promise for trace environmental analysis and removal of heavy metals and toxic anions in waste water clean up. The mechanistic details of how they work, however, are still unclear. Some promising PIM types must be conditioned before use and the membranes are initially flexible but become brittle, and less efficient extracting devices with age, limiting their potential on the industrial scale. Why PIMs exhibit this time dependency is also not well understood.

Few techniques are available that can probe these properties with the required spatial resolution and, historically, methods must infer PIM function from probing surface morphology only. By uptaking a fluorescent dye, however, we can image the PIMs with a range of fluorescence microscopy methods traditionally associated with the biological sciences. This allows us to see the extraction and transport processes both laterally and as a function of depth within the

membrane, in three dimensions with super-resolution and in a time-resolved manner.

We have imaged poly(vinyl chloride)-based PIMs with Aliquat 336 as carrier after extracting fluorescein from aqueous solution using confocal and structured illumination microscopy.<sup>2</sup> We observed that there exist preferential extraction zones within the membrane which increase in size dependent on immersion time in the fluorescein solution. Importantly, correlation of these zones with surface morphology was not found.

We have applied time-resolved confocal fluorescence microspectroscopy<sup>3</sup> to probe the changes in the properties of PIMs with ageing. Clear differences in the time-resolved emission characteristics are observed between PIMs that are infused with fluorescent solution compared with membranes that have been used to extract the fluorophore. Fluorescence decay time distributions evolve as the PIM ages associated with the film stiffening with age.

Extraction of a molecular rotor fluorescent probe<sup>4</sup> was used to measure the microviscosity of the membrane to correlate changes in the PIM efficacy with stiffness and brittleness of the membrane as it ages. Fluorescence anisotropy measurements have also been used to probe the films' internal viscosity.

By applying a range of fluorescence microscopy methods, we have been able to see the extraction of chemical species within the PIMs. This work demonstrates a novel probing method for understanding PIM function and will no doubt inform the design of more stable and efficient PIMs.

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## Poster 33

**Heather Higginbotham<sup>1</sup>,**

*Dr Tich Lam Nguyen<sup>2</sup>, Dr Alison Funston<sup>1</sup>,  
Prof Paul Mulvaney<sup>2</sup>, Dr Toby Bell<sup>1</sup>*

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2. The University of Melbourne

### Investigation of the optical and emission properties of CdSe nanocrystals using defocused widefield microscopy

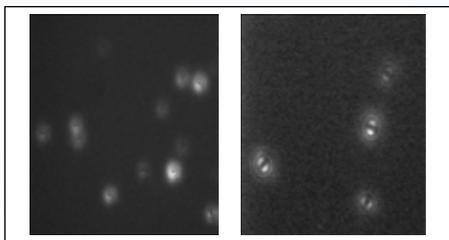
#### Abstract

One of the most researched fluorescent materials of the last decade is semiconductor nanoparticles or quantum dots. Quantum dots are clusters of crystalline semiconducting materials, commonly synthesised from Zn, Cd and Pb metals and Se chalcogenides; the most common of these synthesised from cadmium and selenium. With sizes ranging from a few hundred to a few thousand atoms CdSe quantum dots can be highly fluorescent, are extremely photostable, have a large absorption cross section and a high resistance to photobleaching.<sup>1</sup> Unlike bulk semiconductor materials quantum dots have a tunable bandgap and therefore fluorescence emission is directly related to the size of the quantum particle.

Shape control of semiconductor nanocrystals has now been achieved by modifying the method of synthesis creating nanoparticles in a range of shapes including spheres, rods, rice, and tetrapods.<sup>2,3</sup> Shape alteration should affect optical properties, in particular, quantum rods may adopt a magnetic dipole along the long axis of the wurzite structured nanocrystals leading to linearly

polarised emission and a potential material for data storage.<sup>4</sup>

We have visualised the optical properties of quantum nanocrystal materials using defocused widefield microscopy. Much like conventional widefield techniques defocused widefield applies a focused and collimated laser onto the back focal plane of an objective. However by "defined image defocusing" or the introduction of an aberration in the path of the objective further information about the angular distribution of fluorescence intensity may be obtained.<sup>5</sup> We report the synthesis, optical characterisation and defocused widefield imaging of CdSe quantum nanocrystals of varying shapes. All nanocrystals were characterised using UV-visible spectroscopy, TEM, and widefield microscopy. We show that unlike the CdSe spheres that have been previously shown to contain no discrete emission dipole, more complex shapes such as CdSe rods contain a single and discrete emission dipole. Figure 1a shows defocused widefield images of CdSe spheres with an emission pattern characteristic of a multi-dipole emitter already characterised in the literature. Figure 1b shows that the emission patterns of CdSe rods, however is easily characterised as a single dipole emitter.



**Figure 1:** a) emission pattern of CdSe spheres b) emission pattern of CdSe rods

## Poster 34

**Dr Jennifer Hodgson**, Ahmed Halima,  
Dr Ekaterina Izgorodina, Prof Douglas  
MacFarlane  
Monash University

### Barriers for Proton Transport in Hydrogen-bound Systems Including Protic Ionic Liquids

#### Abstract

There is growing interest in the application of protic ionic liquids in fuel cells and water splitting. In both cases an understanding of the kinetic and thermodynamics of proton transfer is critical. It has been known for some time that neat acids containing intermolecular hydrogen bonding show high intrinsic intermolecular proton conductivity, with proton transport occurring through a Grotthuss-type mechanism similar to the transport of excess charge defects in water.<sup>1</sup> Previous studies have focused on proton conduction in neat phosphoric acid in order to further understand mechanism for phosphate-based systems such as phosphonated polymers and biological systems such as adenosine triphosphate (ATP).<sup>2</sup> However, the same processes occurring in acetic, sulphuric and triflic acid systems have received little attention.

In this work we use computational chemistry to investigate the barriers and mechanisms of proton transfer reactions in these acids. Energy profiles show that the barriers for these reactions are low, as expected. While the charges can be transported by this mechanism over large distances, the movement of individual protons is less than

0.3 Å. A base-doped Grotthuss mechanism allows greater ease of motion of anions and lowering of the barrier, with reactions requiring little translational and rotational motion. However, the more anions there are present the shorter the distance the charge is transferred. In almost pure acid the H-bonded chains are longer leading to longer proton transfer distances. In this case, however, the motion of molecules is hindered by the H-bonding and unfavourable polarisation of the chain, leading to a higher barrier for proton conductivity. Solvent reorganisation is required in order to extend the distance of charge transfer. This work will attempt to further understand the effect of differing amounts of base-doping on the intermolecular proton conductivity of neat acids and protic ionic liquids.

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## Poster 35

**Aidan Karayilan**, A/Prof. Gregory Metha  
The University of Adelaide

### Experimental and Computational Studies on Bimetallic Clusters of Platinum and Cerium

#### Abstract

The interactions between reactant molecules and catalytic systems composed of nanoparticles or clusters deposited on metal oxide surfaces are difficult to study due to their varying composition (cluster aggregation, nanoparticle size distribution, defect sites). As such, it is proposed that the interaction be studied by focussing only on the isolated site at which the catalysis occurs. This can be done by forming and studying gas-phase clusters, both isolated and in the presence of reactant gas molecules, such as carbon monoxide.

Clusters of platinum and cerium oxide are generated via a dual laser ablation source coupled with tuneable dye laser ionisation and linear time-of-flight mass spectrometry. Cluster ionisation energies are determined using photo-ionisation efficiency (PIE) spectroscopy, and compared with theoretical ionisation energies from density functional theory calculations. Additionally, Franck-Condon (FC) calculations are performed on the computationally derived structures to yield simulated Zero Electron Kinetic Energy (ZEKE) spectra, which are then used to construct simulated PIE spectra, against which the experimental spectra are compared.

Good agreement between experiment and theory verifies the structure of the clusters formed and allows further analysis such as the mechanism of charge transfer upon reaction as well as the preferred binding sites of the transition metal component.

## Poster 36

**Dr Tak Kee**<sup>1</sup>, Yin Song<sup>2</sup>,  
Dr Yoichi Kobayashi<sup>2</sup>, Dr Ryan Pensack<sup>2</sup>,  
Prof Gregory Scholes<sup>2</sup>

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### Mapping Charge Generation in an Organic Semiconductor using Two-Dimensional Photon Echo Spectroscopy

#### Abstract

Two-dimensional (2D) photon echo spectroscopy is a nonlinear optical spectroscopic technique that relies on the third-order nonlinear susceptibility of materials. This technique, which is the optical analogue of 2D NMR and 2DIR, offers the opportunity to characterize the coupling between vibronic transitions within a system. In the spectrometer used for the present study, the output of a 12-fs laser with a central wavelength and band width of 580 nm and ~100 nm, respectively, is split into four equal replicas using a diffractive optic in the boxcar geometry. The first three outputs are independent delayed in time using pairs of glass wedges. The generated third order signal is then interfered with the fourth output (local oscillator) on a CCD spectrometer

to yield spectral interferograms. Fourier analyses of the wavelength dependent interferograms results in 2D contour plots that contain information on coupling of vibronic transitions.

In this study, 2D photon echo spectroscopy is used to investigate nanosized aggregates of the conjugated polymer poly(3-hexylthiophene) (P3HT) doped with PCBM, which is a fullerene derivative. It is well established that P3HT has distinct vibronic transitions, e.g., the 0-0, and 0-1 transitions, with wavelengths of 600 nm and 560 nm, respectively. Photoexcitation of the nanosized aggregates using a wavelength within these transitions generates excitons (excited state) in the P3HT domains. Migration of the excitons to domains of PCBM, which function as electron acceptors, enables charge transfer reactions, whereby electrons are transferred to the PCBM domains and the resulting positive charges (hole polarons) reside in the P3HT domains. The presence of hole polarons is often characterized by an induced absorption band around 650 nm. The 2D photon echo results show clear cross-peaks between the polaron absorption band and both the 0-0 and 0-1 transitions. Further analyses of the cross-peaks show that the vibrational coherence consisting of the C=C bonds of P3HT is involved in the charge transfer reaction. These results offer further insight into the photovoltaic effect of P3HT.

## Poster 37

**Thomas Keevers<sup>1</sup>**, Andrew Danos<sup>2</sup>,  
Dr Karl Weber<sup>3</sup>, Dr Scott Watkins<sup>3</sup>,  
Dr Dane McCamey<sup>1</sup>

1. University of Sydney,
2. University of Sydney,
3. CSIRO Materials Science and Engineering

### Probing Spin-Dependent Transport and Recombination in Organic Light-Emitting Diodes through Magnetic Resonance

#### Abstract

The significant disorder and weak Coulombic screening of organic semiconductors leads to sophisticated spin-dependent transport and recombination [1]. These pathways have typically been investigated through magnetic resonance at strong magnetic fields, where the energetics is dominated by the Zeeman splitting. This scenario is somewhat unrealistic in that technological applications typically take place at smaller fields, where zero-field splitting is expected to play a substantial role. A canonical example of a low-field effect is Organic Magnetoresistance, the large changes in resistivity (~10%) seen at small magnetic fields (<50 mT) [2].

The electrical and optical pathways of organic semiconductors can be described through the polaron pair model, in which weakly coupled electron-hole pairs are able to dissociate into free charge carriers, or form strongly exchange-dominated excitons [1]. These pairs display spin-dependent behaviour through

preferred recombination through the singlet channel, and slower carrier transport in the triplet configuration [3]. Despite the importance of spin in organic devices, many basic questions are without consensus, such as the dominant spin relaxation mechanism.

We have custom-built a cryostat system which allows us to perform pulsed electrically and optically detected magnetic resonance at low-field strengths, and at a variety of temperatures. This will provide insight into the spin dynamics which govern optoelectronic efficiencies, and identify the role of thermally-activated processes. We will perform field-swept pulsed Electrically Detected Magnetic Resonance (pEDMR), as described by Baker et al [4], on iridium-doped OLEDs with strong spin-orbit coupling. To our knowledge, this situation has not been investigated theoretically or experimentally, and will identify the effects of spin-orbit coupling on the dynamics of spin resonance in organics. Our devices contain a variety of blend ratios, and this will provide secondary information relating to the structural and spin coupling effects caused by iridium-doping.

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## Poster 38

*Julie Kho, A/Prof Peter Boyd ,  
Dr Ali Hosseini , A/Prof Cather Simpson  
The University of Auckland*

### Photochemical Studies of Self-Assembled Porphyrin-fullerene Complexes through Transient Absorption Spectroscopy

#### Abstract

Porphyrin-fullerene assemblies were discovered over a decade ago as potential artificial photosynthetic mimics due to their photoinduced, multistep electron transfer behaviour<sup>1</sup>. A new class of calix[4]arene-linked bisporphyrin ("jaws" porphyrin) has been constructed that bind fullerene with high affinity<sup>2</sup>. Understanding of the photochemistry of these self-assembled complexes, in particular the charge-separated state lifetime is the focus of this study. For this purpose, state-of-the-art, near-IR transient absorption spectroscopy (TrA) has been utilized to measure the excited state lifetime of fulleride C<sub>60</sub><sup>-</sup>.

In this report, we show results from two different sets of bisporphyrin-fullerene triad systems. The first set is a completely self-assembled system in which a ferrocene secondary donor is coordinated to the Zn-porphyrin primary donor. In the second set, self-assembled porphyrin-fullerene systems are constructed with a variety of distances between the covalently bounded secondary donor and the primary donor.

When photoexcited, the porphyrin donates an electron to the fullerene acceptor. This charge-separation step to form the porphyrin cation and

fullerene anion occurs within the tens of picoseconds. In the triad system, a second electron transfer step from ferrocene to the porphyrin separates the charges further in distance. This additional electron step should slow the charge recombination process, and give rise to a longer charge-separated state lifetime.

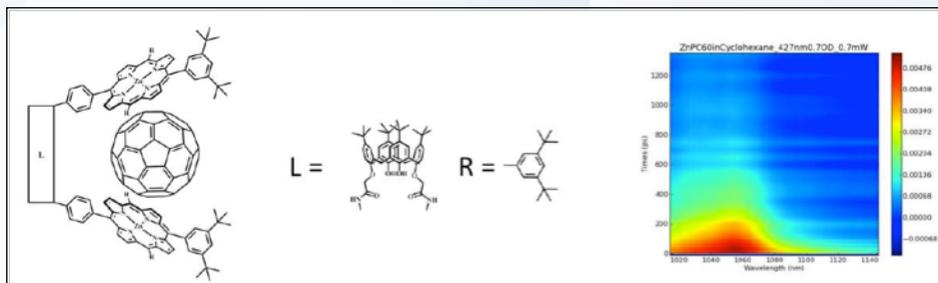
First, we investigated the bisporphyrin-fullerene dyad (Figure 1) in two different solvents (toluene, cyclohexane) which showed that a higher binding constant of C60 to porphyrin in cyclohexane leading to faster charge combination (lifetimes = 560ps and 430ps, toluene and cyclohexane, respectively). We also observed a longer lifetime (2.5 ns) when a tert-butyl pyridine group is coordinated to the bisporphyrin complex. Unexpectedly, the ferrocene-pyridine coordinated triad complex showed no evidence of secondary electron transfer, suggesting that its extended lifetime of 1.5 ns is a coordination effect. A relationship between electronic coupling and lifetimes of the charge-separated state has been demonstrated. For the second set of bisporphyrin fullerene, we observed an increase in charge-separated lifetime (from 1 ns to 3 ns) with increasing distance of the secondary donor to primary donor.

Initial TrA studies of novel solid-state porphyrin-fullerene constructs have been performed as well. These samples have been prepared using self-assembled, co-crystallized structures of various porphyrins with fullerene grounded with KBr into <0.5 mm thick discs. Crystal structures were characterized using X-ray crystallography, and show ordered porphyrin and fullerene packing. The TrA results showed the effects of this packing on the lifetimes of the charge-separated state to explore the effects of crystal packing on the electron transfer process.

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**Figure 1:** (Below) An example of the calix[4]arene-linked bisporphyrin-fullerene constructs (left). A nIR transient absorption spectrum showing decay of C60- signal.



## Poster 39

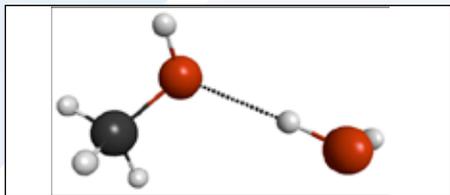
**Michael Morris**<sup>1,2</sup>, **Dr Bun Chan**<sup>1,2</sup>, **Prof Leo Radom**<sup>1,2</sup>

1. The University of Sydney, 2. ARC Centre of Excellence for Coherent X-Ray Science (CXS),

### Excellence for Free Radical Chemistry and Biotechnology How do Bond Dissociation Enthalpies Depend on Protonation State?

#### Abstract

The effect of protonation and deprotonation on the strength of chemical bonds is a topic of particular interest, not least because of the prevalence of proton-transfer reactions. In this connection, we have used high-level *ab initio* calculations to look at how bond dissociation enthalpies (BDEs) change as a result of both adjacent and remote protonation or deprotonation, including partial protonation and deprotonation. Trends in the related gas-phase acidities are also explored, as is the effect of placing various interposing connector groups on the BDEs. The protonation states considered provide a first approximation to the effect of an aqueous solvent on BDEs for a range of pH values.



**Figure 1.** The methanol-water complex, a model for partial protonation.

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## Poster 40

**Miranda Shaw**, **Brian Yates**  
University of Tasmania

### DFT Studies of N<sub>2</sub>O Reactivity with Vanadium and N-Heterocyclic Carbenes

#### Abstract

N-Heterocyclic carbenes have been shown to form stable adducts with kinetically inert nitrous oxide. Following exposure to vanadium(III) complexes, both the NO and NN bonds are sequentially broken, in a mechanistically different reaction to most known metal-N<sub>2</sub>O interactions[1]. The current DFT study has shown that the reaction proceeds by coordination of the NHC-N<sub>2</sub>O adduct to the d<sup>2</sup> metal centre of VR<sub>3</sub> complexes (R = methyl, mesityl), to form an initial η<sup>1</sup>-O triplet complex, from which several reaction paths are available, on both the singlet and triplet surfaces.

The experimental reaction was shown to proceed by intersystem crossing to yield an η<sup>2</sup>-O,N singlet complex, which in turn isomerizes to a highly reactive η<sup>3</sup> complex in which all three atoms of the nitrous oxide molecule are coordinated to the vanadium. NO bond cleavage and simultaneous ligand migration then occurs with a 32 kJ mol<sup>-1</sup> barrier, producing the lower energy vanadium-oxo complex containing a hydrazone-like ligand. The second NN bond cleavage then occurs with a much higher barrier of approximately 130 kJ mol<sup>-1</sup>, though the calculated energies for both reactions are consistent with the experimental reaction conditions. The presence of the carbene changes the expected reactivity

of the nitrous oxide (which typically releases molecular nitrogen following oxygen abstraction) by directly increasing electron density on the terminal nitrogen, which in turn greatly increases the Lewis basicity of the internal nitrogen, allowing it to strongly coordinate to the metal and undergo further insertion and addition reactions. The relatively low energies associated with these reactions show that the nitrous oxide has potential to be exploited as a useful source of both oxygen and nitrogen for organic synthesis.

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## Poster 41

**Donna Whelan**<sup>1</sup>, *Dr Keith Bamberg*<sup>2</sup>,  
*Dr Ljiljana Puskar*<sup>2</sup>, *Prof Don McNaughton*<sup>1</sup>,  
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1. Monash University,  
2. Australian Synchrotron

### Fourier Transform Infrared Spectroscopic Detection of DNA in Cells

#### Abstract

Fourier transform infrared (FTIR) spectroscopy offers a non-invasive method for holistically measuring and 'fingerprinting' the entire biochemical composition of a sample. Because of this, it has long been highlighted as a potential method for disease detection, diagnosis, monitoring and understanding as well as in a broader sense as a fundamental biochemical technique. However actualization of this potential has not occurred

and the anticipated uptake of FTIR spectroscopy in clinical settings also remains elusive. This is, at least in part, due to the discovery of several artefacts in the infrared spectrum of biological samples. Several of these are now known to be due to physical interactions between the sample and the infrared light and can be removed using algorithms. Our research has focussed on deducing the cause of the so-called "Dark DNA" effect and on demonstrating the sensitivity of FTIR spectroscopy to nucleic acid absorptions. The "Dark DNA" effect was based on infrared spectra of cells that appeared to be missing DNA-specific absorptions (1). Because of this, the DNA was hypothesized to be opaque to infrared light due to its high level of compaction. As this was a non-Beer-Lambert interaction and not easily quantified or corrected for, it was cited often as a confounding variable in research attempting to detect cancer and precancer based on DNA absorptions. By working with fully hydrated cells we were able to detect a reversible conformational change of the native B-DNA to A-DNA during dehydration that also coincided with a decrease in absorption intensity. More importantly we found this transition to be reversible both in eukaryotes (2) and, more recently, in functional prokaryotes.

Following this and in a further effort to explain the "Dark DNA" effect, we attempted to quantify DNA spectroscopically in avian erythrocytes. To do this we constructed regression models based on standards on known protein/DNA dry weight ratios. The spectra of avian erythrocytes and extracted nucleic were then fitted to the regression

models to yield accurate estimates of DNA content (average experimental:  $44.2 \pm 6.6\%$  in nuclei,  $12.8 \pm 4.3\%$  in erythrocytes, actual:  $44.3\%$  in nuclei,  $12.5\%$  in erythrocytes) (3)). This result demonstrated the Beer-Lambert nature of the absorption of infrared light by cellular DNA and further work determined that absorption changes were due to a change in the molar extinction coefficient.

Most recently, spectra of >500 live hydrated cells of known age post-mitosis (throughout the G1, S and G2 phases) were acquired at the Australian Synchrotron. Principal Component Analysis of the fingerprint and CH<sub>2</sub>/CH<sub>3</sub> regions of the spectrum allowed successful separation of cells only two hours apart and within the same phase based on changes in DNA, protein and lipid concentration as well as changes to secondary structure and lipid ordering (4). This level of sensitivity achieved non-invasively with live cells is unprecedented and demonstrates the ability of FTIR spectroscopy to detect very subtle biochemical changes in cells. It is anticipated that the ability to consider DNA absorptions in FTIR spectra both quantitatively and with regards to conformation will lead to detection of changes in cell proliferation rate and aneuploidy allowing for detection of cancerous cells.

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### Poster 42

**Duncan Andrews**, Nicholas Hobday,  
Mitchell Quinn, Dr Klaas Nauta,  
A/Prof Meredith Jordan, Prof Scott Kable  
The University of Sydney

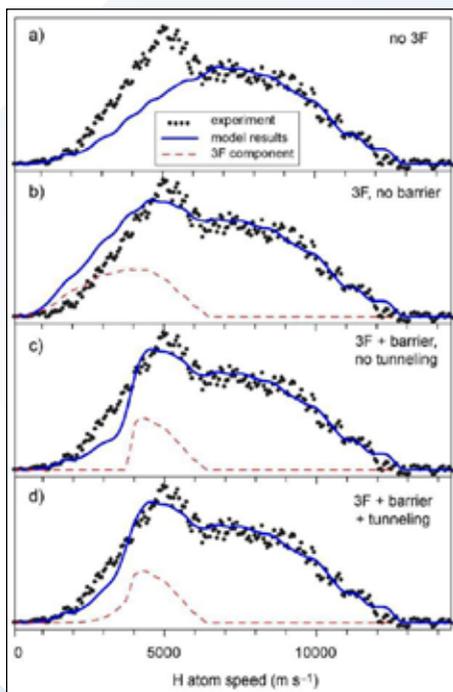
#### An Impulsive Phase Space Theory for Triple Fragmentation

##### Abstract

We describe a simple model for simulating product state distributions in sequential triple fragmentation (3F) reactions, that is, where a molecule breaks into two "hot" fragments and one of these subsequently dissociates on a time scale longer than its molecular rotational period. The model was initially developed to simulate H atom and CO fragment speed, energy and angular momentum distributions for H<sub>2</sub>CO dissociation on S<sub>0</sub> above the 3F threshold. This reaction is modelled as a two-step process. Initially, barrierless C-H bond fission on S<sub>0</sub> forms H + HCO. Those HCO radicals with sufficient internal energy to overcome the small exit channel barrier on the HCO surface undergo secondary fragmentation to form H + CO. Our model treats the first step using phase space theory (PST) and the second using a combined PST-impulsive model, with a tunneling correction. The final velocity of products from the second step is obtained as the vector sum of the HCO parent velocity from the first fragmentation and the velocity imparted to the product fragment during the second fragmentation, assuming that the directions of these

vectors are independent. Angular momentum is explicitly included in the second PST calculation; the HCO angular momentum is set to that arising from the first PST step. There are no adjustable parameters in the model; the parameters are all provided by spectroscopic data or ab initio calculation. The double PST-impulsive model provides a good fit to experimental speed and energy distributions for H<sub>2</sub>CO dissociation on S<sub>0</sub>. Speed and energy distributions have been modelled for H atom and CO fragments for available energies spanning over 7000 cm<sup>-1</sup> and 1000 cm<sup>-1</sup> respectively. H-atom yields (%) arising from reaction on the S<sub>0</sub> and T<sub>1</sub> surfaces are also obtained, at energies below and above the 3F threshold, from the difference between experimental and simulated H atom speed distributions. We show that the triplet mechanism slowly diminishes in importance for energies in excess of the triplet barrier and that triple fragmentation becomes increasingly important as the 3F threshold energy is exceeded. The 3F model is also applied to CH<sub>3</sub>CHO, CH<sub>3</sub>OCHO and CH<sub>3</sub>OCH<sub>3</sub> and used to discriminate products arising from 3F and products arising from "roaming" reactions.

**Figure 1.** For 6943 cm<sup>-1</sup> of available energy, an experimental H-atom speed distribution and calculations for a) no secondary fragmentation; b) secondary fragmentation with no barrier in the HCO exit channel; c) including the effect of a 700 cm<sup>-1</sup> exit channel barrier; and d) allowing tunneling through the barrier.



## Poster 43

**Dr Terry Frankcombe**

*Australian National University*

### Calculating the energetics and dynamics of the interaction of molecules with semiconductor surfaces using fragmentation and ab initio calculations: hydrogen atoms and hydrogen-terminated silicon (111)

#### Abstract

Collins et al. have developed a fragmentation-based methodology for studying large band gap

semiconductors and insulating crystals. Using energies from molecular ab initio calculations at an arbitrary level of theory, the method can model a wide range of properties from structure and lattice dynamics to defect energies. We have applied this fragmentation method to surfaces cleaved from crystals and their interactions with gas phase molecules. Furthermore, the method has been constructed to allow modified Shepard interpolation of the potential energy surface (PES) of each molecular fragment, thus defining the PES of the gas-surface interaction. The dynamics of the gas-surface system can be used to direct sampling of the constituent molecular PESs for building the interpolations. Thus the dynamics of the gas-surface system can be converged with respect to the PES sampling with automatic molecular configuration biasing relevant to the fragmented gas-surface system. While the fragmentation is performed under crystal symmetry, there is no requirement to maintain space group or translational symmetry in the subsequent study of the dynamics. The approach is demonstrated by applying it to hydrogen radicals impacting onto a hydrogen-terminated silicon (111) surface. Cross sections have been calculated for a number of processes including non-reactive scattering, hydrogen abstraction and a range of sticking processes.

## Poster 44

**Dr Olha Krechkivska**, Dr Klaas Nauta,  
Prof Scott Kable, Prof Timothy Schmidt  
The University of Sydney

### A new way to add hydrogen to aromatics: REMPI studies of benzene+H, toluene+H, naphthalene+H

#### Abstract

A new method for generating hydrogenated aromatics has been discovered. Our method has been tested on a few different molecules, such as benzene+H, naphthalene+H that have a known optical spectrum in the gas phase,<sup>1-6</sup> as well as a new system, toluene+H that has not been studied prior to this work. Argon gas containing water vapour was passed through samples of benzene, toluene or naphthalene and hydrogenated species were produced in an electrical discharge followed by supersonic expansion. The role of water being the source of hydrogen was proven using D<sub>2</sub>O vapour in the carrier gas, producing deuterated species, while using fully or partially deuterated aromatics with H<sub>2</sub>O led to the creation of hydrogenated radicals only.

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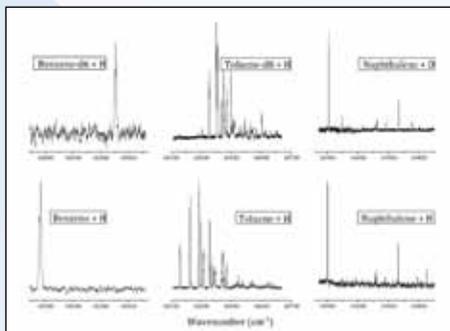
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**Figure 1.** REMPI spectra of hydrogenated and deuterated aromatics

## Poster 45

**Cara Kreck**, Prof Ricardo Mancera  
Curtin University

### Molecular dynamics simulations of the glass transition of water using different intermolecular potentials

#### Abstract

Effective vitrification of water is essential for the successful long-term storage of biological tissues through cryopreservation. This method applies ultrafast cooling rates to induce the formation of the glassy state of water at extremely low temperatures with the help of cryosolvents, thus avoiding the damaging formation and growth of ice crystals and indeed arresting all physical and biochemical processes. Molecular dynamics simulations allow detailed study of the experimentally inaccessible

liquid state of supercooled water below its homogeneous nucleation temperature, and have enabled the characterisation of the glass transition of water promoted by cryosolvents (1, 2).

Simple, non-polarisable intermolecular potential models are commonly used in classical MD simulations of water and aqueous systems due to their low computational cost and their ability to reproduce a wide range of thermodynamic, structural and dynamical properties. As the quality of these predictions vary between the potentials, the predicted glass transition of water is likely to be influenced by the choice of potential. We have thus conducted an extensive comparative investigation of various three, four, five and six point water models in both the NPT and NVT ensembles.

Predictions of the glass transition temperature ( $T_g$ ) for each water potential reveal that, in the NPT ensemble, the number of interaction points in the model appears to be related to the position and height of the peak in the associated heat capacity change. The glass transitions in the NVT ensemble occur in the same order as in the NPT ensemble, but the heat capacity peaks have different heights and slopes, with the most striking changes occurring in the TIP4P family of potentials. The change in  $T_g$  from NVT to NPT appears to be correlated to the change in the magnitude and position of the maximum in the heat capacity change. The  $T_g$  from NPT simulations is also strongly correlated with the temperature of minimum density, whereas the maximum in the heat capacity plot corresponds to

the maximum in the derivative of the density. In the NVT ensemble, these points are instead related to the maximum in the internal pressure and the minimum of its derivative, respectively. A detailed analysis of the hydrogen bonding properties at the glass transition provide further insight into the differences between each water potential investigated.

#### References

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## Poster 46

**Kelvin Lee**, *Stephen Kolmann, Mitchell Quinn, Dr Klaas Nauta, Prof Scott Kable, A/Prof Meredith Jordan*  
*The University of Sydney*

### Quasi-Classical Trajectories on a Zero-Point Energy Corrected Potential Energy Surface

#### Abstract

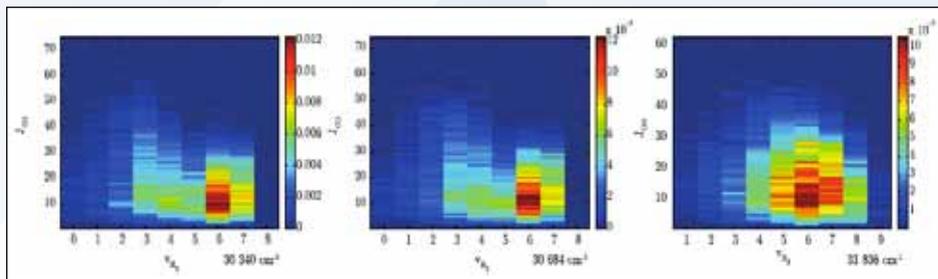
Classical molecular dynamics do not include quantum mechanical expectation values such as Zero-Point Energy (ZPE)<sup>1</sup>. Despite this shortcoming, a classical framework is still favourable for computational ease. Previous attempts to "fill" the ZPE leak have required complex holonomic constraints<sup>2-4</sup> that have been showed to produce unphysical dynamics<sup>5,6</sup>. More recently, this problem has been circumvented by discarding trajectories which violate ZPE conservation, at the loss of statistics and increased computational cost. One would

expect this approach however, to be unsustainable for larger systems. Instead, our group has benchmarked a consistent method of including ZPE without introducing artificiality in the product state distributions. As a proof-of-concept, we reproduced "Roaming" reaction dynamics in the bimolecular abstraction reaction  $\text{H}+\text{HCO} \rightarrow \text{H}_2 + \text{CO}$  on a modified Shepard Interpolated surface. In this work, we have included a zeroth-order ZPE correction to the CASSCF potential energy surface, with observables in good agreement with previous theoretical<sup>7,8</sup> and experimental<sup>9,10</sup> work. We have since extended the work to exploring the reaction  $\text{CH}_3\text{CO} + \text{H} \rightarrow \text{CH}_4 + \text{CO}$ , comparing with roaming

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**Figure :** *Reproduced correlations from our quasi-classical trajectory simulations between vibrational states of H<sub>2</sub> and rotational states of CO. Rotationally cold CO fragments are correlated with highly vibrationally excited H<sub>2</sub>, as seen in velocity-mapped imaging experiments<sup>9</sup>*



## Poster 47

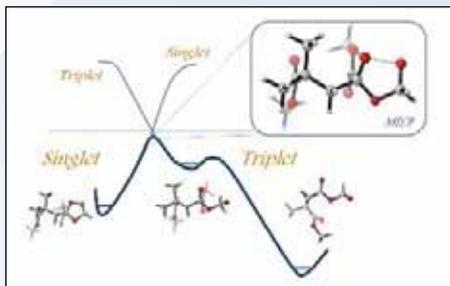
**Richmond Lee**, Michelle Coote  
Australian National University

### New Insights into 1,2,4-trioxolane Stability and the Crucial Role of Ozone in Promoting Polymer Degradation Richmond Lee

#### Abstract

Poly(methyl methacrylate) (PMMA) and its derivatives are the primary constituents of many outdoor products, such as paints and building materials, and are often highly exposed to pollutants, heat and ultraviolet radiation (UV). A fundamental understanding of their chemical degradation mechanisms provides a crucial first step toward the design of more resistant polymers. Whilst the conventional mechanism of polymer autooxidation assumes that oxygen plays a key role in helping to propagate autooxidative damage,<sup>1</sup> there is growing evidence that for polymers such as PMMA, the situation is more complicated<sup>2-5</sup> and that oxygen itself may even help to retard degradation.<sup>6, 7</sup> Interestingly, previous studies have also revealed that nitric oxide retards PMMA degradation,<sup>7</sup> which has prompted us to cast the spotlight on ozone, since NO reduces O<sub>3</sub> to O<sub>2</sub>. Intuitively, in absence of NO, O<sub>3</sub> may participate in PMMA degradation and play a more critical role in environmental polymer degradation. Ozone chemistry is of crucial importance in atmospheric science, plant biology, organic syntheses, drugs, and materials. Cognizant of its huge and diverse impact and in an attempt to consolidate our

efforts to computationally design more durable PMMA, in the present work we use quantum chemical calculations to study the reactivity of ozone towards PMMA, reporting herein the mechanism for ozone initiated polymer degradation and depolymerisation.<sup>8</sup> Our quantum chemical calculations reveal that common defects found in PMMA such as a vinyl terminated chain end reacts expediently with ozone to form a 1,2,4-trioxolane intermediate 4 (Figure 1). Subsequent decomposition of trioxolane involves intersystem crossing from singlet to triplet, through the minimum energy crossing point (MECP, calculated  $\Delta E_{MECP} = +41.9$  kcal/mol) and in the process generates an alkoxy biradical intermediate 5 which causes further chain degradation in a series of kinetic and thermodynamically favourable processes.



**Figure 1.** Pathway for proposed ozone initiated polymer degradation. Values are SMD/G3(MP2)-RAD//B3LYP/6-31+G(d) Gibbs free energy in solution (kcal/mol) relative to starting materials.

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exists as the major species in most polar organic solvents, however the tautomerisation is poorly understood. In this study, nuclear magnetic resonance spectroscopy is used to monitor deuteration of curcumin at the  $\alpha$ -carbon position in several deuterated solvents. The Ha peak around 6 ppm decays as a function of time, which is indicative of proton exchange of curcumin with deuterated solvent. Furthermore, the rate of tautomerisation of curcumin, which is inferred from the rate of deuteration, is deduced by fitting the data using rate equations from a kinetic model. Additionally, the rate of tautomerisation exhibits a strong temperature dependence and the activation energy of tautomerisation of curcumin is determined in several polar organic solvents.

## Poster 48

**Mandy Leung**, Prof Stephen Lincoln,  
Dr Tak Kee  
The University of Adelaide

### A Kinetic Study of Keto-Enol Tautomerisation of the Medicinal Agent Curcumin with NMR Spectroscopy

#### Abstract

Curcumin, the major yellow pigment in turmeric, has been under intense investigation for its medicinal benefits. The structure of curcumin enables tautomerisation, which results in two distinct forms: the diketo and keto-enol tautomers. Recent work has established the link between tautomerisation and the medicinal effects of curcumin. It is well known that the keto-enol form of curcumin

## Poster 49

**Kamron Ley**<sup>1</sup>, Dr George Yiapanis<sup>1</sup>,  
Dr Dave Winkler<sup>2</sup>, Dr Shane MacLaughlin<sup>3</sup>,  
Dr Evan Evans<sup>3</sup>, Prof Irene Yarovsky<sup>1</sup>

1. RMIT University,
2. CSIRO Materials Science and Engineering,
3. BlueScope Steel Research Laboratories

### Flexible or Rigid? Investigating the Effect of Surface hardness on Anti-Fouling performance

#### Abstract

Responsive surfaces have attracted attention largely due to their ability to resist contamination, a property important for many industrial applications including paint coatings. Recently the bio-contamination of these surfaces attracted significant

attention, and Specifically, bio-fouling by class I Hydrophobins, a family of small, amphiphilic fungal proteins. These proteins are best known for their ability to self-assemble into stable monolayers, on hydrophobic as well as hydrophilic surfaces[1-2] due to distinct amphipathic characteristics and can condition the surface, regardless of the starting substrate's polarity and morphology, thus facilitating further microbial growth[3].

We present an all-atom molecular dynamics study on the binding of a class I Hydrophobin, EAS[4], onto some typical industrial coating surfaces modified with poly(ethylene glycol) (PEG) chains for potential antifouling protection[5]. We investigate the effects of surface flexibility and PEG coverage density on the interaction between the protein and PEGylated substrates, as well as the evolution of the secondary and tertiary structure of the protein during adsorption. Results show that PEG modifications of the surfaces induce an increase in Hydrophobin mobility and perturb the secondary structure of the protein.

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## Poster 50

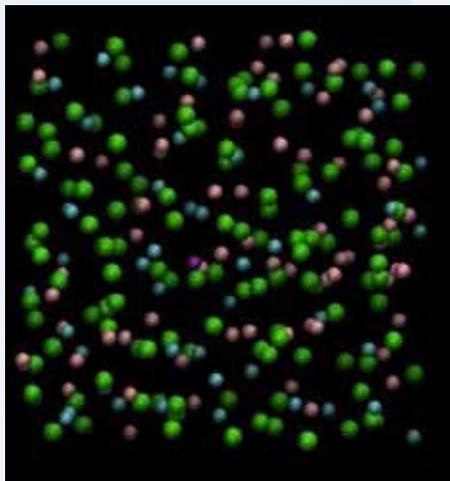
**Cassandra Lutzko**, Maoyan Liu,  
Angus Gray-Weale  
The University of Melbourne

### Free Energy of Solvation for a Uranium ion in the LiCl-KCl Eutectic

#### Abstract

Molecular dynamics simulations of the LiCl-KCl eutectic containing a uranium ion are studied to obtain the free energy of solvation. As opposed to current trends, our method involves the use of classical mechanics to calculate the solvation thermodynamics. Our technique uses a three-step model for the simulations. The first step involves thermodynamically integrating the uranium ion from U<sup>3+</sup> to U<sup>4+</sup> to obtain a free energy of solvation for the oxidation reaction. The second step involves using the Widom

Insertion method to insert a neutral chlorine atom in various locations throughout the eutectic and thus obtain a chemical potential for the insertion. The third step involves using thermodynamic integration for reducing the chlorine atom from ClO to Cl<sup>-</sup> to obtain the free energy of solvation for the reaction. Currently simulations have been done for the temperatures 800K to 2000K.



## Poster 51

**Rowan MacQueen**, Yuen Yap Cheng,  
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### Nanostructured Upconverters for Solar Energy Applications

#### Abstract

The energy conversion efficiency of quantum solar energy collectors is limited by a mismatch between the step-like nature of the band gap and the continuous energy distribution of sunlight. Photon upconversion is one approach to overcome this, where photons with energies insufficient to cause excitation across the band gap have their energies combined, yielding upconverted light that can be absorbed by the collector. Using triplet-triplet annihilation upconversion (TTA-UC), which exploits the strong broadband absorption of molecular chromophores, we have measured small but clear improvements in the output of solar cells under low solar concentration (~several suns). TTA-UC is a bimolecular process, so in order to improve the efficiency under one-sun illumination we are working to dramatically increase the chromophore density. This necessitates a move to solid materials, where we use nanostructured scaffolds to support high loadings of chromophores while impeding aggregation-induced quenching. To this end, mono-carboxylic acid tetrakisquinoxalino palladium porphyrin was coupled to silica nanospheres functionalised with aminopropyltrimethoxysilane using peptide coupling chemistry. Kinetic studies of the functionalised silica were carried out, and the results

compared to free dye solutions at equivalent concentration. The phosphorescence lifetime of the dye was longer when tethered than in solution, suggesting a disruption of aggregation. Quenching of the porphyrin sensitizer by rubrene emitter was slightly slower in the tethered system, likely due to hindered diffusion. The output of an amorphous silicon solar cell was enhanced by the tethered upconverter system, but unremarkably so. We are working to improve the dye loading and kinetic parameters of the tethered-dye TTA-UC system. Initial challenges and results from this venture are reported.

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## Poster 52

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2. Monash University, Melbourne, Australia

### In situ High-Resolution Raman Imaging of Erythrocytes from Whole Blood

#### Abstract

In the presented studies, red blood cells (RBCs) from whole blood were studied using confocal Raman microscopy. High-resolution Raman imaging of the RBCs in thin smears of whole blood as well as RBCs in buffered solutions enabled us to obtain spatial information on the oxidation states of haemoglobin (Hb) inside the cells. The excitation of RBCs using 488 nm and 532 nm laser gave an enhancement of Raman signal of the Hb chromophore through the

pre-resonance with the Soret band and Q band, respectively.

High-resolution Raman imaging of thin smears of whole blood shows the existence of a thin outer layer of haemoglobin in RBCs, where the Fe<sup>3+</sup> state of the haem dominates. The Fe<sup>3+</sup> layer may protect the internal parts of RBCs from oxidation. Such behaviour of RBCs may also suggest that in air-dried blood preparations haemichrome is created on the outer surface of RBCs, while haemochrome resides inside the cells. The interactions with blood plasma show that carotenoids may have an impact on the oxidative processes in RBCs. Moreover, it was possible to observe the oxidation of the haem iron in situ of RBCs treated with different external oxidants and reductants. To fully understand and evaluate the results obtained from thin smears, the measurements of functional RBCs in buffered solutions are compared

#### Acknowledgement:

This work was supported by the European Union under the European Regional Development Fund (grant coordinated by JCET-UJ, POIG.01.01.02-00-069/09) and Go8 European Fellowship.

## Poster 53

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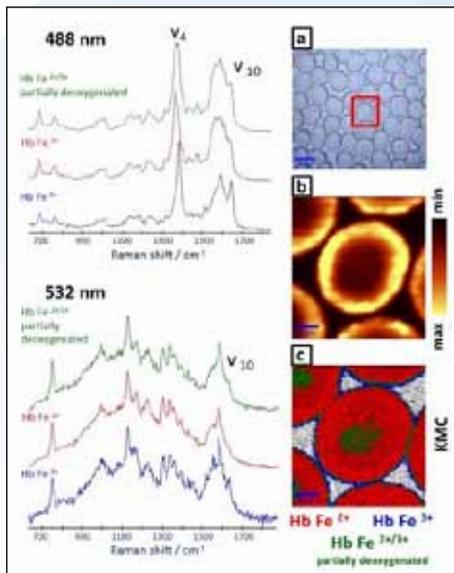
### Ramps: A new type of basis function for faster quantum chemistry calculations

#### Abstract

Gaussian basis sets are ubiquitous in computational chemistry due to their unparalleled mathematical properties. However, Gaussians have no cusps and their use is an inefficient way to model the cusp and core region of real orbitals; this leads to a undesirably large number of Gaussians in conventional basis sets to describe the core region, which is generally chemically unimportant. We propose the introduction of a new type of basis function, namely a ramp, which has the basic form:

$$\phi_n(r) = (1-r)^n, 0 \leq r \leq 1$$

Ramps have cusps at the origin, but decay entirely at 1 bohr. This allows many of the new integrals involving ramp basis functions to be calculated via interaction of the multipole moments or even neglected entirely, in stark contrast to the difficulty of calculating integrals involving the cusped Slater functions that were historically used before the introduction of Gaussian basis sets. Modelling non-concentric ramp-Gaussian shell pairs as a sum of ramps further simplifies two-electron integrals because this means that only two-center integrals are required, as is the case for two-electron integrals using Gaussian-only basis sets after application of



**Fig. 1** (a) Microphotographs of the (a) fresh human RBCs (full blood, smear on the CaF<sub>2</sub> slide) with the labeled (red) investigated area; (b): Integration maps of Hb bands in the spectral region of 1350-1380 cm<sup>-1</sup> (v<sub>4</sub>, for 488 nm laser wavelength); (c): The K-means Clustering (KMC) results with the 3 main classes of dominance of Hb Fe<sup>3+</sup> (blue), Hb Fe<sup>2+</sup> (red) and partially deoxygenated Fe<sup>3+</sup>/2<sup>+</sup> (green). The spatial resolution was equal to 0.33 μm. The average spectra of the respective 3 classes from the K-means Clustering (KMC) were obtained with the use of laser wavelengths of 488 nm and 532 nm (spectral resolution of 3 cm<sup>-1</sup>).

the Gaussian product rule and Boys differentiation. Efficient basis sets can be formulated by combining localized ramp functions, for the treatment of nuclear-electron cusps, with Gaussians, for the intermediate and valence regions. These mixed ramp-Gaussian basis sets have far fewer primitive basis functions than the standard Gaussian basis sets. As integral evaluation and code development for these new classes of integrals is optimised in the future, these smaller mixed basis sets may have the potential for faster calculations without limiting the ability of the basis set to describe the chemically important valence region. With this methodology, we develop a preliminary efficient Fortran implementation for Hartree Fock calculations involving a mixed ramp Gaussian basis set. In conventional notation, this involves the replacement of the "6" in the 6-31+G basis set by a "R" (1 ramp and 1 Gaussian) along with calculation of all required integral types. Consequently, we present results for small molecules to demonstrate that these mixed basis sets reproduce the chemistry of their parent basis set.

## Poster 54

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*Joseph Black Building, King's Buildings,  
Edinburgh*

### Using 2-Aminopurine to Study Excitation Energy Transfer in DNA

#### Abstract

Transfer of excitation energy between DNA bases and the fluorescent, modified adenine base 2-aminopurine (2AP) has been shown to occur by using 2AP as an energy acceptor in 2AP-containing dinucleotides and by exciting at wavelengths in the region where the 2AP absorbance is minimal (approximately 260 nm). 2AP emission has been observed at the characteristic wavelength of 370 nm when the dinucleotide samples are excited at 260 nm which suggests that excitation energy transfer is occurring between the donor DNA base and the acceptor 2AP base. Energy transfer efficiencies were calculated from absorption and fluorescence spectra at room temperature it has been found that energy transfer efficiency is only significant in the case of adenine acting as the donor base while in the cases of cytosine, guanine and thymine acting as the donor bases, the energy transfer efficiency is minimal. By freezing the 2AP-containing dinucleotide samples to the low temperature of 77 K, the excitation energy transfer has been shown to greatly increase, thus opening up further work on investigating the fluorescent decay properties of 2AP-containing DNA when excited at 260 nm.

## Poster 55

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2. Center for Free-Electron Laser Science, Hamburg, Germany,
3. Center for Ultrafast Imaging, Universität Hamburg, Hamburg Germany

### A new semi-confocal high-resolution FTMW spectrometer

#### Abstract

A high-resolution, cavity-based, Fourier-transform microwave spectrometer is being commissioned in Hamburg. The spectrometer is based around the COBRA design (Coaxially Oriented Beam Resonator Arrangement [1]). It consists of a semi-confocal arrangement of a

planar mirror and a spherical curved mirror ( $R=2\text{ m}$ ). The molecule source is a pulsed valve that creates a supersonic expansion, which enters the resonator through the centre of the planar mirror. The electronics consist of a 0–20 GHz analogue signal generator (3 in figure 1). A frequency doubler increases the spectral range to 40 GHz. This signal is mixed with a 30 MHz carrier frequency (5) and then coupled to the cavity. The molecular response is amplified (11) and measured by a 12.5 GS/s digitiser (1). The resolution is expected to be on the order of 3 kHz, limited by transit-time and Doppler broadening. This instrument will allow investigations of nuclear quadrupole hyperfine structure, internal rotations and, in combination with a source of cold, slow molecules, chirality effects.

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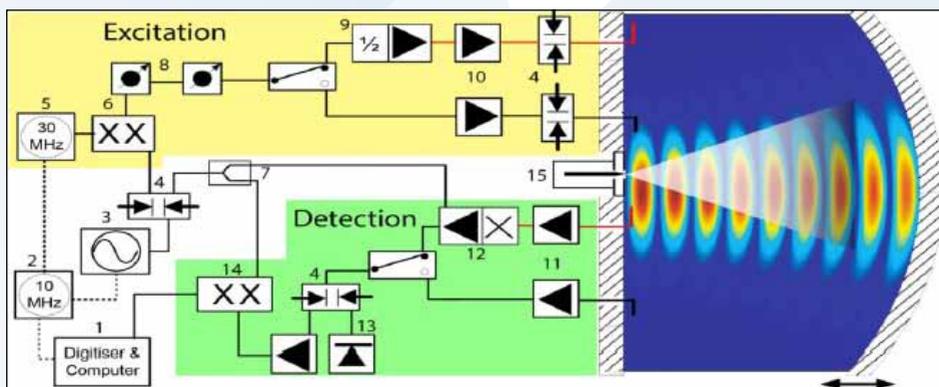


Figure 1: Scheme and block diagram of the electronic setup of the new semi-confocal FTMW spectrometer.

## Poster 56

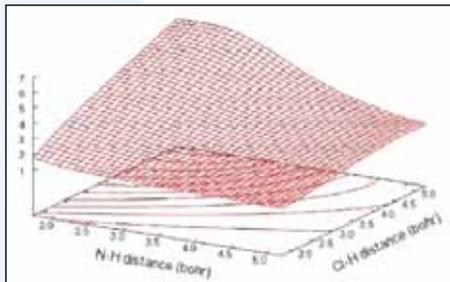
**Michael Morris**, A/Prof Meredith Jordan  
The University of Sydney

### Building Dipole Moment Surfaces with Modified Shepard Interpolation

#### Abstract

An essential component required for the prediction of rotation-vibration spectral line intensities is the molecular dipole moment surface (DMS). Knowledge of the DMS can also be used to predict the first order response of a molecule to an external electric field,<sup>1</sup> as well as the experimental dipole moment, ( $\psi_0$  |  $\mu$  |  $\psi_0$ ).

In practice, DMSs are often constructed using functional forms fit to *ab initio* or experimental data. Constructing an accurate DMS in this manner, however, can be difficult due to fitting errors and errors arising from the nature of the functional form used. Even when a large number of parameters are used in conjunction with high-level *ab initio* and experiment data, problems can persist. In light of such difficulties, it is worthwhile to consider alternative methods for the generation of accurate DMSs. We investigate whether the modified Shepard interpolation scheme of Collins and co-workers<sup>2</sup> is a viable alternative for building accurate DMSs using the water molecule as a test species. Some applications of this scheme are also considered.



**Figure 1.** The DMS of CIH:NH<sub>3</sub> as a function of its C-H and N-H bond lengths.

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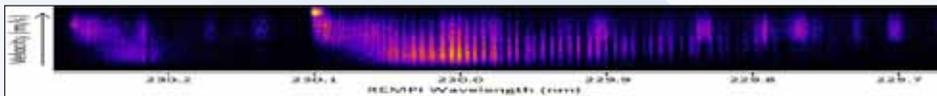
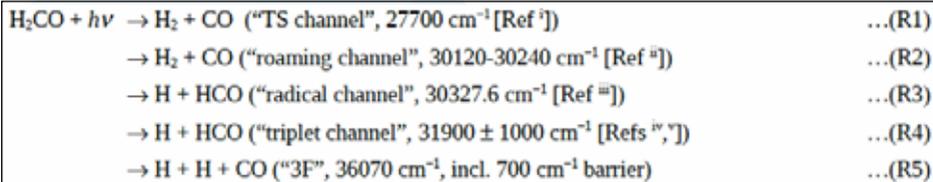
## Poster 57

**Dr Klaas Nauta**, Nicholas Hobday,  
Mitchell Quinn, Gaby de Wit, Duncan  
Andrews, A/Prof Meredith Jordan,  
Prof Scott Kable  
University of Sydney

### Triple-fragmentation of Formaldehyde: using Velocity Map Imaging and 2D REMPI to determine complete photochemical quantum yields

#### Abstract

Formaldehyde, H<sub>2</sub>CO, is a well-studied molecule where its photochemistry is concerned. The S<sub>0</sub>-S<sub>1</sub> absorption spectrum covers a range of ~28,000 cm<sup>-1</sup> to 40,000 cm<sup>-1</sup>, with discrete vibronic structure up to approximately 38,000 cm<sup>-1</sup>. Within that range a variety of photochemical processes can occur. These are listed below with their approximate energetic thresholds.



The first four processes have been well studied, both experimentally and theoretically and are reasonably well understood. The fifth process, triple-fragmentation, was recently investigated by us using Velocity Map Imaging.

With the VMI apparatus we have looked at the velocity distributions of nascent hydrogen atoms as well as rotationally resolved CO fragments as a function of photolysis energy across the entire S1-S0 absorption spectrum. With hydrogen atoms, the velocity distributions show a clear signature of triple-fragmentation at photolysis energies above  $\sim 36,000 \text{ cm}^{-1}$ , while the distributions also allow us to distinguish hydrogen atoms formed in reactions R3 and R4.

Rovibrationally resolved, 2D VMI-REMPI scans of the CO fragment allow us to separate out fragments formed in reactions R1, R2 and R5. Together, the H-atom and CO distributions form a complete picture of the photochemical fate of S1-excited formaldehyde and allow us to extrapolate quantitative branching fractions for all photochemical products. Combined with published total quantum yields for the CO and HCO fragments, we can try to infer the quantum yields for each of the reactions R1-R5 at a wide range of excitation energies.

## Poster 58

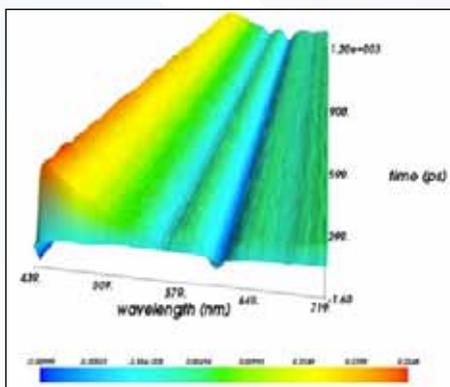
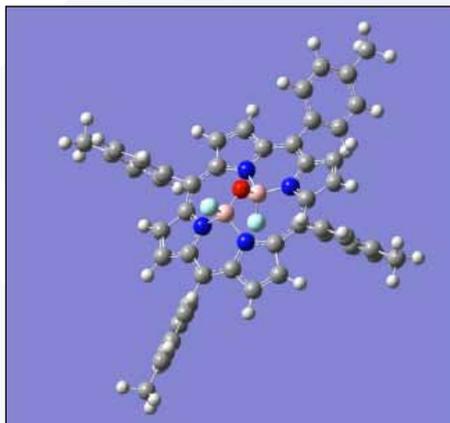
**Nina Novikova**, A/Prof Cather Simpson,  
Prof Penelope Brothers  
The University of Auckland

### Spectroscopic investigation of boron porphyrin/porphyrinoid complexes

#### Abstract

Porphyrin complexes of transition metals and many main group elements have been extensively studied in the past years due to the important roles they play in many biological processes. The number of new applications for porphyrin compounds is increasing continuously in such fields as medicine, photovoltaic devices, biological imaging, polymer materials and oxygen sensing. With this driving the research and with advancements in analytical techniques, a more in-depth examination of porphyrin complexes with semi- and non-metallic elements is underway. Boron porphyrins and boron porphyrinoids in particular are attractive candidates for a wide range of potential applications due to their unique structural features, surprising versatility and unusual

chemical reactivity.<sup>2</sup> The most distinctive feature exhibited by boron porphyrin complexes is coordination of two boron atoms within the cavity of porphyrin macrocycle, where each boron atom is coordinated to two nitrogen atoms. This results in a large tetragonal elongation of the porphyrin ring along the B-B axis.<sup>3</sup> The similarity in structure of some of the boron-porphyrin complexes to the BODIPY dyes used in fluorescent labelling is another feature that offers intriguing potential for the application of these complexes. To examine this possibility, spectroscopic analyses of boron-porphyrin complexes, synthesised by previously reported methods,<sup>1,2</sup> have been carried out using femtosecond transient absorption spectroscopy, fluorescence, IR and Raman spectroscopy as well as DFT calculations. Transient absorption spectroscopy was used to study the dynamics of the transient species by exciting the molecule with a ~100 fs pulse of light at the wavelength corresponding to the Soret and Q band absorptions of those complexes and recording a UV/Vis absorption spectrum at a series of time delays after the excitation. The results from this study will be presented and discussed.



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[3] Brothers, P. J., *Chem. Commun.* 2008, 2090-2102.

## Poster 59

**Gerard O'Connor**, Dr George Bacskay,  
Gabrielle Woodhouse, Dr Tyler Troy,  
Dr Klaas Nauta, Prof Scott Kable,  
A/Prof Timothy Schmidt  
The University of Sydney

### Jet-Cooled Excitation Spectra of Large Benzannulated Benzyl Radicals: 9-anthracenylmethyl (C15H11) and 1-pyrenylmethyl (C17H11)

#### Abstract

The jet-cooled D1 ← D0 excitation spectra of two benzannulated benzyl radicals (BBRs), 9-anthracenylmethyl (9-AnMe) and 1-pyrenylmethyl (9-PyMe), have been obtained using mass-resolved resonant two-colour two-photon ionization spectroscopy (R2C2PI). Analysis of the spectra in view of symmetry and calculated vibrational frequencies indicate significant vibronic coupling. From the spectrum of 9-AnMe we elucidate significant anharmonicity in the excited state.

This anharmonic behaviour is examined computationally through both TDDFT and ab initio methods. Excited state properties of 9-AnMe and 1-PyMe are examined with reference to the existing spectra of smaller BBRs. Trends in the observed spectra of BBRs allow spectroscopic properties of larger BBRs to be predicted. These predictions suggest the D1 ← D0 transitions of large BBRs are unlikely to be carriers of the diffuse interstellar bands.

## Poster 60

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Clare Henderson<sup>1,2</sup>, Trevor Smith<sup>1,2</sup>

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### Self-Assembled Nanostructures for High Resolution Characterisation

#### Abstract

Self-assembled ordered arrays of mono and binary colloidal systems comprising micro- and nanometre-sized spheres can form patterned nano-structures. These have the potential to be used in many applications including photonic bandgap devices, chemical sensors, biosensors and biomaterials templates. Self-assembled patterned nano-structures also provide excellent test samples for new high-resolution X-ray/extreme ultraviolet (XUV) coherent diffraction imaging (CDI) and super-resolution optical imaging methods. CDI allows images to be reconstructed from X-ray/XUV diffraction patterns of a sample, and optical imaging methods can provide comparable and complementary information if one or both of the binary colloids fluoresces.

In this work we have generated binary colloidal arrays of fluorescent and non-fluorescent particles on silica and silicon nitride substrates. These arrays have been imaged with both XUV CDI in order to characterise the algorithms for the CDI reconstruction process, and structured illumination (SIM) and stimulated emission depletion (STED) microscopy. Each sample exhibits

controllable morphological features or order and disorder on the micro-to nanometre scale. Preliminary CDI experiments using an ultrafast laser based high harmonic generation source confirm that these ordered arrays show promise as test samples for this emerging technique. In addition, with the use of fluorescent spheres, we are able to demonstrate time-resolved fluorescence lifetime imaging and characterise a range of super resolution microscopy methods.

## Poster 61

**Matthew B. Prendergast<sup>1</sup>,**

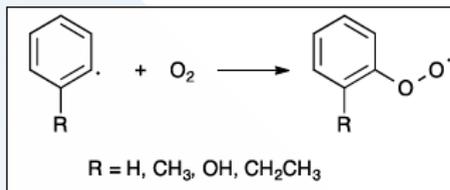
*Benjamin B. Kirk<sup>1</sup>, Stephen J. Blanksby<sup>1</sup>, Gabriel da Silva<sup>2</sup>, Adam J. Trevitt<sup>1</sup>*

1. University of Wollongong,  
2. The University of Melbourne

### Product Branching Studies of ortho-Substituted Phenyl + O<sub>2</sub> Reactions: Experimental and Theory

#### Abstract

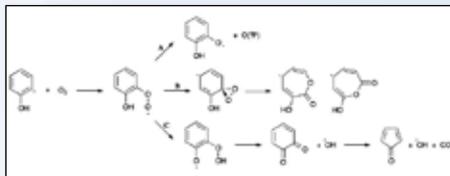
The study of aryl-radical + O<sub>2</sub> reactions is fundamental to understanding combustion chemistry as aromatic hydrocarbons comprise a large fraction of transportation fuels. To comprehend the function of aromatic fuel additives in combustion, and tune performance, detailed molecular understanding of aryl-oxidation is essential. In this presentation we describe the experimental and theoretical investigation of ortho-substituted phenyl + O<sub>2</sub> reactions shown in Scheme 1.



**Scheme 1**

The experimental apparatus employs a reactor flow tube coupled with kinetically resolved photoionisation mass spectrometry. Radical reactions initiated by photolysis in the presence of O<sub>2</sub> (298 K, 4 Torr) are probed using tunable synchrotron radiation (Advanced Light Source, LBNL) and time-of-flight mass spectrometry, with isomer specificity afforded by photoionisation spectra. Quantum chemical calculations and RRKM/Master Equation modelling are utilised to provide additional insight into the oxidation mechanisms and rationalise observed reaction products.

Scheme 2 depicts the dominant reaction pathways predicted for 2-hydroxyphenyl + O<sub>2</sub>. Similar to phenyl + O<sub>2</sub>, pathways A and B are accessible.



**Scheme 2**

The new pathway, C, afforded by the proximity of the hydroxyl-hydrogen, allows for ROO → QOOH isomerization and subsequent OH elimination to produce 1,2-benzoquinone. The benzoquinone species, implicated in coal and wood combustion, undergoes

CO elimination to produce cyclopentadienone. ortho Substitution of phenyl radicals opens up new chemistry and reaction products in aryl-radical + O<sub>2</sub> reactions relevant to combustion.

## Poster 62

**Paul Raston**<sup>1</sup>, *Tao Liang*<sup>2</sup>, *Emmanuel Obi*<sup>2</sup>, *Gary Douberly*<sup>2</sup>

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2. University of Georgia

### Helium Nanodroplet Isolation Spectroscopy of the Hydroxyl Radical and of its Complexes with Carbon Monoxide and Methane

#### Abstract

The hydroxyl radical and its complexes with carbon monoxide and methane have been characterized in cold (0.4 K) helium nanodroplets by infrared depletion spectroscopy. For OH and OD, two sharp Q branch lines were observed, with a separation that indicates a large increase in the  $\Lambda$ -type doubling in helium nanodroplets (relative to the gas phase). From an analysis of the Stark spectrum of the Q(3/2) branch transitions of OH, the  $\Lambda$ -doublet splittings are determined to be 0.198 cm<sup>-1</sup> and 0.369 cm<sup>-1</sup> in the ground and first excited vibrational states, respectively. These splittings are 3.6 and 7.2 times larger than their respective gas phase values. A factor of 1.6 increase in the Q(1/2)  $\Lambda$ -doublet splitting was previously reported for the helium solvated NO radical [K. von Haefen, A. Metzethin,

S. Rudolph, V. Staemmler, and M. Havenith, Phys. Rev. Lett. 95, 215301 (2005)]. A simple model is presented that predicts the observed  $\Lambda$ -doublet splittings in helium solvated OH and NO. The model assumes a small parity dependence of the rotor's effective moment of inertia and predicts a factor of 3.6 increase in the OH ground state ( $J=3/2$ )  $\Lambda$ -doubling when the B<sub>0</sub> e and B<sub>0</sub> f rotational constants differ by less than one percent. Other species probed include the linear OH-CO complex, for which we searched for the weakly bound, higher energy, OH-OC structural isomer, but to no avail., suggesting that it is either relatively unstable with respect to isomerization, or that the long-range interactions in helium nanodroplets guide the molecules to the global minimum (OH-CO) on the associated potential energy surface. The OD-CO complex was also investigated with the hope that the lower zero-point energy might stabilize the higher energy isomer. Stark spectroscopy was performed on this important atmospheric complex, and its analysis shall be presented at the meeting. Addition of CH<sub>4</sub> to OH doped helium droplets results in the formation of the rather floppy OH-CH<sub>4</sub> complex which has a very rich rotationally resolved spectrum. Measurements of deuterated complexes have been made (OD-CH<sub>4</sub>, OH-CD<sub>4</sub>, and OD-CD<sub>4</sub>), the relative line widths of which provide information about the flow of vibrational energy in the complexes, and the line spacings and relative intensities of which provide clues as to the spectroscopic assignment and equilibrium structure.

## Poster 63

**Jason Rigby**, Dr Ekaterina Izgorodina  
Monash University

### New spin-component scaled MP2 coefficients to approximate CCSD(T) for charged systems

#### Abstract

Accurate electronic structure calculations of charged species is a challenging aspect of computational chemistry, particularly when charge transfer and dispersion forces are significant. Density Functional Theory, in most cases, has shown to be poorly suited to the task<sup>1, 2</sup>, both in terms of the charges themselves and accurate dispersion energies. We therefore must resort to fully ab initio correlated methods in order to best account for these interactions. Highly accurate methods, such as Coupled Cluster theory, show poor scalability with molecular size and are typically limited to small molecular systems. An additional bottleneck arises from basis set superposition errors (BSSE) which is usually corrected via the counterpoise (CP) correction scheme by Boys and Bernardi.<sup>3</sup> The CP correction scheme requires a number of time-consuming calculations, which becomes non-trivial for larger clusters. Recently our group has shown that for charged systems such as ionic liquids, CP correction was necessary to closely reproduce CCSD(T)/CBS interaction energies.<sup>2</sup> Spin-component scaled MP2 (SCS-MP2)<sup>4</sup> has been shown to significantly improve energies with respect to high-level CCSD(T) calculations which, when coupled with a triple- $\xi$  basis set, exhibited a fortuitous cancellation of errors for

neutral species<sup>5</sup> and ionic liquids.<sup>2</sup> Therefore, SCS-MP2 can provide a route by which CP correction could be avoided. In this study, we expand upon this by presenting a refined set of SCS-MP2 scaling factors for the parallel and antiparallel spin components, as well as for the scaled opposite-spin MP2 (SOS-MP2)<sup>6</sup> variant, determined by multivariate least squares regression analysis. The spin components of 17 popular basis sets are fitted to counterpoise corrected CCSD(T)/CBS interaction energies of a wide range of ionic liquids including a variety of energetically accessible conformations and validated against the S66/S22 datasets<sup>7, 8</sup> as well as several charge transfer complexes. We demonstrate that while SCS-MP2 methods are sensitive to the choice of basis set, remarkable agreement with CCSD(T) energies below spectroscopic accuracy can be achieved while avoiding costly CP correction.

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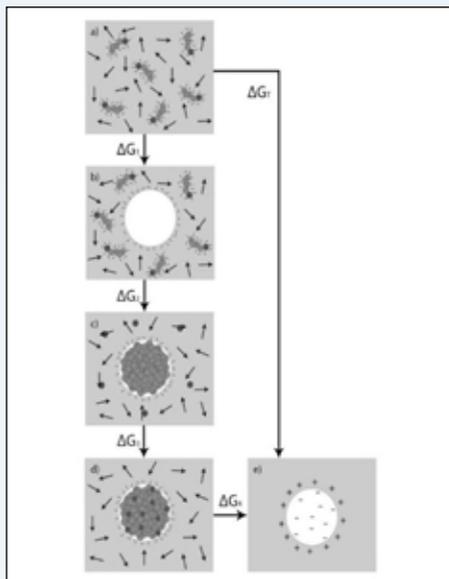
## Poster 64

**Cameron Ritchie**, Dr Angus Gray-Weale  
The University of Melbourne

### Permanent Dipole Correlations Drive Self-Assembly in Various Solvents

#### Abstract

A simple theoretical model for self-assembly consisting of a combination of permanent dipole correlations and a Debye-Hückel approximation was employed to calculate properties of micellation such as the cmc and aggregation number of surfactants. The driving force for micelle formation is described by a series of competing solvophobic, solvophilic and electrostatic steps. We build upon previous work by Chandler et al.<sup>3</sup> and Klein et al.<sup>4</sup> by describing solvent effects with permanent dipole correlations which provides a model for self assembly capable of predicting all known dependences of micelle formation and micellar properties. The theory is validated against experimental data for both ionic and non-ionic surfactants in a number of different solvents. The theoretical calculation of size, salt and temperature dependence of ionic and non-ionic micellation, and a solvent's capacity for self-assembly all agree with experiment. This model allows for calculations of properties of self-assembly where cmc computations become infeasible. Applications of this theory include prediction of new solvents capable of supporting self-assembly, and manipulation of micellar properties to promote desired nano and micro scale structures.



**Figure:** Thermodynamic steps which contribute to micellation

## Poster 65

**Patrick Robertson**, Isabella Lobo,  
Dr Evan Robertson, Dr David Wilson  
La Trobe Institute of Molecular Science

### Conformational analysis of biomolecules in the gas-phase by optical spectroscopy? Don't amide if I do

#### Abstract

Conformational analysis of neurotransmitter and other biologically important molecules and their analogues has significant implications in understanding their biological activity, pharmaceutical design and fundamental character. A number of optical spectroscopic techniques have been used to determine the conformational

preferences of a variety of biologically relevant molecules in the gas phase. Resonance enhanced multi-photon ionisation spectroscopy (REMPI), UV-UV and IR-UV hole burning have identified and assigned a number of unique conformers present in jet-cooled expansions of 4-vinyl imidazole and phenelzine. Comparison of spectral data to ab initio and DFT calculations has assisted in the assignment of conformational preferences in each compound.

## Poster 66

**Charu Rohatgi**

*The University of Adelaide*

### Near-IR Femtosecond Transient Absorption Spectroscopy of Poly(3-hexylthiophene) Nanofibres

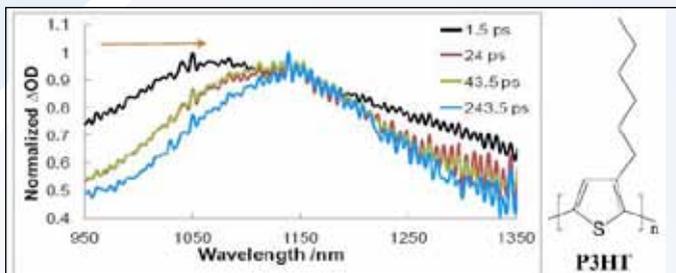
#### Abstract

Exciton generation and charge recombination play a major role in determining the efficiency of an organic solar cell. The investigation into exciton and charge dynamics is therefore an important step towards understanding the ultra-fast photovoltaic conversion. This research aims to investigate the

exciton and charge dynamics in ordered, interconnected poly(3-hexylthiophene) (P3HT) nanofibres<sup>1,2</sup> using femtosecond transient absorption spectroscopy. The high-energy excited states of P3HT nanofibres in anisole were studied via two-pulse/ pump-probe and three-pulse/ pump-repump-probe techniques. The excited-state absorption spectra (Figure 1) obtained from the pump-probe experiment exhibit a broad photo-induced absorption band in the near IR region (approx. 850 to 1450 nm)<sup>3</sup>. The red shift of this absorption band over time indicates the decrease in the energy of singlet excitons. The pump-repump-probe experiment involved generating an exciton population with first laser pulse and then re-pumping these excitons with a second near IR laser pulse to promote them to highly excited states. The results suggest that re-pumping the excitons leads to exciton dissociation to yield free charge carriers.

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**Figure 1:** Excited state absorption spectra for P3HT nanofibres in anisole excited at 400 nm and chemical structure of poly(3-hexylthiophene) (P3HT).

## Poster 67

**Julian Sanelli**, *Dr Nahid Chalyavi*, *Dr Viktoras Dryza*, *Prof Evan Bieske*  
*the University of Melbourne*

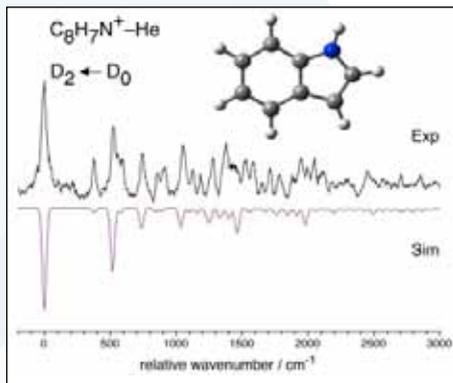
### Electronic Spectroscopy of Cyclic Hydrocarbon Cations in the Gas Phase using Resonance-Enhanced Photodissociation

#### Abstract

Hydrocarbon ions are believed to play an important role in combustion chemistry, where they are found as reactive intermediates in the formation of aromatic rings, and in interstellar chemistry, where they are considered as candidates for carriers of absorption features in the interstellar medium. Despite persistent efforts, there still exist many fundamental cyclic and polycyclic hydrocarbon ions that have escaped spectroscopic characterisation in the gas phase. Examining molecular ions in isolation, free from the perturbing effects of solvent or matrix, is essential for a rigorous understanding of their intrinsic structure and energetics. We have recently recorded the electronic spectra of several cyclic hydrocarbon cations in the gas phase, employing resonance-enhanced photodissociation spectroscopy in conjunction with tandem mass spectrometry. The molecular cations are generated by electron impact on a supersonic expansion seeded with vapour from a suitable precursor. In most cases, the cations are 'tagged' with a weakly-bound rare-gas atom (He or Ar). The parent ion complexes are initially mass-selected using a quadrupole mass filter, then exposed to light

from a tunable laser. Electronic excitation of the molecular cation can lead to rupture of the weak intermolecular bond and release of the rare gas atom following either internal conversion from the excited electronic state or fluorescence to a vibrationally excited level in the ground state. The cation photofragment is mass-selected with a second quadrupole mass filter and passed through to the ion detector. An absorption spectrum is produced by monitoring the photofragment signal as a function of excitation wavelength.

Molecular species studied using this approach include radical cations (e.g., indene<sup>+</sup>, indole<sup>+</sup>, and cyclopentadiene<sup>+</sup>) and closed-shell protonated cations (indeneH<sup>+</sup> and pyridineH<sup>+</sup>). The technique also allows the effects of microsolvation on the ion's electronic transitions to be examined. For example, in the case of pyridineH<sup>+</sup>, we have investigated the effect of microsolvation by H<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub> molecules. Experimental observations are compared with theoretical predictions made using time-dependent density functional theory (TD-DFT). Ground and excited state geometry optimisations and vibrational frequencies are calculated with the B3LYP functional and cc-pVDZ basis set, allowing theoretical simulation of the vibronic spectrum and assignment of Franck-Condon active vibrational modes.



**Figure 1:** *Vibrationally resolved D<sub>2</sub>-D<sub>0</sub> electronic transition of indole radical cation. Experimental (top) spectrum of He-tagged indole<sup>+</sup> in the gas phase; simulated spectrum (bottom) from calculated Franck-Condon factors determined using TD-DFT.*

## Poster 68

**David Scarborough**, Christopher Thompson, Ekaterina Izgorodina  
Monash University

### MCSCF models and competing mechanisms of [4π + 2π] cycloadditions

#### Abstract

Polymeric methanal azine was first synthesised in 1893 and two structures, corresponding to [2π + 2π] and [4π + 2π] cycloadditions, have been proposed. Previous (unpublished) work suggests that there is a preference for the [4π + 2π] cycloaddition mechanism and therefore the polymerisation by this route has been modelled to predict reaction energies and barriers. Computational studies indicate that cycloaddition reactions cannot be

modelled accurately using single reference methods and can proceed by concerted, asynchronous biradical or stepwise biradical transition states, as observed in the iso-electronic butadiene dimerisation system. This research aims to use MCSCF methods to determine the preferred reaction pathway and the effect of dynamic correlation on the calculated MCSCF energies. The first systematic study of the influence of active space and basis set size on the butadiene dimerisation and butadiene-ethene reaction is performed to act as a benchmark for the methanal azine calculations. Active spaces include a minimal to full selection of π orbitals and lone pairs of electrons; encompassing active spaces of (4, 4) through to (14, 14) where relevant. The basis sets STO-3G, 3-21G, 6-31G(d) and 6-31+G(d) are also used. Here we show that dynamic correlation is vital to providing an accurate model of reaction barriers, larger basis sets improve MRMP2 results whilst increasing active space size has little effect, indicating that the inclusion of lone pairs of electrons and all π orbitals in the active space may be unnecessary. The performance of single reference methods is also revisited.

## Poster 69

**Kathryn Schroeder**, Jason Alvino,  
Trystan Bennett, Gregory Meth  
The University of Adelaide

### Photocatalysis of CO<sub>2</sub> and H<sub>2</sub>O using Au<sub>n</sub> cluster doped TiO<sub>2</sub> nanoparticles

#### Abstract

Climate change and decreasing fuel reserves have forced the development of alternative methods of producing energy. One area is conversion of solar energy into chemical bonds, which allows the energy to be easily stored. These reactions do not readily occur. Research has been done into water splitting and CO<sub>2</sub> reduction to methane, methanol or higher order hydrocarbons<sup>1-3</sup>. A catalyst in the form of nanoparticles of the semiconductor TiO<sub>2</sub> has been widely studied for their photocatalytic properties to drive reactions. UV light is harnessed to excite an electron to the conduction band, leaving a valence band hole. The photo-generated electron drives the reaction of CO<sub>2</sub> with protons to form hydrocarbons and the hole drives reactions to split water<sup>4-6</sup>. To improve the efficiency of the TiO<sub>2</sub> nanoparticles, they can be doped with noble metals, which trap photo-excited electrons which reduces electron hole recombination.

Gold clusters, which have different properties to bulk gold, were chosen as the dopant in this study. The atomically precise Au<sub>8</sub>, Au<sub>9</sub>, Au<sub>101</sub> clusters were chemically synthesised and ligand protected. Treatments of the catalysts affect the ligands involved in synthesis of the gold

clusters, and the interactions of the clusters. Post-synthesis treatments involved calcination under pure O<sub>2</sub> atmosphere at 200 °C for 2 h and calcination under pure O<sub>2</sub> at 200 °C for 2 h followed by calcination in H<sub>2</sub> at 200 °C for 2 h<sup>7,8</sup>. Gas phase photocatalysis experiments were undertaken to test anatase TiO<sub>2</sub> nanoparticle catalysts doped with gold clusters. Powdered catalysts were deposited on discs that were placed in the reaction cell, which was connected by a pulse nozzle to an RGA mass spectrometer as part of a vacuum system. Water vapour (~18 Torr) was allowed into the cell and then Ar (for water splitting experiments) or CO<sub>2</sub> (for CO<sub>2</sub> reduction experiments) was pulsed into the cell to 300 Torr. The reaction was illuminated with a 365 nm ± 5 nm UV LED light, with an adjustable power that has a maximum of ~38 mW illuminating the catalyst disc. The reaction was monitored over time by the RGA mass spectrometer to determine the reaction rate of over time. The gold catalysts have shown ability to split water by producing hydrogen. Oxygen production has not been seen, possibly due to involvement in other reactions. Anatase TiO<sub>2</sub> with untreated Au<sub>8</sub> gold clusters is shown in Figure 1 as an example of the H<sub>2</sub> production. Comparisons have been made to catalysis with Pt/TiO<sub>2</sub> in the same system.

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Semiconducting tri-block copolymer PFM-F8BT-PFM

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## Poster 70

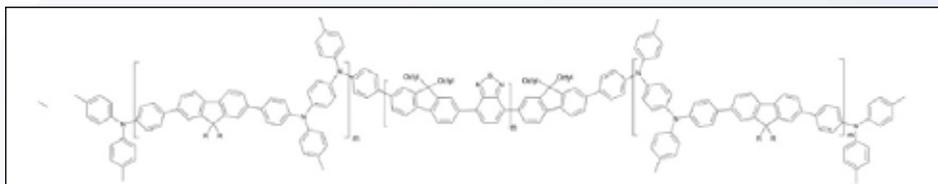
**Kyra Schwarz**, Prof Ken Ghiggino,  
A/Prof Trevor Smith  
The University of Melbourne

### Transient Absorption Spectroscopy of Novel Semiconducting Block Copolymers for Organic Solar Cells

#### Abstract

Efficient conversion of solar energy to electricity in low-cost organic photovoltaic (OPV) devices requires the complex interplay between multiple processes and components over various length and time scales. Exciton diffusion to the donor-acceptor interface and charge transport to electrodes (related to thin film blend morphology) as well as geminate charge recombination are currently regarded as the main loss mechanisms limiting device performance. Novel block copolymers including PFM-F8BT-PFM, synthesised in-house, have been designed to phase separate on the 20-30 nm scale – a domain size ideal for maximising exciton collection at the donor-acceptor interface. Ultrafast transient absorption spectroscopy provides a means of elucidating charge transfer dynamics in a backlog of novel solar cell materials that lack photophysical characterisation. Using a high repetition-rate laser system, polymers are investigated both in solution and as bulk heterojunctions in the solid state with spectral and femtosecond temporal resolution. This work reveals the means by which these new materials can lead to smart design to overcome current obstacles in OPV efficiency.

**Acknowledgement:** We thank Dr David Jones for providing the copolymer sample and ARENA for the provision of a postgraduate scholarship (to KNS) and funding through the Australian Centre for Advanced Photovoltaics.



## Poster 71

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### Phototautomerisation of Carbonyls to Enols at Atmospheric Pressure of N<sub>2</sub>

#### Abstract

The production of enols under atmospheric conditions might have a significant effect on the yield of organic acids in the troposphere, the production of which is generally under-estimated in atmospheric models. For example, vinyl alcohol (VA) will react readily with OH radicals and in a couple of subsequent reaction steps produce formic acid.

Phototautomerisation of common atmospheric carbonyls, such as acetaldehyde, has recently been discovered as a likely source of enols. Previously, we reported the phototautomerisation quantum yield,  $\Phi_{VA}$ , for neat CH<sub>3</sub>CHO [1]. Here we report  $\Phi_{VA}$  under atmospherically realistic conditions of 1 atm of N<sub>2</sub>. Quantum yields for photolysis and phototautomerisation of acetaldehyde were measured at a variety of wavelengths ( $\lambda = 300 - 330$  nm) and pressures ( $P_{acet} = 2-20$  Torr and  $P_{N_2} = 0-760$  Torr). Photolysis was carried out in a static cell, placed inside an evacuated FTIR spectrometer, using a pulsed, frequency-doubled dye laser. The sample was irradiated at 10 Hz, for 7 minutes, whilst recording the FTIR spectrum every 30 seconds.

Stable reaction products were identified by FTIR spectroscopy, revealing the production of primary photolysis products: CO and CH<sub>4</sub>, and secondary products of photolysis to HCO + CH<sub>3</sub>: CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>CO, (CH<sub>3</sub>)<sub>2</sub>CO, and (CH<sub>3</sub>CO)<sub>2</sub>. The primary phototautomerisation product: vinyl alcohol, VA (CH<sub>2</sub>=CHOH) was observed at all wavelengths and pressures. In addition, the production of 1-propanol (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH) was observed, which was attributed to the secondary reaction of VA with primary CH<sub>3</sub> radicals, followed by H addition.

At 1 atm, the quantum yield for VA production increased from ~1% at 300 nm to a peak of 5% at 320 nm, reducing to 1% again at 330 nm. When the production of 1-propanol is included, the overall phototautomerisation quantum yield was as high as 17% at 320 nm and 1 atm N<sub>2</sub>. In general,  $\Phi_{VA}$  increased as N<sub>2</sub> pressure was lowered, with a maximum of  $\Phi_{VA} = 23\%$  for irradiation of 10 Torr of neat CH<sub>3</sub>CHO at 320 nm.

The photolysis quantum yield,  $\Phi_{ph}$  was determined to be between 5 and 80% depending on pressure and wavelength.  $\Phi_{ph}$  was reduced with longer wavelength and with increased pressure of N<sub>2</sub>. Our values of  $\Phi_{ph}$  are in broad agreement with previously published values by Horowitz and Calvert [2] and Moortgat and co-workers [3].

If photo-tautomerization is a general feature of aldehyde and ketone photochemistry then this mechanism may provide the origin of the missing organic acid yield in atmospheric models.

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## Poster 72

**Dr Alessandro Soncini**

*The University of Melbourne*

### Vortex magnetic states in frustrated molecular metal rings: towards single-molecule spin torque effects despite the weak spin-orbit coupling

#### Abstract

A theoretical model for sequential spin tunnelling through frustrated antiferromagnetic molecular rings in the weak spin-orbit coupling (SOC) limit is presented. The metal rings are shown to support vortex magnetic states (toroidal spin states), originating from the interplay between strong frustrated exchange interactions and weak spin-orbit coupling. The model predicts that these toroidal states can be harnessed to exert a spin-torque on an input spin-current, inducing an output spin current with opposite spin-polarization. Thus, the proposed model suggests that strong SOC is not a necessary condition to achieve spin torque and spin accumulation in molecular devices, as previously believed.

## Poster 73

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*Prof Harry Ridgway<sup>2,3</sup>, Prof Stephen Gray<sup>1</sup>,  
A/Prof Todor Vasiljevic<sup>1,4</sup>,  
Prof John Orbell<sup>1,4</sup>*

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2. AquaMem Scientific Consultants, New Mexico, USA,
3. King Abdullah University of Science and Technology, Kingdom of Saudi Arabia,
4. Victoria University

### Predicting the outcomes of oxidising processes: The development of a QM/MM hybrid simulation method

#### Abstract

The use of chemical oxidants is a common feature in the treatment and preparation of drinking water. These agents - commonly ozone, chlorine, chlorine dioxide and chloramines - are utilised for two properties; they have the capacity to both remove microorganisms (i.e. disinfection) and oxidise organic molecules. The ability to oxidise organic molecules is an important feature, as this allows for greater control of water quality parameters such as taste and odour control, as well as removing - or, at least, transforming - potentially harmful micropollutants which are present in many surface waters. Organic compounds of particular importance are pesticides, endocrine disrupting compounds (EDC's) and pharmaceuticals and personal care products (PPCP's); all of which are commonly found in the surface waters that undergo treatment to produce drinking water.

However, due to the typically slow reaction rates for the oxidation of these organic compounds, the dose of oxidant (concentration and/or contact time) used in treatment plants is frequently not sufficient to completely remove all of the potentially harmful EDC and PPCP molecules from solution, leading to the generation of transformation products (TP's). The TP's of certain compounds have previously been shown to display enhanced toxicity and/or estrogenicity, compared to the parent compound, which generally is assumed to be due to chlorination (in cases where a chlorine-based oxidant is applied). Many attempts have been made experimentally to determine how partial oxidation affects the toxicological and/or endocrinological profiles of selected EDC's and PPCP's, as well as attempting to identify which TP's are produced and, ultimately, responsible for this change in observed activity. Whilst there have been a number of experimental studies that have successfully identified stable TP's following oxidation, it is unclear whether these products represent the full gamut of TP's, given the wide use of solvent extraction techniques and chromatographic separation analysis; techniques which some generated products may not be suitable for.

In order to provide further insights into the potential reactions occurring, and hence TP's being produced, when organic molecules are partially oxidised, a novel theoretical method has been developed and is currently under evaluation. This method, which the team has named 'Stepped Forced Molecular Dynamics' (SFMD), is an iterative method that combines dynamic quantum chemical

calculations of the potentially reactive species, with a molecular mechanics treatment of the surrounding milieu. This SFMD method will be detailed here, along with some of the initial benchmarking work completed using this SFMD method to study reactions of 1,4-dioxane with hydroxyl radicals.

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## Poster 74

**Patrick Tapping**, Dr Tak Kee,  
Dr David Huang  
The University of Adelaide

### Simulation of Energy Transport in Conjugated Polymer Systems

#### Abstract

Conjugated polymers are organic semiconductor materials that possess interesting optical and electronic properties and thus have applications in organic optoelectronic and photovoltaic devices. In a conjugated polymer solar cell, photoexcitation of the polymer produces an exciton – a delocalised excited state – that must migrate to the donor-acceptor interface for the energy to be harvested as electricity. The primary mechanism for exciton transport is through a resonance energy transfer process, where the exciton “hops” between spectroscopic units. The efficiency of the migration is heavily dependent on the morphology of the polymer domains, so an accurate simulation of energy transport therefore requires realistic representations of these systems.

In this research, realistic structures of a polymer commonly used as the electron donor in organic solar cells, poly(3-hexylthiophene) (P3HT), are generated using a coarse-grained molecular dynamics model, in which groups of atoms from an accurate atomistic model are mapped onto a smaller set of coarse-grained sites. Energy transport through these systems is then simulated using a fully quantum mechanical model of the exciton. The simulations produce results that can be directly compared to experimental data, including time resolved fluorescence, fluorescence anisotropy and steady-state absorption and fluorescence.

Importantly, the simulations can highlight phenomena that are difficult to observe experimentally, such as the exciton diffusion pathways and location of "trap" sites – areas where the exciton movement is hindered, reducing the efficiency of a solar cell. Ultimately these simulations provide detailed molecular-level insight into energy transport mechanisms and how they depend on polymer microstructure, which can potentially be applied to the rational design of organic optoelectronic devices.

## Poster 75

**Asya Tawfiq<sup>1</sup>**, Dr Graham E. Ball<sup>2</sup>,  
A/Prof John A. Stride<sup>2</sup>

1. University of Wollongong,
2. University of New South Wales

### Distance dependent parallel interactions of graphene with a variety of aromatic molecules

#### Abstract

The interaction between aromatic species, some containing ring nitrogen atoms and substituent fluorine atoms, with graphene - (6,6) – an array of 6 x 6 fused aromatic rings of carbon - has been studied using dispersion corrected density function theory (DFT). The  $\square$ B97X-D/6-31G(d,p) functional/basis combination was employed to probe the interaction as a function of distance between the graphene and aromatic species, along with the faster semi-empirical PM6 method for comparison with a lower level, non-dispersion corrected method.

The energetics of the interaction between graphene and the aromatic molecule when held parallel, that are largely van der Waals' in nature, was investigated. Beyond a separation corresponding to an energy minimum that was found to be dependent upon the nature of the interacting aromatic species, the interaction becomes increasingly weak with increased separation between the graphene sheet and aromatic species. Significant differences in the energies of interaction were observed when changing the group substituents from hydrogen to a halogen such as fluorine.

## Poster 76

**Sarah Thompson**<sup>1,2,5</sup>,

*Dr Charles Rohde*<sup>1</sup>, *Dr Erin Griffey*<sup>4,5</sup>,  
*A/Professor Cather Simpson*<sup>1,2,3,5</sup>

1. The Photon Factory, 2. School of Chemical Sciences, 3. Department of Physics, 4. Department of Art History, 5. The University of Auckland

### Seeing Red: Using Femtosecond Transient Absorption Spectroscopy to Investigate Photodegradation in Anthraquinone Dyes and Pigments

#### Abstract

Anthraquinones are a family of molecules that share a common 9,10-anthraquinone core structure. In use since around 2000 BC, 1 anthraquinones remain the second most industrially synthesised class of dyes, with applications stretching from their origins as natural artistic pigments and dyes, to synthetic compounds with roles in medicine, solar energy harvesting, clothing and food. In almost all of their applications, both modern and ancient, it is the anthraquinones' interaction with light that makes them useful, whether as a dye, a pigment, or a photosensitizer. This interaction with light, however, comes with the attendant danger of photodegradation and loss of the molecule's desired function. Nowhere is this more obvious than in the case of the natural anthraquinones found in historic red pigments; madder (principally alizarin and purpurin), carmine (carminic acid) and lac (principally laccaic acid A). These anthraquinones were and are highly valued for their intensity

and colour, but notorious for their photolability<sup>2</sup>, the mechanism of which is not well understood. Ultrafast transient absorption (TrA) spectroscopy has been used to evaluate the response of these natural anthraquinone chromophores to light, in order to probe their photodegradation timescales and mechanisms. In addition, the relationship between the molecules' microenvironment and their lifetimes and photodegradation rates has also been examined. The TrA and photodegradation studies presented here represent the first femtosecond time-resolved spectroscopic studies on the majority of these compounds. They indicate that very small structural differences can have a profound impact upon the excited state lifetimes (and by extension, photodegradation) of these chromophores, and show that the relative rates of photodegradation in different anthraquinones may be related to the presence or absence of free protons/hydrogen bonding opportunities in their microenvironment. In the case of madder, the results demonstrate for the first time the ultrafast underpinnings of the long-known disparity in the photolability of the two main components of madder: the reported superior macroscopic photostability of alizarin compared to purpurin<sup>3</sup>.

This work bridges the fields of art and science to work toward a deeper understanding of the fundamental interactions that occur between light and molecular structures. Future work will extend the investigation to cover the molecules' degradation in the solid state and the possibility of photochemical or photophysical physical reversal of degradation.

## Poster 77

**Rhys Tilbury**, Ashley Mulder,  
Michael Walter, Dr Massiliano Massi,  
Prof Mark Buntine  
Curtin University

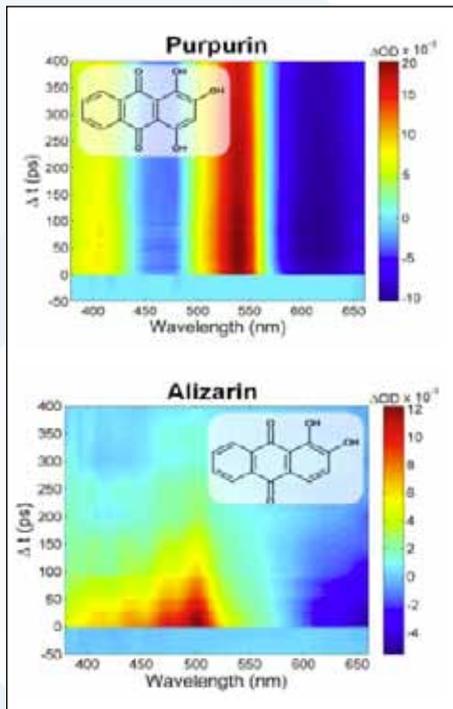
### Ligand-mediated control of the surface plasmon resonance in metal nanoparticles generated by laser ablation

#### Abstract

Metal nanoparticles were generated by the Laser Ablation Synthesis in Solution (LASiS) approach, encapsulated and stabilised by a variety of ligands in solution. The encapsulation ligands were designed and synthesised to allow the attachment of phosphorescent transition metal complexes on their outer shell, whose distance to the nanoparticle core can be varied to facilitate energy transfer between the complex-centre excited state and the surface plasmon resonance of the core. This exploitation of the electronic structure of the nanoparticle surface has insinuations for a variety of photovoltaic applications.

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## Poster 78

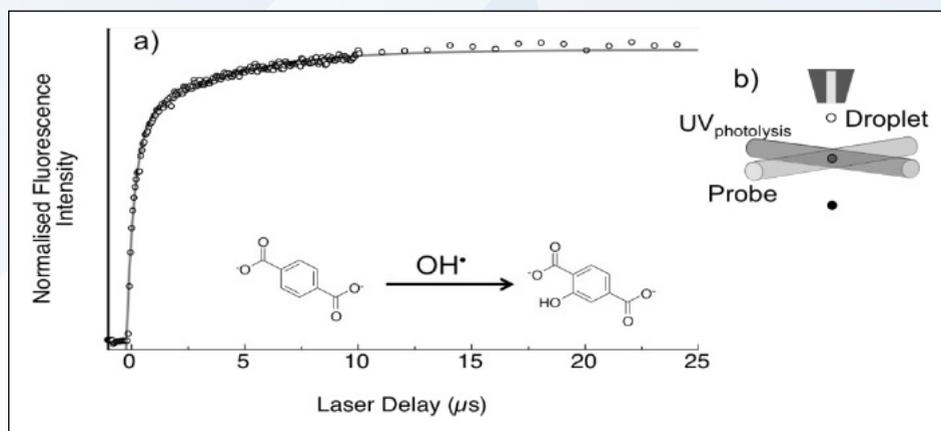
**Bartholomew Vaughn**, Phillip Tracey,  
Dr Adam Trevitt  
The University of Wollongong

### Measuring photo-initiated radical chemistry in single microdroplets

#### Abstract

Aerosol systems are complex chemical environments containing a range of microparticles/droplets that vary in size, shape and composition. Particle sizes extend from the nano- to micrometer scale, providing an environment rich in surface chemistry arising from the high ratio between the surface area and volume. This complicates the fundamental study of aerosol as there is a mix of homogeneous and heterogeneous chemistry. Studying single microdroplets with controllable characteristics provides insight into these single-particle processes without obscurement from ensemble averaging.

This poster will describe experiments that probe OH radical kinetics in free-falling water microdroplets. Using a precisely timed two laser-pulse setup, as shown in Figure 1 (b), radical chemistry is followed by monitoring a growth in fluorescence signal in single microdroplets of water – one at a time – containing known concentrations of a profluorescent molecule, terephthalate, and a hydroxyl radical precursor ( $\text{H}_2\text{O}_2$ ). OH radicals are liberated in solution by a UV laser pulse ( $\lambda = 266 \text{ nm}$ ). Then a second pulse ( $\lambda = 310 \text{ nm}$ ), timed by a scanned delay, irradiates the same droplet exciting the fluorescent product. The resulting fluorescence signal is measured as a function of delay time thus allowing measurement of the kinetics (Figure 1 (a)). Using this technique the kinetics of radical reaction in single droplet are trackable, allowing acquisition of second order rate coefficients allowing comparison with both the bulk system and gas-phase environments.



**Figure 1.** a) Kinetic plot of experiment data (points) and fitted curve (line) showing production of 3-hydroxy terephthalate. b.) Example of the timed laser pulses irradiating a droplet.

## Poster 79

**Dr Yun Wang**, Dr Haimin Zhang,  
Dr Porun Liu, Prof Huijun Zhao  
Griffith University

### Origin of visible-light activity of fluorinated titanium dioxides: A DFT study

#### Abstract

Titanium dioxides (TiO<sub>2</sub>) are prominent photocatalysts for applications in the clean environment and energy fields. Nevertheless, the wide bandgap of TiO<sub>2</sub>-based photocatalysts (3.0 - 3.4 eV) has been one of the major obstacles limiting the practical applications of such materials because their poor sunlight utilization capability. Doping methods are commonly employed to reduce their bandgap to achieve visible-light (VL) activities. Among all doping techniques, the fluorination approach is unique since it does not introduce any intermediate energy band, enabling the retention of high photocatalytic activity of TiO<sub>2</sub>. The fluorination method has been widely accepted as an effective means to enhance the photocatalytic activity of TiO<sub>2</sub>-based photocatalysts. Although a noticeable progress has been made on experimental fronts, the origin of the VL activity of the fluorinated TiO<sub>2</sub> still remains a mystery. On one hand, this could be partially attributed to the controversial experimental observations as not all fabricated fluorinated TiO<sub>2</sub> photocatalysts are VL active. However, on the other hand, this can be largely due to the lack of mechanistic understanding on the origin of the bandgap shrinking of the fluorinated TiO<sub>2</sub>. Therefore, the precise theoretical understanding

on the nature of the VL activity of the fluorinated TiO<sub>2</sub> photocatalysts is of a scientific interest and practical importance, although highly challenging.

In this work, the origin of the VL activity for fluorinated TiO<sub>2</sub> is confirmed for the first time via comprehensive theoretical studies. The 3-coordinated surface F atoms with higher 1s binding energy have been precisely identified to be the VL activity origin by systematically analyzing the 1s core-level shifts (CLSs) of various types of F atoms in the fluorinated TiO<sub>2</sub>. Further analyzing the electronic structures of the fluorinated TiO<sub>2</sub> via semi-local density functional theory and non-local hybrid density functional theory calculations demonstrate that the introduction of the surface 3-coordinated F atoms leads to the formation of Ti<sup>3+</sup> ions in the sub-surface that causes the bandgap shrinking, giving a rise for VL activity. The results also reveal that the presence of 3-coordinated surface F atoms strengthens the adsorption of hydroxyl groups on their vicinity to enhance the photocatalytic activity. The findings of this work address a long-standing scientific question and provide useful guidance for design and development of high performance VL photocatalysts.

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[3] Y. Wang, H. M. Zhang, P. R. Liu, T. Sun, Y. B. Li, H. G. Yang, X. D. Yao and H. J. Zhao, *J. Mater. Chem. A*, submitted.

## Poster 80

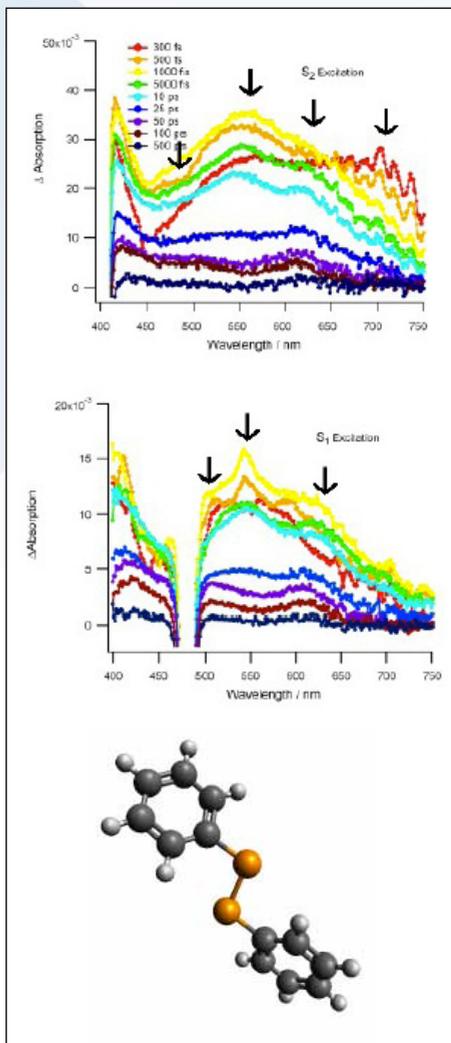
**Xindi Wang, Jennifer Stott,**  
A/Prof M Cather Simpson  
University of Auckland

### Time-resolved resonance Raman spectroscopy of aryl- diphosphenes

#### Abstract

Recent advances in main group chemistry have spurred increased interest in the synthesis and characterization of heavier main group analogues of carbon compounds. This project builds on the work already done by the Simpson group in identifying the phosphinidene analogue of the nitrene fragment.<sup>1</sup> The excited state dynamics of an aryl diphosphene, dmp diphosphene, have been investigated using femtosecond transient absorption (fsTrA) and computationally using the CASSCF method, which have shown the photo-excited S<sub>1</sub> and S<sub>2</sub> states to be mostly P=P in character. The time-resolved resonance Raman experiment will focus on characterising the short-lived species that contribute the absorption bands in the 500-650nm region of the S<sub>1</sub> and S<sub>2</sub> fsTrA spectra with picosecond resolution.<sup>1a</sup> This will ascertain whether the absorptions observed in the fsTrA spectra belong to the same transient species. At the same time, our group is gaining more information about the excited state potential energy surfaces (PES) using various ab initio techniques including CASSCF/CASPT2 and a model diphosphene: diphenyl diphosphene. We have begun to explore the interactions between the lowest excited state and ground

state surfaces and found new conical intersections which are pending characterisation.



**Figure 1.** (a) Peng, H.-L.; Payton, J. L.; Protasiewicz, J. D.; Simpson, C., P=P Bond Photophysics in an Ar-P=P-Ar Diphosphene. *Dalton Transactions* 2012; (b) Payton, J. L. The photophysical behaviour of aryl-diphosphenes and aryl-phosphaalkenes: a theoretical study. Case Western Reserve University, Cleveland, 2010.

## Poster 8f

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Department of Biochemistry and  
Molecular Biology

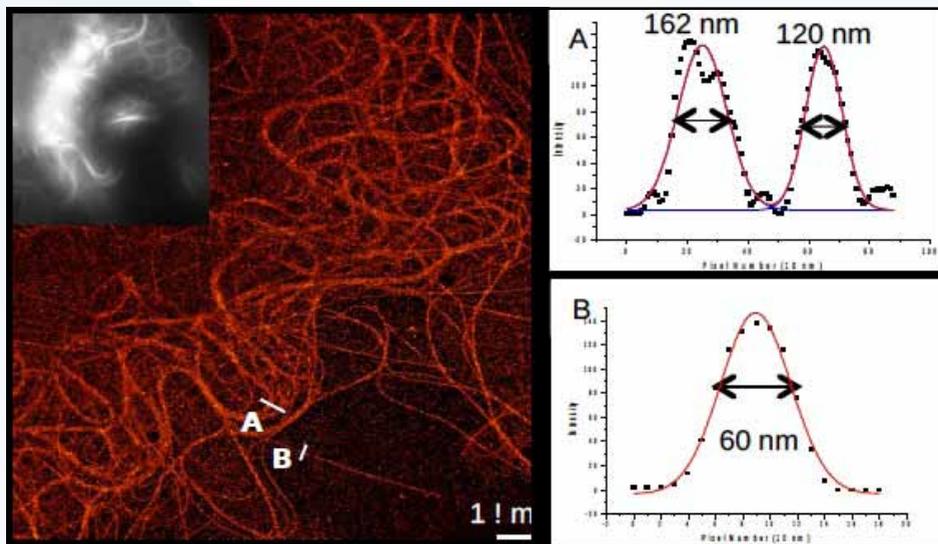
### Super-Resolution Fluorescence Microscopy for Imaging Virally Induced Changes to the Cell Cytoskeleton

#### Abstract

Super-resolution fluorescence microscopy (SRFM) allows sub-diffraction imaging of highly complex nano-structures with a spatial resolution of 10-20 nm routinely achieved. The clear advantages of visualizing nanomaterials and cell structures at a spatial resolution a magnitude improved from conventional fluorescence imaging has resulted in a number of SRFM techniques being introduced internationally over the past decade.

Using off-the-shelf components we have constructed a home-built set-up capable of several of these SRFM techniques.

The single-molecule localization techniques this set-up is capable of obtain SRFM images by detecting the emissions of single fluorophores so that the resulting point spread function distribution of photons can be solved for the precise localization of the emitting molecule. Separation of the fluorophores is achieved temporally by switching the majority of emitters into a temporary dark state and only imaging a small number of emitters at any one time. The most straightforward method for achieving this is called direct stochastic optical reconstruction microscopy (dSTORM (1)) and utilizes high laser flux and a reducing environment to convert fluorophores into a non-emitting state. Tens of thousands of images are then acquired over several minutes with each image showing a different subset of fluorophore PSFs.



Application of SRFM to biologically relevant questions requires extensive optimization of conventional immunostaining protocols of the target molecule as well as of optimization of imaging and buffering parameters. Microtubules (MTs) make an ideal target as they are polymeric in nature and well-established as a SRFM benchmarking protein. They have also recently been indicated as a target molecule for the Rabies virus interferon (IFN)-antagonist protein P3.

Using conventional biochemical methods and diffraction-limited microscopy the association of P3 with MTs and the importance of this association to the lethality and pathogenicity of the virus could be deduced (2). The true extent of MT architectural changes required SRFM. Wildtype P3 was observed to bundle MTs (diameter=50 nm when stained) and induce unusual curvature (diameter of bundles=100-200 nm). An attenuated interferon-sensitive P3 protein of diminished lethality was observed to have less bundling with a lower overall average diameter. A singly mutated P3 protein (N226-H) with known impaired MT-association, nuclear localization and IFN-antagonistic function was observed to cause only slightly more bundling than in control cells. These direct observations of sub-diffraction changes to the structure of the MT cytoskeleton give previously inaccessible insight into the role of the P3 protein in Rabies viral infection. Furthermore, these results demonstrate a spatial-resolution of 10-20 nm on our homebuilt SRFM set-up and the applicability of this new technique to important biological questions.

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## Poster 82

**Andy Wong**<sup>1</sup>, *Prof Don McNaughton*<sup>1</sup>,  
*Dr Dominique Appadoo*<sup>2</sup>, *Ruth Plathe*<sup>2</sup>,  
*Dr Evan Robertson*<sup>3</sup>,  
*A/Prof Sigurd Bauerecker*<sup>4</sup>

1. Monash University,
2. Australian Synchrotron,
3. La Trobe University,
4. Technische Universität Braunschweig

## Infrared Spectroscopy of Ethylene Aerosols using Synchrotron Radiation

### Abstract

Ethylene can be readily found in interstellar media and is one of the many organic molecules formed during photo-chemical reactions in Titan's stratosphere<sup>1</sup> – the largest moon orbiting Saturn. With the exception of Signorell et al<sup>2</sup>, many of the previously reported infrared data have been recorded via the deposition of ethylene onto a cold surface or through matrix isolation<sup>3</sup>. We present here, mid infrared data of ethylene in the aerosol phase using Synchrotron radiation.

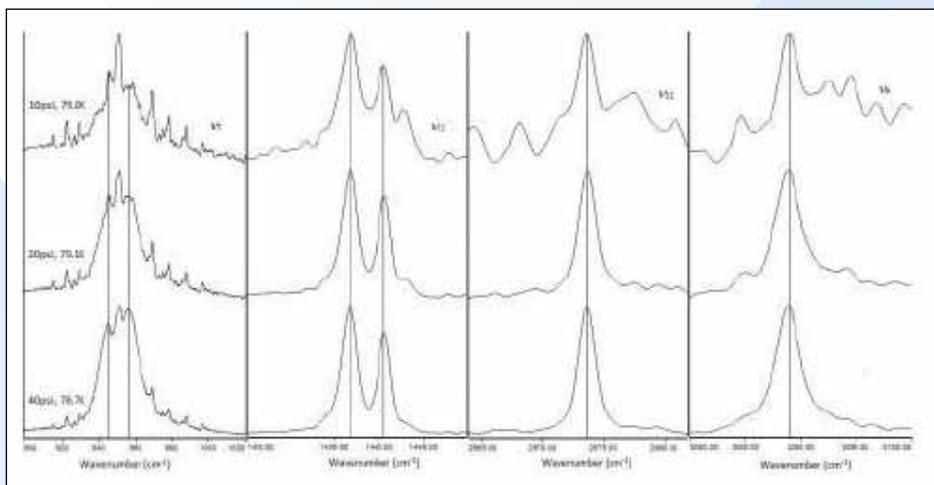
Synchrotron infrared radiation was used to interrogate the physical properties of ethylene particles in the mid infrared region. These

particles were made using the unique instrumental setup at the FIR beamline at the Australian Synchrotron. The fundamental modes:  $\nu_7$  (CH<sub>2</sub> wag),  $\nu_{12}$  (CH<sub>2</sub> def),  $\nu_{11}$  (C-H str) and  $\nu_9$  (C-H str) were the main focusses of this experiment. Band shapes, wavenumber shifts and phase transitions were studied as a function of temperature change, from 5 -7 K, under varying experimental conditions.

**Figure 1:** A comparison of ethylene particles formed at  $78.9 \pm 0.2$  K using 200 mbar of He buffer gas and a sample mixture of 1 % ethylene in He.

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