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Foreword

PhysChem 2019: RACI Australian Conference on Physical Chemistry, Perth, 11–14 February 2019

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Introduction

It is my great pleasure to contribute this foreword for a special issue of the *Australian Journal of Chemistry* which is dedicated to the Australian Conference on Physical Chemistry. The conference was held at The University of Western Australia, Perth, from 11 to 14 February and represented the latest in the roughly biennial series that has been running since 1995. It was the first time that this conference has been held in Western Australia; however, it is of course important to note that the RACI Physical Chemistry Division came into being due to a successfully held national meeting as part of the ANZAAS meeting in Perth in 1974.

Australian Physical Chemistry conferences are a fantastic opportunity for physical chemistry researchers in Australia to refresh old, or forge new, friendships and collaborations, and to share their latest research with a supportive community. In addition, the meetings are also highly valuable for students who are, sometimes for the first time, exposed to the wonderful and world-class physical chemistry research being undertaken in Australia. I still vividly remember attending my first conference in this series, in Brisbane 1998 chaired by Sean Smith, and I highly value the friendships made there and in subsequent meetings. My own students have come away from these events invigorated with a resolve to work harder, excited by brilliant new understandings and ideas, and propelled by the fact that they are not alone in this field in Australia. Sometimes, it certainly may feel this way when we are toiling away as a small part of a larger multi-disciplinary school or university.

The conference in Perth attracted close to 140 participants (most of whom are shown in Fig. 1), and featured presentations from 58 academic staff and 12 post-doctoral researchers, and for the first time in this conference series, 12 short presentations from PhD students in the three minute thesis format (3MT). The conference attracted international delegates from India, France, New Zealand, Germany, Poland, and the USA. There were six plenary speakers, two of whom were recent RACI Physical Chemistry Division medallists (Professor Irene Yarovsky, RMIT (2017) and Professor Michelle Coote, ANU (2019)), included in the 60 conference oral presentations. We were also enticed, entertained, and inspired by the four invited international plenary speakers: Dr Steven Lee (Cambridge University), Dr Johannes Hunger (MPI for Polymer Research, Mainz), Professor Henrik Kjaergaard (University of Copenhagen), and Professor Yunjie Xu (University of Alberta). Several keynote speakers were chosen by the organising committee, and justified their choices with fantastic presentations.

The conference program centred around three broad themes—'Spectroscopy', 'Computational Chemistry' and 'Physical Chemistry of Solutions, Surfaces, Interfaces'—with sessions not dominated by one theme, but with speakers selected using a random number generator – the intention being to showcase the breadth of our field on each day, and within each session. Poster sessions were held over two nights, and it was pleasing to observe the interaction between students, post-doctoral researchers, and academics. Again, I think back to my first conference in this series in 1998 where I presented a poster as an honours student. I drew so much from the advice provided by academics who were willing to spend their time talking with me. At the conference in Perth, poster prizes were awarded to Patrick Kelly (University of Wollongong), Blair Welsh (University of New South Wales), Maggie Corrigan (Sydney University), and Jack Buntine (Melbourne University). In addition, prizes were awarded to the best 3MT presenter from each session (determined by popular vote): Simone Waite (University of Adelaide) and Alexandra Stuart (University of Newcastle). I urge you to keep an eye out for these rising stars on the Australian physical chemistry landscape.

Other highlights from the conference included participation in the IUPAC Global Women's Breakfast (organised by Associate Professor Sarah Masters of Canterbury University, New Zealand), the delightful Jeff Reimers waving and saying 'Hi' to those in the audience whom he acknowledged for their contributions to the work he presented, and the overall sense of goodwill,

Duncan Wild received his Ph.D. degree from Melbourne University in 2003. He was an Alexander von Humboldt and MPI Research Fellow at the MPI for Biophysical Chemistry in Göttingen from 2003 to 2007, and is now a Senior Lecturer at the University of Western Australia. His research interests include laser spectroscopy, the nature of intermolecular interactions, and van der Waals complexes. He also performs ab initio *calculations to support the experiments and collaborates with UWA colleagues to determine reaction intermediates, transition states, and mechanisms in chemical syntheses. With Allan McKinley, he co-chaired the RACI Australian Conference on Physical Chemistry, 11–14 February 2019, in Perth.*

Fig. 1. Participants at PhysChem 2019.

support, and cohesion within our community. The conference was made possible by the generous support of our sponsors, who are acknowledged on the conference website www.physchemperth2019.com.au. I am particularly thankful for the support of The University of Western Australia, Murdoch University, the Perth Convention Bureau, Tourism WA, and of course the RACI.

The remainder of this foreword is an introduction to what you, the reader, will find within this special issue. Contributions have been made by active researchers across Australia in the broad field that is described as physical chemistry, and also from international contributors who travelled to Perth from France, New Zealand, and India. The papers represent a snapshot of the fantastic research being done, and showcases the diversity in our field, at the time of the conference.

Contributions to this Special Issue

In the spirit of the conference, the order of the papers for the special issue was determined using the now (in)famous random number generator!

The first article, 'New Perspectives on Photosystem II Reaction Centres',[1] is contributed by Elmars Krauz and co-workers and describes circular polarisation (CPL) and magnetic CPL (MCPL) optical spectroscopic experiments on isolated photosystem II (PS II) reaction centres (RCs). Energies, exciton couplings, and heterogeneities of the chromophore site are analysed from the data. An anomalous MCPL signal near 680 nm at 1.8 K, inconsistent with exciton coupling of Qy states of either Chl-a or pheophytin-a (Pheo-a), was proposed to arise from transient excited state luminescence, with the state created by photo-induced charge separation within the RC. When CD spectra are compared to modelling of RC preparations with varying pigment numbers, the non-conservative nature of the spectra aligns with 'special pair' pigments PD1 and PD2.

In their article, 'Predicting Octanol-Water Partition Coefficients of Fluorinated Drug-like Molecules: A Combined Experimental and Theoretical Study',[2] Junming Ho and co-workers provide an analysis of several popular empirical fragment-based methods, and quantum chemical solvent models (SMD and SM12) which they compare against a dataset of experimentally determined octanol-water partition coefficients (log P) of functionalised fluorinated compounds (amides, esters, indoles, and ethers). They found that the empirical methods worked the best overall, with the lowest mean absolute deviations, and went on to make recommendations for fast predication of log P for neutral organic solutes with moderate accuracy.

Toby Bell and co-workers present a collaborative effort between Monash University, Latrobe University, University of Würzburg, and KU Leuven. They describe advances in super-resolution microscopy in their paper titled '"Live and Large": Super-Resolution Optical Fluctuation Imaging (SOFI) and Expansion Microscopy (ExM) of Microtubule Remodelling by Rabies Virus P Protein'.[3] A brief outline of the SOFI and ExM techniques is provided, accompanied by results from an investigation into the remodelling of microtubules by rabies P proteins. SOFI allows for the real time visualisation of live cell transfection. This highlight article showcases the rapidly evolving field of super-resolution microscopy and its multi-disciplinary applications.

The next paper in this issue is a contribution from my group at UWA, 'Evidence For a Water-stabilised Ion Radical Complex: Photoelectron Spectroscopy and *Ab Initio* Calculations' and it describes a serendipitous result.[4] In our work, we were initially targeting van der Waals complexes formed between ethanol and halide anions; however, from a chance alteration in ion-source conditions, we produced a novel anion…radical molecule complex. Combining results from the mass spectrometry (peak at 174 *m/z*, rather than 173 *m/z* for $I^- \cdots CH_3CH_2OH$), the observed electron binding energy of the complex (3.54 eV and 4.48 eV), and high level *ab initio* calculations, we were able to conclusively identify the species as $I^- \cdots H_2O \cdots CH_3CH_2^{\bullet}$.

Rosalind Cox and co-workers from Monash University present results for 45 molecules embedded in a poly-(methylmethacrylate) (PMMA) film in their paper 'Electron Transfer in a Naphthalene Diimide System Studied by Single Molecule Delayed Fluorescence'.[5] Forward and reverse electron transfer (ET) rates were calculated from single-molecule fluorescence measurements, and by utilising the Marcus-Hush theory description of electron transfer, they are able to demonstrate that both the variation in electronic coupling and the driving force for electron transfer occurs between molecules in the PMMA film, and also for individual molecules over time.

Using ion-trap mass spectrometry, Adam Trevitt and collaborators follow the reactions between radical cations and ethylene in their contribution 'Barrierless Reactions of Three Benzonitrile Radical Cations with Ethylene'.[6] They have determined branching ratios for the products formed and the kinetics for the reactions, and have suggested reaction mechanisms with the support of quantum chemical calculations. The rate coefficients are in the order of 10^{-11} cm^3 molecule s^{-1}, while the reactions form radical addition and addition-elimination product ions. Pre-reaction van der Waals adducts are of importance, and form with no energy barrier with respect to the reactant energies.

In the first of the theory development or review papers in this special issue, Tim Gould and Stefano Pittalis present 'Density Driven Correlations in Ensemble Density Functional Theory: Insights From Simple Excitations in Atoms'.[7] This work describes the extension of the usual Kohn-Sham formalism to quantum state ensembles that involve ground and excited states. This paper centres on density-driven (DD) correlations, and reports work on atoms with S-P and S-S transitions which indicated that the behaviour of DD correlations depends on orbital angular momentum of the involved states. The approximated DD correlations are comprised of exact conditions, K-S inversion, and assumptions for systems that are weakly correlated.

Franca Jones and Andrew Rohl of Curtin University apply empirical molecular modelling to unravel the effect of organic additives on the inhibition of crystallisation, and the resulting crystal morphology, in their paper 'Using Molecular Modelling to Understand and Predict the Impact of Organic Additives as Crystal Growth Modifiers'.[8] Conductivity data allowed them to determine that the replacement energy correlated well with degree of inhibition, and that this energy can also predict the effect of organic molecules on crystal growth modification.

Following on with the theme of molecular modelling, Konstantin Momot and co-workers have investigated water-like molecules in liquids in their contribution 'Effects of Hydrogen Bonding on the Rotational Dynamics of Water-Like Molecules in Liquids: Insights from Molecular Dynamics Simulations'.[9] The key driver of this work is to better understand the complex reorientational behaviour of water by studying the similarly shaped molecule H_2S which does not exhibit strong hydrogen bonding. The lack of oscillatory behaviour in the simulations, as seen with water, was attributed to the absence of hydrogen bonding in H_2S.

The next paper in the issue, 'Diatomic Rovibronic Transitions as Potential Probes for Proton-to-Electron Mass Ratio Across Cosmological Time',[10] Laura McKemmish and co-workers propose that a suite of molecular probes might be useful in astrophysics for determining proton-to-electron mass variation. They detail how the application of molecular probes is constrained by the available telescopes and, while none of the 11 molecules they studied would be observable, that due to accidental near-degeneracies at higher temperatures, five of the species show promise. This insight allows for screening of all astrophysical diatomics as potential probes, and indicated that CN, CP, SiN, and SiC are promising candidates.

As a freely available paper via Open Access, Tim Schmidt and co-workers provide a review on how the pre-quantum theories of Lewis and Langmuir relate to post-quantum theory of Linnett in their paper 'Electronic Wavefunction Tiles'.[11] The calculation of the wavefunction tile, being a 3N-dimensional repeating structure of the N-electron wavefunction, is reviewed with new results presented for unusual systems and cases such as the bent bonds of cyclopropane, and electron correlation in Be-O-Be. They demonstrate that by analysing the full dimensionality of the wave function, classical chemical concepts which are absent from many theoretical treatments emerge. The work puts previously empirical or conceptual models on a firm theoretical footing.

In the first paper of this special issue from an international delegate to the conference, Elangannan Arunan and Sharon Priya Gnanasekar from the Indian Institute of Science, Bangalore, provide 'A Detailed Classification of Three-Centre-Two-Electron Bonds'.[12] They use the atoms in molecules (AIM) and natural bond orbital (NBO) approaches to evaluate three-centre two-electron (3c-2e) bonds and thereby propose a classification system for these bonds which is based on the way the three centres are bonded and the electron density topology.

Warren Lawrance and Jason Gascooke of Flinders University present the next paper, 'The Case for Methyl Group Precession Accompanying Torsional Motion'.[13] They explain that molecules which contain a methyl group require many more constants than rigid molecules in order to fit high resolution spectra; however, the additional terms have unclear physical meanings. They show, using substituted toluenes as examples, that the dominant contribution to a number of the constants is torsion-vibration coupling, and that a number of the constants required for fitting the spectral data arise from methyl group precession.

David Wilson and co-workers' paper, 'Theoretical Investigation of Main-Group Element Hydride Insertion into Phosphorus-Heterocyclic Carbenes (PHCs)',[14] reports on an investigation of a series of ring expansion reactions involving main-group hydrides and PHCs, thereby forming an expanded heterocyclic ring. The roles of electronic and steric effects on PHCs and their reactivity are elucidated through their systematic computational study.

Sarah Masters' group from the University of Canterbury, New Zealand, provide us with the second paper from international delegates to the conference, 'Utilising the Combined Power of Theory and Experiment to Understand Molecular Structure – Solid-State and Gas Phase Investigation of Morpholine Borane'.[15] They detail the molecular structure of

morpholine borane in both the solid state and gas-phase, using the techniques of single-crystal X-ray diffraction and gas electron diffraction, with the support of computational chemistry. Differences in the molecular structure were observed in the solid state, compared with the gas phase. Following on from this, computational studies were undertaken to explore the hydrogen storage potential of morpholine borane.

Using broadband dielectric spectroscopy (BDS), Claire Lesieur and co-workers from the Institut Rhônalpin des Systèmes Complexe, Lyon, and the University of Lyon investigate the molecular fluctuations of proteins that are essential in sustaining protein folding and function, in their paper 'Analysis of Nanoconfined Protein Dielectric Signals Using Charged Amino Acid Network Models'.[16] The frequency range of BDS makes it suitable for investigating slow motions in proteins, and provides access to fluctuations on different length-scales. The authors also integrate network-based models to offer perspectives on the relationship between local perturbations and larger-scale conformational changes.

The final paper in this special issue, 'Probe Intramolecular Hydrogen Bonding of Stereoisomers Using Computational Spectroscopy',[17] by Feng Wang and co-workers reports on utilising computational chemistry of model stereoisomers to provide fingerprints of intramolecular hydrogen bonding. They find that observables such as infrared band positions and splittings, ionisation energies of core electrons, and valence electron binding energies can be used for this purpose. The test suite for their calculations included the model species ferrocene, methoxyphenol, and furfural.

I close this foreword by extending my heartfelt gratitude to all authors for their contributions to this special issue related to the 2019 RACI Australian Conference on Physical Chemistry. I have thoroughly enjoyed taking on the role of guest associate editor for the issue.

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