

**PLENARY PRESENTATIONS ICP2019**

<b>Code:</b>	Plenary	<b>Abstract Title:</b>	Optical Manipulation in Chemistry
<b>Presenter:</b>	Hiroshi MASUHARA (TWN)	<b>Abstract:</b>	Photochemistry and spectroscopy study various dynamics and mechanism of molecules and materials induced by their interaction with light. Optical force is another interaction between light and matter, which was experimentally confirmed by Lebedev in late 19th century. Utilizing this force Ashkin proposed as "Optical Tweezers" in 1986 and demonstrated high potential in application to bio-science, which was awarded Nobel Prize Physics last year. Optical force was also expected to control molecular motion in solution and eventually chemical reaction. In 1988 we started to explore new molecular phenomena characteristic of optical force by combining optical trapping with fluorescence, absorption, electrochemical, and ablation methods. We have studied on microparticles, microdroplets, nanoparticles, polymers, supramolecules, micelles, amino acids and proteins in solution and reported their unique behavior. The remarkable achievement was performed in 2007 when the trapping laser was focused at solution surface. Various amino acids are crystalized, giving one single crystal at the position where trapping laser is focused and at the time when irradiated. This optical manipulation at solution surface is extended to dielectric and gold nanoparticles and to glass/solution interface. The initially trapped polystyrene nanoparticles at the focus form their periodical structure and scatter/propagate the trapping laser, shifting trapping site outside of the focus and forming a single large circle assembly. Due to intense scattering of the laser by gold nanoparticles, their assembly evolves to swarming where the nanoparticles dynamically fluctuating like bees. These dynamics and mechanism are considered as "Optically Evolved Assembling". In this lecture we will summarize these developments and show high potential of optical manipulation at solution surface and interface in photochemistry and spectroscopy.
<b>Co-Author(s):</b>			
<b>Institution:</b>	National Chiao Tung University		
<b>Code:</b>	Plenary	<b>Abstract Title:</b>	Photochemistry in the Gas and Condensed Phases as Drivers of Environmental Change
<b>Presenter:</b>	Barbara J. Finlayson-Pitts (USA)	<b>Abstract:</b>	Most issues involved in recent years in environmental change, including air and water quality, acid deposition, toxic compounds and climate change, are driven by photochemistry either directly or indirectly. In the atmosphere, there are thousands of individual compounds encompassing both the gas and condensed phases, where the latter includes liquids, solids and multiphase mixtures. This complexity presents special challenges in relating sources and chemistry to impacts. However, understanding the fundamental, molecular processes that occur in such systems is essential for developing reliable predictive models that can be used to develop policy and regulatory options. While important problems remain to be explored in the gas phases, much less is know about processes in and on solids (so-called "heterogeneous chemistry"), in liquids and at interfaces between the phases. This talk will explore some current challenges in elucidating mechanisms of heterogeneous and multiphase chemistry that play a role in air quality, toxic compounds and climate change.
<b>Co-Author(s):</b>			
<b>Institution:</b>	Department of Chemistry, University of California Irvine		
<b>Code:</b>	Plenary	<b>Abstract Title:</b>	UV photoelectron spectroscopy of biochromophores in the gas-phase and in aqueous solution
<b>Presenter:</b>	Helen Fielding (GBR)	<b>Abstract:</b>	Photoelectron spectroscopy is an attractive technique for probing the electronic structure and relaxation dynamics of biochromophores in the gas-phase and in solution. However, the interpretation of solution-phase photoelectron spectra is complicated by inhomogeneous broadening and inelastic scattering of photoelectrons causing the measured electron kinetic energies to be lower than their true values. In this presentation, we will discuss how comparing analogous UV photoelectron spectroscopy measurements in the gas-phase and in aqueous solution can help us to unravel the role of an aqueous environment on electronic structure.
<b>Co-Author(s):</b>			
<b>Institution:</b>	University College London		
<b>Code:</b>	Plenary	<b>Abstract Title:</b>	Ultrafast photo-isomerisation in microbial retinal proteins and biomimetic molecular switches
<b>Presenter:</b>	Stefan Haacke (FRA)		

<b>Co-Author(s):</b>		<b>Abstract:</b>	The ultrafast trans/cis photo-isomerization dynamics and reaction quantum yield of protonated retinal Schiff bases (PRSB) in microbial retinal proteins is known to depend critically on the amino acid composition, but a detailed understanding is still lacking. Through a combined experimental and theoretical investigation of the reaction dynamics of all-trans PSBR in Anabaena Sensory Rhodopsin and its mutants(1-2), we propose that non-adiabatic mixing of the first two excited states (S1 and S2) determine the excited state energy profile (PES), and thus controls the isomerization speed. Since only the reactive S1 has charge transfer character, the reaction dynamics are modulated via the electrostatic properties of the protein environment or by mutation-induced steric effects (3). Remarkably, the same mechanism is operative for the PRSB-mimicking N-alkylated indanylidene-pyrroline (NAIP) photoswitches in methanol (4). Here, substituting the pyrroline moiety with a methyl group introduces a $\approx 15^\circ$ twist of the ground state conformation for Z-1. Quantum chemistry calculations show that S1 and S2 are separated, allowing for a barrierless and ballistic isomerization, leading to low-frequency wavepackets in the ground state. Taken together, both model systems provide now a generalized mechanism for ultrafast photo-isomerization, and confirm predictions for rhodopsin, the visual photoreceptor of vertebrates (5). 1. Marin, M. D. C., et al., J Am Chem Soc 2019, 141, 262-271. 2. Agathangelou, D., et al., Faraday Disc. 2018, 207, 55-75. 3. Roy, P. P.; Abe-Yoshizumi, R.; Kandori, H.; Buckup, T., J.Phys. Chem. Lett. 2019, 10, 1012-1017. 4. Gueye, M.; et al., J., Nat Commun 2018, 9, 313. 5. Luk, H. L.; et al., Proc Natl Acad Sci U S A 2015, 112, 15297-302.
<b>Institution:</b>	University of Strasbourg & CNRS, IPCMS, F-67034 Strasbourg Cedex		
<b>Code:</b>	Plenary		
<b>Presenter:</b>	Graham Richard Fleming (USA)	<b>Abstract Title:</b>	Two Dimensional Electronic Vibrational (2DEV) Spectroscopy A New Method to Observe the Conspiracy of Electrons and Nuclei in Motion
<b>Co-Author(s):</b>		<b>Abstract:</b>	Two-dimensional electronic vibrational (2DEV) spectroscopy includes two optical interactions (UV/Vis) and two infrared interactions. Because of the two different sets of transition moments involved, 2DEV spectroscopy is very sensitive to electronic coupling within molecular complexes, can reveal rapid changes in electronic structure during large amplitude motion such as motion to, and through a conical intersection, and explore whether multi-component reactions such as proton-coupled electron transfer are truly concerted. Because the method, associated theory, and methods of analysis are still being developed this talk aims to illustrate both the potential and complexity of 2DEV spectroscopy via examples taken from photosynthetic light harvesting, a conical intersection system, and a proton-coupled electron transfer system (the latter being a collaboration with T. Moore, A. Moore, D. Gust and co-workers) and a strongly vibronically coupled dimer system along with associated theory and modeling.
<b>Institution:</b>	University of California at Berkeley, Lawrence Berkeley National Lab, Kavli Energy Nanoscience Institute		
<b>Code:</b>	Plenary		
<b>Presenter:</b>	Michael R Wasielewski (USA)	<b>Abstract Title:</b>	Quantum Coherence in Photo-driven Electron Transfer Processes
<b>Co-Author(s):</b>		<b>Abstract:</b>	Quantum coherence has been implicated in natural and artificial photosynthesis and is central to the emerging field of quantum information science (QIS). We will present examples from our recent work in both contexts. First, we will discuss photo-driven electron transfer in donor-acceptor (D-A) compounds that link one donor to one or two equivalent acceptors. Sub-picosecond ET from the lowest excited singlet state of the donor to both acceptors is about 2.5 times faster than ET to one acceptor at room temperature, but about 5 times faster at cryogenic temperatures, resulting from ET to a superposition state of the two acceptors with correlated system-bath fluctuations. Second, we will present our recent results on electron spin state teleportation in an ensemble of covalent organic donor-acceptor-stable radical (D-A-R $\cdot$ ) molecules. Following preparation of a specific electron spin state on R $\cdot$ in a magnetic field using a microwave pulse, photoexcitation of A results in the formation of an entangled electron spin pair D $\cdot$ +-A $\cdot$ -. The spontaneous ultrafast chemical reaction D $\cdot$ +-A $\cdot$ -->R $\cdot$ -> D $\cdot$ +-A-R- constitutes the quantum measurement step necessary to carry out spin state teleportation. Quantum state tomography of the R $\cdot$ and D $\cdot$ ++ spin states using pulse electron paramagnetic resonance spectroscopy shows that the spin state of R $\cdot$ is teleported to D $\cdot$ ++ with high fidelity. This result affords the possibility that chemical synthesis can create complex nanostructures for QIS applications.
<b>Institution:</b>	Northwestern University		
<b>Code:</b>	Plenary		
<b>Presenter:</b>	Christy F. Landes (USA)	<b>Abstract Title:</b>	Super-Resolved Protein Dynamics at Nanoscale Interfaces
<b>Co-Author(s):</b>		<b>Abstract:</b>	Understanding nanoscale protein dynamics at interfaces is crucial for topics ranging from disease inception to drug delivery to separations science. Recent efforts by our group and others have shown the promise of applying single molecule methods to link mechanistic detail about protein adsorptions to macroscale observables. Although the best super-resolution methods achieve high 2D spatial resolution, the temporal resolution remains low. We developed a new phase mask that provides 3D super-localized spatial information while simultaneously improving the temporal resolution of traditional cameras by 20 times. This improvement is achieved by rotating a new stretching phase mask in the Fourier plane during data acquisition and then recovering the temporal information by fitting the PSF orientations. The feasibility of this technique is verified with both simulated and experimental adsorption/desorption and transport. When STRem is applied to measure protein adsorption/desorption at a nanostructured interface, previously unresolvable dynamics are revealed.

**Institution:** Rice University

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**Code:** Plenary

**Presenter:** Paul Mulvaney (AUS)

**Co-Author(s):**

**Abstract Title:** Surface Plasmon Spectroscopy of Gold Nanocrystals

**Abstract:**

In this talk, I will discuss the emergence of nanocrystals for applications in optical switching, sensing and signal modulation. These potential applications arise from the unusual nature of surface plasmon resonances (SPRs). Surface plasmon resonance frequencies or wavelengths depend on the electron density of the gas, particle size and shape, and also the medium refractive index. I will show that we can modulate the particle response by altering the electron density, through hydrostatic loading and by modifying the refractive index of the medium. We also demonstrate how electro-optical effects lead to a method for direct modulation of light, that could be used in high speed signal processing. I will demonstrate detection of 100 electrons using single gold rods as sensors [1-4] and that directed assembly of nanocrystals into arrays opens up single nanocrystal spectroscopic sensing.

[1] T. Kawawaki, H. Zhang, H. Nishi, P. Mulvaney, T. Tatsuma, "Potential-Scanning Localized Plasmon Sensing with Single and Coupled Gold Nanorods," J. Phys. Chem. Lett. 8, (2017) 3637.

[2] S.S.E. Collins, X. Wei, T.G. McKenzie, A. M. Funston, P. Mulvaney, P., "Single Gold Nanorod Charge Modulation in an Ion Gel Device", Nano Letters, 16, (2016), 6863-6869. doi:10.1021/acs.nanolett.6b02696.

[3] C. Martín-Sánchez, G. González-Rubio, P. Mulvaney, P., A. Guerrero-Martínez, L.M. Liz-Marzán, F. Rodríguez, "Monodisperse Gold Nanorods for High-Pressure Refractive Index Sensing", J. Phys. Chem. Letters 10, (2019) 1587 – 1593. DOI: 10.1021/acs.jpcllett.9b00636.

[4] C. Martin-Sanchez, J. A. Barreda-Argüeso, S. Seibt, P. Mulvaney, F. Rodríguez, "Effects of Hydrostatic Pressure on the Surface Plasmon Resonance of Gold Nanocrystals", ACS Nano, 13, (2018), 498-504.

Acknowledgements: The author acknowledges funding from the ARC through grant CE170100026.

**Institution:** University of Melbourne

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