DCU research project proposals for potential Notre Dame interns – January 2013

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2. Chris J. O'Brien	Chemical Sciences
3. Jens Ducree	Physics/Biomedical Diagnostics Institute [BDI]
4. Lampros Nikolopoulos	Physics/NCPST
5. Enda McGlynn	Physics/NCPST
6. John T. Costello	Physics/Faculty of Science and Health/NCPST
7. Fiona Regan	Chemical Sciences and NCSR

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A collaborative project between Dr Bríd Quilty (brid.quilty@dcu.ie), School of Biotechnology and Dr Mary Pryce, School of Chemical Sciences

Title *- An innovative approach for the photodisinfection of water using novel photosensitisers and sunlight*

Project outline

Photosensitisation of microorganisms was first reported at the start of the 20th century when Oscar Raab observed the phototoxicity of acridine hydrochloride against *Paramecia caudatum* (Raab, 1900). The underlying principal of the technology relies on the activation of a dye or photosensitiser by visible light. Cytotoxic species are generated which kill the cells. The technology was largely ignored until recent times when with the increase in antibiotic resistance, photodynamic antimicrobial therapies were explored in the treatment of antibiotic resistant microorganisms.

The light source used in photosensitisation can be natural sunlight making the technology an interesting option in environmental applications (Ergaieg and Seux, 2009). Furthermore, this is an attractive alternative approach to the traditional disinfection techniques such as chloronation, ozonolysis, irradiation with UV light because it is low cost, low environmental impact and low maintenance. Research continues to design more effective systems for use in environmental applications (Hamblin, 2012). The cytotoxic species generated in the reaction include singlet oxygen and free radicals and differently structured photosensitisers show a variable degree of phototoxic efficiency depending on the composition of the outer layers of the bacterial cell (Lazzeri et al., 2004).

Aims and Objective

The objective of this project is to investigate the efficacy of water insoluble singlet oxygen ($^1O_2$) generating porphyrins for the photodisinfection of water.

The aims are to;

- Screen a range of porphyrins for antimicrobial activity against target microorganisms,
- Optimise the environmental conditions for selected porphyrins and
- Immobilise selected porphyrins and test under optimal environmental conditions.

The student interested in this project should have good microbiological technique.

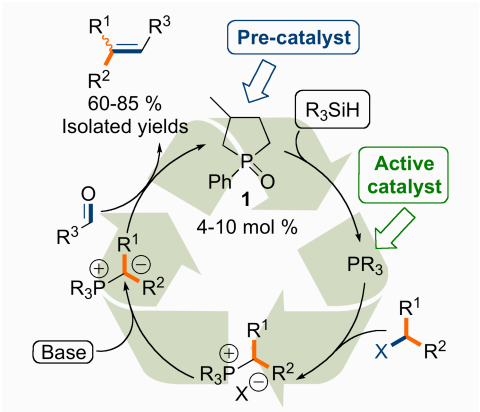
Ergaieg, K. and Seux, R. (2009). A comparative study of the photoinactivation of bacteria by meso-substituted cationic porphyrin, rose bengal and methylene blue. Desalination 246, 353–362

Hamblin, M.R. (2012). Antimicrobial photodynamic therapy and photodynamic inactivation, or killing bugs with dyes and light. Photochemictry and photobiology, 88, 496-498.

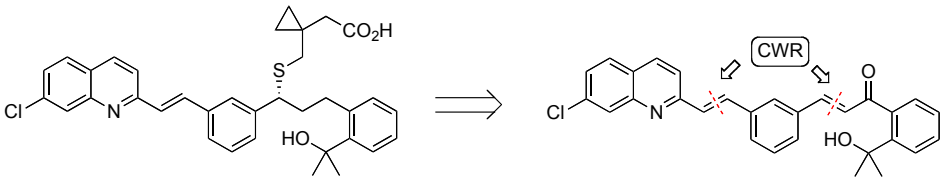
Lazzeri, D., Rovera, M., Pascual, L and Durantini, E.N. (2004). Photodynamic studies and photoinactivation of Escherichia coli using meso-substituted cationic porphyrin derivatives with asymmetric charge distribution. Photochem. Photobiol. 80, 286 – 293.

Raab, O. (1900). Ueber die Wirkung fluorizierender Stoffe auf Infusorien, Z. Biol. 39, 524–546.

Project 1: *Further Development of the Catalytic Wittig Reaction (CWR): Synthesis of montelukast (Singulair)*

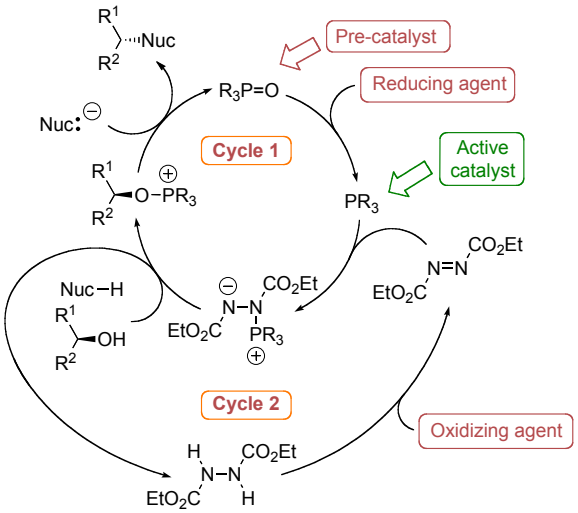


The formation of carbon-carbon double bonds is among a select group of key transformations on which much synthetic chemistry is based. This is not surprising, as the fabrication of many natural products and drugs necessitate their assembly *via* alkenes. Arguably the most important olefination methodology was discovered in 1953 by Georg Wittig and is known as the Wittig reaction. This involves treatment of an aldehyde or ketone with a phosphonium ylide, yielding an alkene with the concomitant generation of phosphine oxide. Nevertheless, the Wittig reaction suffers from several limitations: 1) The current process is stoichiometric; 2) Complete removal of the phosphine oxide byproduct is not always straightforward. The lack of a catalytic protocol, due to cost/benefit, removes from serious consideration the possibility to control the olefination by alteration of phosphine structure. Recently we reported the first catalytic Wittig reaction, above, some 57 years after the parent was discovered. This project will apply the CWR methodology to the synthesis of montelukast (Singulair an anti asthma drug) shown below.



Montelukast

Project 2: *Realisation of a Catalytic Mitsunobu Reaction*



Discovered in 1967 by Prof. Oyo Mitsunobu his reaction is extensively employed in academic and industrial laboratories due to its scope, stereospecificity, and mild reaction conditions. However, like the Wittig reaction the Mitsunobu reaction often suffers from problems related to product isolation and purification. These issues occur due to the formation of phosphine oxide and hydrazine byproducts. Encouraged by our success in achieving the first catalytic Wittig reaction we became interested in whether this methodology could be extended to the Mitsunobu protocol. There are three possible ways the Mitsunobu reaction can be made catalytic: 1) in phosphine; 2) in hydrazine; and 3) in both. The most challenging protocol to develop would be the dual catalytic protocol, which would necessitate a reducing agent (phosphine oxide to phosphine) and an oxidizing agent (hydrazine to azo compound) being present in the same flask! This project will develop a dual-catalytic Mitsunobu reaction as detailed above.

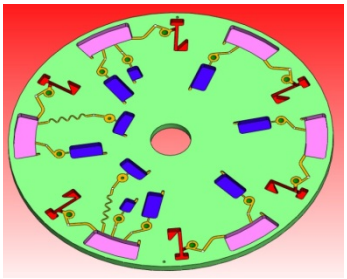
Lab-on-a-Disc Platform

Supervisor: Prof. Jens Ducrée (School of Physical Sciences, DCU)

So-called microfluidic "Lab-on-a-Chip" technologies provide many elegant solutions to common applications, often biomedical related. The design and fabrication of these versatile, credit-card sized labs occurs in highly multidisciplinary teams in which physicists play a pivotal role.

Over the recent years, the microsystems group headed by Prof. Jens Ducrée in the School of Physics has focused on a special kind of lab-on-a-chip platforms. These centrifugal "Bio-Disc" platforms look very akin to commercial CD or DVD systems. However, instead of "playing" charts music, they analyse samples like patients' blood for common disease markers, e.g. in the fields of infectious diseases, cardiovascular function or cancer. The centrifugal force is used to transport the liquid and to sediment particles.

In the project, essential modules for a biological "Compact Disc" will be developed. This Bio-Disc will be designed to carry out complete biomedical diagnostics for later installation in a doctor's office. The CD will be read using an optical reading device similar to a CD/DVD player.



Project work involves the computer-aided design, manufacture and test of new, more optimised systems for finer and improved flow control while studying or even simulating the forces involved in such a complex system. The student will be given the opportunity to acquire hands-on-experience and produce significant scientific results while embedded a highly cooperative team and a world-class facility associated with the world-leading Biomedical Diagnostics Institute (BDI) at DCU.

Background Information

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2. Robert Gorkin *et al*., **Centrifugal microfluidics for biomedical applications,** Lab Chip, 2010, 10, 1758–1773.
3. N. Pamme, *Lab on a Chip*, **6** (2006), pp. 24-38. (on magnetism and microfluidics)
4. www.dcu.ie/microfluidics
5. www.bdi.ie

Naughton Fellowship Project Proposal

School of Physical Sciences, Dublin City University

Lampros Nikolopoulos

Title: Theory of atomic systems under FEL radiation[1]

Scientific background

Coherent radiation in the Vacuum Ultraviolet (VUV) was generated in February 2000 at Deutsches Elektronen-Synchrotron (DESY) in Hamburg, based on the Free Electron Laser technique. It was the first VUV/FEL source in the world, offering coherent radiation in the range of 80 - 180 nm (high energetic photons) with a peak brilliance 10^3 larger than the most modern synchrotron sources existing at that time. Phase II of the FEL started operating in 2005 in the VUV and the soft X-ray wavelength regime from 100 down to 6 nanometers [1]. Until 2009 it was the only available facility of its kind, until another FEL source started its operation at LCLS, California. Since then, other countries are developing their own X-ray sources [Japan-SACLA (2012), Italy-Fermi (2012), Switchzerland-SwissFEL (planned for 2016). Furthermore, in addition of these sources, in Hamburg, through a multinational project a European-XFEL source is under construction (planned to operate 2016) which will provide radiation with unique properties. Briefly, X-FEL will provide coherent radiation in the hard X-ray wavelength (6 - 0.1 nm) with an enhancement of the peak brilliance, compared with the best storage ring-based synchrotrons, of about 9 orders of magnitude and pulse duration is expected to be of the order of 50-100 fs.

X-ray sources are of great importance in a number of research areas not restricted to physics or chemistry sciences (i.e. atomic,molecular physics, clusters, plasma, condensed-matter physics) but to biology and medicine sciences (molecular biology, bioimaging,..). *The fact that this short-wavelength radiation is coherent, intense and of short duration allow to explore, for the first time, new manifolds of states of complex systems (ranging from small quantum systems to large biological structures) in an atomic-scale time resolution down to few femtoseconds.*

More specifically and from the atomic physics point of view, the inside regions of multielectron atomic and molecular systems can be probed by direct interaction of the radiation with the tightly bound electrons of the inner shells. This is in contrast with the radiation in the regime of long-wavelength lasers where only the outer electrons are affected no matter how intense is the field. Therefore, for multielectron atomic systems under FEL radiation the degree of complexity is increased since there is significant probability of exciting inner-shells electrons, additionally to those of the outer shells (optical shells), thus making theoretical approaches based on 'frozen' core-electrons inappropriate.

Research on laser-matter interactions in realistic applications requires in depth knowledge of sophisticated theoretical methods, advanced computational techniques and the ability to make connections between approaches to problems with various settings.

Formally, the dynamics of an atomic or molecular system with N-electrons with an electromagnetic field, at the quantum level, is described by the time-dependent Schrödinger Equation (TDSE) [2],

$$i\frac{\partial}{\partial t}\psi(\mathbf{r}_1,\mathbf{r}_2,...\mathbf{r}_N;t) = \left[H_0 + \sum_{i=1}^{N}\mathcal{E}(\mathbf{r}_i,t)\hat{e}\cdot\mathbf{r}_i\right]\psi(\mathbf{r}_1,\mathbf{r}_2,...\mathbf{r}_N;t).$$

where H_0 is the Hamiltonian of the atomic/molecular system, $\mathbf{r}_i, i = 1,2,...,N$ represent the position of the i-th electron while $\mathcal{E}(\mathbf{r},t)$ represents the time-dependent EM field. From a mathematical point of view the TDSE is a multidimensional partial differential Equation (PDE) in space and time. The dimensionality in space depends on the number of electrons. This latter fact makes almost impossible to solve ab-initio the TDSE, even numerically, when more than 2-electrons are

[1] Free-Electron Laser

involved. In addition, at the current stage of FEL radiation, the field $\mathcal{E}(\mathbf{r},t)$ suffers from strong amplitude and phase fluctuations. The latter characteristic adds an extra complication in the description of the interaction of FELs with atomic systems.

Project description

The purpose of the present project is to study the effects of the stochastic fluctuations of an x-ray FEL field on the dynamics of the innermost 1s-shell electron of the neon atomic system (see Fig. 1). This study will concentrate to the ionization yield and electron's kinetic energy spectrum.

In the present case we'll be following an alternative quantum description of the dynamics, by considering the Liouville equation for the density matrix of the system [3]:

$$i\frac{d}{dt}\rho(\mathbf{r},t) = [H(\mathbf{r},t), \rho(\mathbf{r},t)].$$

The stochastic variations of the field will be modelled as a Gaussian, stationary stochastic processes in the dipole approximation. Thus, the TDDM equations become a system of stochastic differential equations (due to field's stochastic variations) and appropriate techniques needs to be adopted. The assumption of stationarity simplifies considerably the mathematical aspects of the problem and an averaging technique can be followed avoiding the use of alternative, computationally demanding direct techniques (Monte Carlo).

It is worth noting that in viewing, the TDDM equations as a system of partial differential equations the present problem is formally equivalent to stochastic problems that frequently appears in risk analysis of finance market.

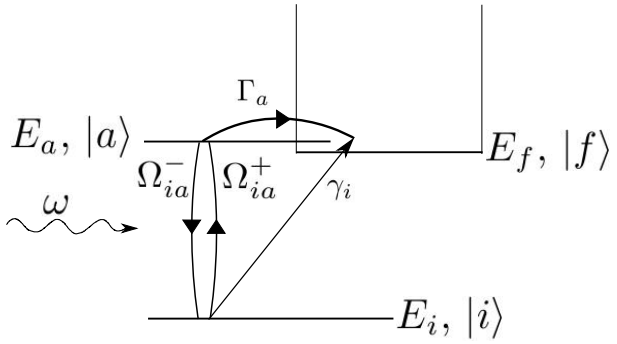

Figure 1: A simplified two-level view of the process that is taking place. The 1s-core electron of neon ($|i\rangle$) interacts with the x-ray radiation of frequency ω and neon is excited to the 3p ($|a\rangle$) state. Two of the most domininant possibilities for the excited electron is to be de-excited back to the ground state $|i\rangle$ or to be ejected (Auger electron) accompanied by a fluorescence photon $\omega_R \neq \omega$ (see refs. [3],[4]).

In solving the stochastic TDDM equations for this system in the x-ray field, the student will work as follows:

1. Will come into contact with the density matrix approach as an alternative of the incomplete description of TDSE in terms of the state wavefunction.
2. Will analytically formulate the density matrix equations in terms of stochastic ordinary differential equations (SODE).
3. Will develop a model for the stochastic variations of the electric field of an the x-ray FEL field.
4. Will write a code for the solution of a system of the obtained SODE.

Skills required: The skills required for the present project is a basic knowledge of the quantum mechanics concepts, programming languages (f77 or f90 or C++ or C) and UNIX/Linux/Mac OSX operating systems. Since, eventually, the project may also depend heavily on the development of a theoretical framework around the solution of the TDDM equation it is suited for students with strong interest in the theoretical/computational aspects of atomic physics.

Keywords strong light-matter interactions, free-electron laser, FLASH,LCLS,XFEL, density matrix, stochastic differential equations, Auger transitions

References

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2 L. A. A. Nikolopoulos and P. Lambropoulos. Helium double ionization signals under soft-x-ray coherent radiation. *J. Phys. B*, 39:883–893, 2006.

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Modelling growth of ZnO nanowires – effects of wire shadowing on growth

Dr. Enda McGlynn, School of Physical Sciences and National Centre for Plasma Science and Technology (enda.mcglynn@dcu.ie)

ZnO is a promising semiconducting material with many exciting applications and a strong propensity to grow in nanostructured form. ZnO nanostructures display a wide range of morphologies which are sensitive to growth parameters such as temperature, substrate type and the method used to generate source species [1]. Because of this sensitivity and morphological diversity, a greater theoretical understanding of the growth process is required in order to reproducibly grow specific ZnO nanostructure morphologies, especially on an industrial scale.

Our group has undertaken a number of theoretical/ computational studies of ZnO nanowire growth via the Vapour Phase Transport (VPT) growth method and reasonable overall agreement between theory and experiment has been found, e.g. in terms of average nanowire properties such as length, diameter etc. [2-4]. However, experimental results also show a substantial degree of scatter in physical quantities such as nanowire lengths [4] and the origin of this scatter is at present still unclear.

One physically plausible possibility is that the scatter in nanowire lengths is related to shadowing effects/competition for available source material amongst closely spaced nanowires and some experimental data support this hypothesis [4]. The summer intern project proposed here is to develop a theoretical/computational model and to test this hypothesis, building on the existing studies performed in our group and adding to these by incorporating the effects of shadowing/competition into those models, e.g. perhaps by Monte-Carlo techniques.

This summer intern project would suit a physics, engineering, materials science or physical chemistry student with an interest in nanoscience and an interest and ability in mathematics and computational science.

Further details can be obtained by contacting Dr. Enda McGlynn by email, at the email address given above.

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Time Resolved Spectroscopic Diagnostics of Laser Ablated Metal Nanoparticle Solutions

John T. Costello, School of Physical Sciences and National Centre for Plasma Sci. and Technol.

Laser ablation, leading to heated and partially ionized plasma plumes, underpins a number of key commercial analytical techniques employed across a wide range of domains including materials science, biopharmaceuticals, security/forensics, environmental monitoring, etc. One example is LIBS or laser induced breakdown spectroscopy. LIBS permits elemental classification and quantification by analyzing the radiation emitted from a laser-produced plasma formed on the surface of (usually) a liquid or solid sample [1]. LIBS can provide a limit-of-detection or LOD for any element in any host, solid or liquid, down to a few parts per million (ppm) [2]. The typical experimental setup for LIBS [3] and stagnation layer formed between two counter-propagating and colliding laser-plasmas is shown in figure 1 [4].

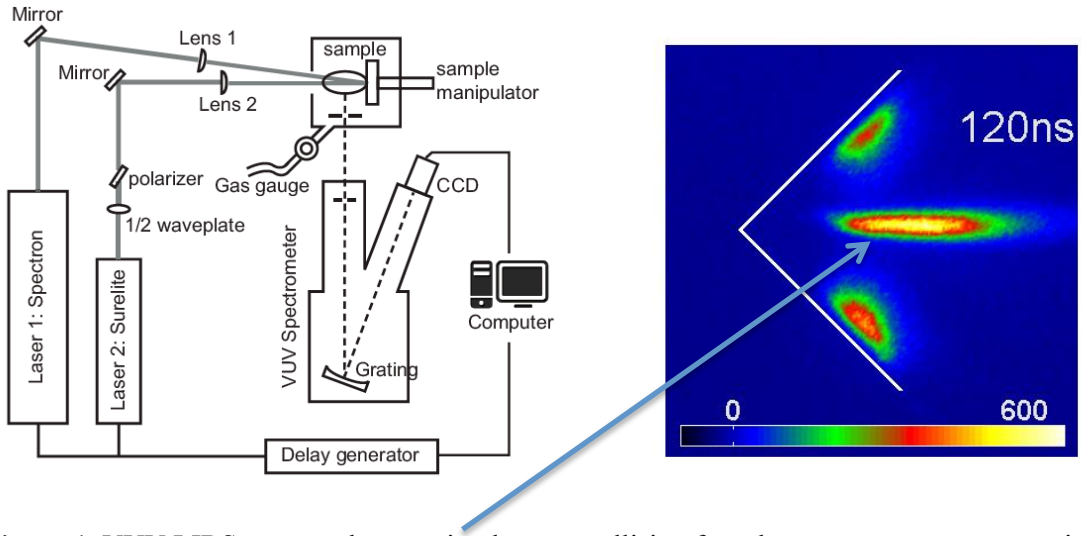

Figure 1. VUV LIBS setup and stagnation layer at collision front between counter-propagating plasmas

Laser ablation of metallic targets submerged in liquids has been the subject of much recent detailed research. The plasma-liquid interaction leads to the formation of significant numbers of nanoparticles [NP] which form a collidial suspension. Although well established as a NP fabrication methodology with even commercial suppliers now in the market [5] there is still little known about the plasma conditions during the early plasma ignition, formation and expansion phases. Working in collaboration with a PhD student at DCU, the main objective of this summer project is to track the key parameter evolution [geometry, temperature, density, etc.] of laser ablated plasmas in liquids from birth to death using time-gated and intensified CCD imaging and spectroscopy [6]. We may also use time-resolved shadowgraphy [7]. If time permits fluorescence lifetime measurements using femtosecond laser excitation [using a Coherent Micra oscillator] with picosecond time resolved spectroscopy [using a Hamamatsu Streak Camera] will also be undertaken. The project is a milestone on the roadmap to the control of key parameters for NP formation in liquids.

References

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Notre Dame Summer Intern Projects

Prof. Fiona Regan, School of Chemical Sciences, Marine and Environmental Sensing Technology Hub, NCSR, DCU
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Project 1 Development of nano-antimicrobial materials for the reduction or prevention of biofouling

Biofouling is a challenge for any devices that are placed in water for any period of time. The development of strategies for the reduction in biofouling is highly desirable.

This project will involve the development of **superhydrophobic materials based on nano-particle technology**. The nano-particles offer anti-microbial potential and also a mechanism of generating a hydrophobic surface. The project will involve synthesis and characterisation of the generated nano materials. Anti-microbial testing will be carried out in the laboratory and in the field. Materials will be assessed for application to surfaces or generation of filter or other extraction materials.

The project is multidisciplinary and the intern will be involved with students in wider MESTECH projects of sensing, data, monitoring, engineering etc,

The School offers a range of equipment such as SEM, NMR, IR, UV suitable for application to the project.

Project 2 Bio-inspired design of novel anti-fouling materials for marine applications

Over the years a number of devices and developments have taken knowledge from nature to improve technologies. Here we propose to investigate surface features of marine organisms, fish and crustaceans that do not undergo fouling to inform us on how to develop novel surface topography for the prevention of fouling on deployed structures. To date we have learned that the surface features of the shark or crab play a significant role in prevention of fouling.

This research will involve a study of marine organism surface features and chemistry. This information will direct the next stage of work in taking features of non-fouled organisms to develop designs for novel anti-fouling materials. The second stage of the work will involve design of surfaces and testing using simple estabished anti-fouling laboratory and field tests.

We will investigate the surfaces of crustaceans and algal samples to indentify marine inspired materials.