Nottingham Raman Microscopy and Spectroscopy Symposium

One-day symposium celebrating the broad ranging applications of Raman spectroscopy and featuring talks from world-leading experts.

Highfield House

University Park

University of Nottingham

Monday 29th June 2015

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1 Programme

The programme has been designed to appeal to both current users and potential future users of the NNNC Raman instrument.

Morning Session

09:30 Registration / Tea and Coffee

09:55 Welcome – Prof. Andrei Khlobystov

Invited presentations

10:00 Dr. Ioan Notinger (School of Physics and Astronomy, University of Nottingham)
"Spontaneous Raman microscopy for biomedical applications: from nanomaterials to live cells and tissues"

10:30 Dr. Ian Hutchinson (Space Research Centre, University of Leicester)
"Raman spectroscopy on Mars: challenges & opportunities"

11:00 Prof. Michael George (School of Chemistry, University of Nottingham)
"UNICAS & Raman spectroscopy – from fundamental science to engineering solutions"

User presentations

11:30 Francesco Tres (School of Pharmacy)

11:40 Jonathan Birchall (School of Medicine)

11.50 Dr Vladimir Korolkov (School of Physics and Astronomy)

12.00 Flash Presentations (Dr. Kim Hardie, Dr. Xue Han, Dr. Raphael Horvath, Dr. Tamara Monti, Yuyoung Shin, David Tiemessen)

12:30 Lunch and poster session

Afternoon Session

Invited presentations

14:00 Prof. Andrew Beeby (School of Chemistry, Durham University)
"Shining light on medieval manuscripts"

14:30 Dr. Paul Pudney (Unilever Research)
"The use of confocal Raman in the fast moving consumer goods industry"

15:00 Dr Cinzia Casiraghi (School of Chemistry, University of Manchester)
"Raman spectroscopy of graphene"

User presentations

15:30 Dr Jonathan Burley (School of Pharmacy)

15:40 Tina Patel (School of Pharmacy)

15:50 Dr Andrew Davies (School of Physics and Astronomy)

16:00 Closing remarks – Dr Graham Rance

2 Abstracts – Oral presentations

Spontaneous Raman microscopy for biomedical applications: from nanomaterials to live cells and tissues

Ioan Notingher

School of Physics and Astronomy, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.

Advances in our understanding of the molecular biology of cells have led to a revolution in the treatment of many diseases, development of a wide range of therapies, as well as fundamental understanding of the links between cell biochemistry and biological function. However, understanding the molecular interactions which are responsible for cellular processes and diseases require new methods for studying biological nanomaterials and imaging of cells and tissues. Such methods must be able to provide detailed biochemical information in biological samples without using labelling or other invasive procedures and be suitable for dynamic molecular processes in live cells.

The talk will introduce the main features of spontaneous Raman microscopy for biomedical studies. Examples of several techniques based on Raman microscopy will be presented as follows:

- Bio-nanomaterials: molecular orientation in individual peptide nanotubes (combined polarised Raman spectroscopy - Atomic Force Microscopy)
- Label-free studies of live cells: from Raman-activated cell sorting of stem cells and time-lapse molecular imaging of cells
- Tissue imaging and diagnosis: towards automated histopathology of skin cancers.

2 Abstracts – Oral presentations

Raman spectroscopy on Mars: challenges & opportunities

Ian Hutchinson

Space Research Centre, School of Physics and Astronomy, University of Leicester, University Road, Leicester, LE1 7RH, UK.

In 2018, a planetary rover jointly developed by the European and Russian space agencies will start its nine month journey to Mars. A primary aim of the mission (called ExoMars) will be to search for evidence of extinct and/or extant life. In order to achieve this, the rover will carry a suite of analytical instruments, including the first Raman spectrometer to be deployed on another planet.

In this talk, we will describe the current status of the mission, discuss the challenges involved in designing and developing a spectrometer for space applications and present results obtained from field studies (that have been recently undertaken in order to verify and optimise the performance of the instrument). In addition, we will also outline a number of ongoing technology development programmes associated with proposals for the next generation of planetary exploration instruments and will discuss potential terrestrial applications for such instruments.

2 Abstracts – Oral presentations

UNICAS & Raman spectroscopy – from fundamental science to engineering solutions

Michael George

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.
Department of Chemical and Environmental Engineering, University of Nottingham Ningbo China, 199 Talking East Road, Ningbo 315100, China

This lecture will aim to cover applications of Raman spectroscopy in both fundamental science and materials characterisation as well addressing engineering problems. In particular we aim to cover (i) monitoring processes using time-resolved Raman measurements to contribute to areas such as solar energy and solar fuels; (ii) monitoring phase behaviour of supercritical fluids for applications in CCS and the production of nanomaterials. In addition, examples from early UNICAS events will be presented highlighting how Raman spectroscopy can be used in a variety of applications particularly in food science, plant science and forensics.

2 Abstracts – Oral presentations

Real time Raman mapping and in-line UV-Vis to monitor the dissolution mechanisms of oral dosage forms

Francesco Tres,[1] Stephen A. C. Wren,[2] Jonathan W. Aylott,[1] Jonathan C. Burley[1]

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A major pharmaceutical challenge is the development of formulations required for active ingredients with low aqueous solubility. Whilst there are strategies which in principle address this challenge, e.g. amorphous solid dispersions, a current limitation is the lack of understanding of the factors which govern the dissolution performance. Raman spectroscopic mapping offers high chemical specificity and ability to readily differentiate between crystalline and amorphous forms and therefore was employed along with in-line UV-Vis to relate changes in dissolution profile to physico-chemical changes that occur to the solid form.

We investigated the dissolution performance of poorly soluble felodipine, bicalutamide and indomethacin formulated as amorphous solid dispersions as a function of drug loading and environmental pH. Raman maps were collected as a function of time using a HORIBA LabRAM HR confocal microscope/spectrometer equipped with an automated xyz stage. For Raman data analysis, the novelty arises from the use of concatenated timepoint maps to create one large dataset which vastly improves the signal:noise ratio in Raman chemical mapping.[1]

Raman maps of the high drug-loaded bicalutamide-copovidone VA64 extrudate generated by multi-variate curve resolution (MCR) of the 16184 spectra collected across a 2946 minutes time-frame indicated that amorphous bicalutamide re-crystallises into polymorphic metastable form II and stable form I.[2] As a result, the drug release profile observed by UV-Vis is limited. To probe the re-crystallisation mechanism, we undertook a kinetic analysis which included first-order rate constants for the processes A → II, A → I and II → I. The analysis distinctly pointed towards a mixed crystallisation mechanism. The appearance of form I directly from the amorphous form is favoured compared to the conversion II → I.

We have demonstrated that Raman mapping offers an alternative method to probe in real time the dissolution performance of amorphous solid dispersions. The dissolution behaviours and mechanisms observed in this work are likely to have significant implications for drug delivery and bioavailability optimisation, and to apply to a wide range of molecular dispersion formulations.

[1] Tres et al. (2014), J. Control. Release, 188, 53
[2] Tres et al. (2015), Mol. Pharmaceutics, 12, 1512

2 Abstracts – Oral presentations

Using Raman spectroscopy to improve hyperpolarised noble gas lung imaging techniques

Jonathan Birchall,[1] Jason Skinner,[1] Hayley Chung,[2] Nicholas Whiting,[3] James Carriere,[4] Linda West,[4] Michael J. Barlow,[1] Boyd M. Goodson[5]

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Ultra-low frequency Raman spectroscopy may be used to perform rotational temperature measurements of nitrogen in spin-exchange optical pumping (SEOP) experiments. SEOP can be used to produce hyperpolarised noble gases such as ^{129}Xe for use in Magnetic Resonance Imaging (MRI) of the human lungs.[1] The SEOP process involves transfer of angular momentum from circularly polarised resonant photons to alkali metal (Rb) electrons, and then onto ^{129}Xe nuclei. This technique results in an enhancement of the net spin polarisation by 4-5 orders of magnitude relative to the thermal Boltzmann polarisation.[2]

Increasing the NMR signal requires maximisation of the available spin polarisation. However, this is made difficult by complex system dynamics and co-dependence of many variables such as Rb vapour density and spin-exchange rate of the ^{129}Xe with Rb electrons. To better understand these dynamics, Raman spectroscopy of N_2 can be utilised to acquire *in situ* rotational temperature measurements.[3] Nitrogen is present as a buffer gas to quench re-emission of photons with random polarisation from the excited states of Rb (radiation trapping) that would lead to loss of polarisation. Our Raman setup uses an in-line pump and probe arrangement with volume holographic grating notch filters to facilitate the detection of Stokes scattering close to the laser wavelength, dramatically improving low frequency Raman scattering resolution.[4] Raman spectroscopy compliments more commonly used techniques within SEOP such as low-field NMR spectroscopy and optical absorption spectroscopy to provide a more complete insight into the energy deposition and transport processes that occur during the SEOP process.

Xenon density affects energy transfer during the SEOP process by increasing the rate of laser absorption, as well as reducing the thermal conductivity of the overall gas mixture.[5] Analysis of the acquired Raman spectra can provide valuable information on the sensitive and constantly changing dynamics of the sample. Obtaining results from optical cells with a variety of ^{129}Xe/N_2 gas mixtures and oven temperatures as functions of cell position and time should provide greater insight into the co-dependence of energy transport mechanisms during the SEOP process. This may further optimise the efficiency of noble gas hyperpolarisation in the future, improving the diagnostic capability of hyperpolarised MRI in the clinical setting.

[1] Salerno et al. (2001), Eur. J. Radiol., 40, 33
[2] Walker and Happer (1997), Rev. Mod. Phys., 69, 629
[3] Hickman and Liang (1972), Rev. Sci. Instr., 43, 796
[4] Newton et al. (2014), Appl. Phys. B, 115, 167
[5] Nikolaou et al. (2013), Proc. Nat. Am. Sci., 110, 14150

2 Abstracts – Oral presentations

Molecular adsorption and organisation on boron nitride and molybdenum disulphide

Vladimir V. Korolkov,[1] Alex Summerfield,[1] James Kerfoot,[1] Simon A. Svatek,[1] Neil Champness,[2] Lixu Yang,[2] Nick A. Besley,[2] Takashi Taniguchi,[3] Kenji Watanbe,[3] Peter H. Beton[1]

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The adsorption of a range of molecules on layered materials has been investigated using high resolution atomic force microscopy (AFM). We have observed several arrangements of molecules which are stabilized by hydrogen bonding including a bimolecular layer formed by perylene tetracarboxylic di-imide (PTCDI) and melamine which form an open nanoporous array in which the planar PTCDI molecules are adsorbed parallel to the substrate. The networks are deposited from solution by immersion of BN and MoS_2 substrates and the ordering may be improved by post-annealing in an inert atmosphere. We have also investigated the adsorption of 5,10,15,20-tetrakis(4-carboxylphenyl)porphyrin (TCPP), a dye molecule with a planar porphyrin macrocycle as its core. This molecule forms an open square array, also stabilized by hydrogen bonding through carboxylic acid pendant groups which steer the arrangement so that macrocycle lies parallel to the surface. In this arrangement the molecular layer is strongly fluorescent showing lines which are red-shifted from solution. When molecules are adsorbed on MoS_2 they form similar structures but the resulting islands are smaller and less ordered, and, due to the smaller band gap of MoS_2, fluorescence is quenched. We also present density functional theory calculations of the conformation of adsorbed molecules and numerical estimates of the hydrogen bonding and adsorption energies. We discuss this approach as a route to the molecular functionalization of two-dimensional materials and the formation of hybrid molecular devices.

2 Abstracts – Oral presentations

Shining light on medieval manuscripts

Andrew Beeby

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Anyone looking at an illuminated medieval manuscript does so in awe of the skills and creativity of the scribes and illuminators. In the past, scholars made educated guesses as to the materials used in manuscripts, sometimes drawing spectacularly incorrect conclusions. The ability to use spectroscopic methods provides unambiguous identification of pigments and hence provides a solid basis for the understanding of pigment and book production technologies of the time.

Any techniques employed need to be non-contact and cause no damage to the precious and often fragile manuscripts. Our methods of choice, reflectance spectroscopy and imaging and Raman spectroscopy all look at light scattered by the pigments, providing unequivocal forensic evidence as to their identity. The exceptionally high insurance valuations of manuscripts effectively prohibits the movement of books to laboratory based instrumentation: equipment has to move to the books. Our early work on manuscripts of Durham Cathedral Library was facilitated by moving cumbersome research instrumentation to Palace Green Library, a luxury not possible for work at other UK libraries.

We have constructed dedicated high-performance instrumentation, designed for portability and flexibility yet retaining research-level sensitivity, readily transported by train or car and requiring minimal set-up time: typically less than 30 minutes. Our capability is exemplified by 15 visits and the examination of over 80 manuscripts in libraries across the UK in the past year, indicating the proficiency of our team. The presentation will focus upon our choice of instrumentation and the results obtained using this equipment from a variety of manuscripts from the 7th to 15th centuries.

2 Abstracts – Oral presentations

The use of confocal Raman in the fast moving consumer goods industry

Paul D. A. Pudney

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In the FMCG industry, there are many challenges from physio-chemical perspective such as understanding individual ingredients properties to whole product structures and also a more recent focus on how products interact with consumers i.e. people. This talk will show how Raman Spectroscopy is in the prime position to contribute to all these areas. I will show examples of natural structure of a food, tomato, manufactured structure, a spread. Then how Raman can be used in-vivo to look at people, where I will concentrate on skin. To understand the uptake into the body of bioactive 'healthy' molecules from fruits and vegetables it is necessary to know where they are located within the original plant structures and what path they take as the plant is processed before consumption. This means not only the location but also the physical state of the molecule e.g. crystalline or solvated, as this affects uptake. I demonstrate how confocal Raman microspectroscopy can be used to follow these changes of the physical state of carotenoids in tomatoes during these processes.[1,2] Emulsions and colloids are the basis of many common products that people buy every day. These have very complex structures on the micron length scale that determine their properties. Quantifying the microstructures of these complex composite soft solid materials presents a great measurement challenge. Confocal Raman spectroscopy has all the attributes to potentially measure these structures quantitatively. It will be shown how Raman can do this by illustrating it with a very complex 'real life' system, a dairy spread, by separating it into component images and how that compares to the optical structure.

Raman has been used for some time now to measure the skin and has now been described to be in the forefront of skin research. I will show how molecules that can benefit these areas of the body can be measured to see if and when they are delivered to the body. The skin benefit agent retinol, which increases the production of collagen synthesis, is shown to penetrate a different amount depending on which delivery vehicle it is in.[3] However many products go on more difficult areas to measure such as the scalp and axilla (underarm). I show how new probe has been built which allows these areas to be measured effectively and gives new insights into these areas of the body. The probe allows the window to be placed against the subject in more curved and recessed areas of subject's body and for them to be more comfortable whilst the measurements take place. The scalp and axilla strata cornea (SC) show significant differences from the 'normal' SC of the volar forearm.[4] For instance, the scalp is observed to have lower amounts of natural moisturising factors (NMF) compared to the volar forearm within the same subjects. Also for both the axilla and scalp the lipids show a change in order as compared to the lipids in the volar forearm and differences from each other. In addition, we have studied the stratum corneum (SC) of dandruff scalp to observe how it compares with the non-dandruff scalp. The dandruff SC has lower NMF than the non-dandruff SC (0.16 compared with 0.39 a.u.), lower hydration, elevated levels of urea and lower levels of lactic acid.[5] Treatment of dandruff with an anti-dandruff shampoo containing 1% ZnPTO for six weeks substantially restores the levels of each of these components close to the non-dandruff levels.

[1] Pudney et al. (2011), Appl. Spectrosc., 65, 127.
[2] Svelander et al. (2011), J. Food Sci., 76, 215.
[3] Mélot et al. (2009), J Controlled Release, 138, 32.
[4] Pudney et al. (2012), Appl. Spectrosc., 66, 882.
[5] Bonnist et al. (2014), J. Cosmet. Sci., 36, 347.

2 Abstracts – Oral presentations

Raman spectroscopy of graphene

Cinzia Casiraghi

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Raman Spectroscopy is the most used technique to probe the properties of graphene. In this talk I will give an overview on the use of this technique to identify graphene, and to probe amount of defects, doping, strain and superlattices.[1-5] If time allows, I will also show preliminary results on ultra-narrow and precise graphene nanoribbons, small stripes of graphene, which could be used in transistors.[6-7]

[1] Ferrari et al. (2006), Phys. Rev. Lett., 97, 18740
[2] Pisana et al. (2007), Nature Mater., 6, 198
[3] Zabel et al. (2011), Nano Lett., 12, 617
[4] Eckmann et al. (2012), Nano Lett., 12, 3925
[5] Eckmann et al. (2013), Nano Lett., 13, 5242
[6] Narita et al. (2014), Nature Chem., 6, 126
[7] Narita et al. (2014), ACS Nano, 8, 11622

2 Abstracts – Oral presentations

Probing phase transitions using low-wavenumber Raman spectroscopy

Jonathan Burley, Aalae Alkhalil, Jagadeesh Babu Nanubolu

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The efficacy of phonon-mode spectral data (20–400 cm^{-1}) in identifying and characterising phase transitions is for the first time compared directly with traditional "fingerprint" intra-molecular spectral data (400–3800 cm^{-1}) for a model molecular system, using a range of statistical approaches and algorithms. Both data sets were collected in the same experiment, allowing a direct comparison.

We find that phonon-mode data offer a reliable method of identifying phase transitions, whereas the intra-molecular are inherently unsuitable. Our results are likely to apply widely to solid-solid transformations. [1]

[1] Alkhalil et al. (2012), RSC Advances, 2, 209.

2 Abstracts – Oral presentations

The effect of co-formulants on dermal uptake – A Raman study

T. Patel,[1] D. Salazar,[2] G. Bell,[2] J. Wright,[2] B. Parr-Dobranzski,[1] A. Ghaemmaghami,[1] P. Williams,[1] C. J. Roberts,[1] F. R. A. J. Rose[1]

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The Organisation for Economic Co-operation and Development (OECD) guidelines on the conduct of *in vitro* dermal absorption investigations have attempted to standardise global practises. However, these have yet to be established for the standard tape stripping methods used to investigate epidermal accumulation due to the large variation in the depth of epidermis removed using these techniques. Thus, there is a strong need to develop alternative methods to investigate compound localisation within skin samples. Confocal Raman spectroscopy (CRS) is a label free, rapid, optical method which allows compounds to be identified within dermal tissue. Here, CRS has been developed to determine testosterone localisation within *ex vivo* 300 µm dermatomed pig skin samples treated with the compound in solutions ((1:1) *v/v*) containing either; emulsogen, propylene glycol or tween 20. A Lab Ra HR CRS was employed for the analysis of the treated skin samples (n=6), using an IR laser at 785 nm and a x50 objective lens coupled with a Synaspe CCD detector. Spectra were obtained from the surface of the skin to a maximum depth of -150 µm (-50 µm increments) at 0, 1, 2, 3, 4, 5 and 6 hour time points to mimic real-time exposure. CRS spectra for the dermatomed pig skins demonstrated good reproducibility with some spectral differences noticed. Spectral intensity decreased with increased depth as expected. Furthermore, it was noticed that the presence of either emulsogen or propylene glycol delayed the absorption of 30.0 mg mL-1 testosterone through the skin. However, tween 20 appeared to increase the rate of compound absorption through the skin samples. Spectra also suggested that the stratum corneum was the main barrier of testosterone absorption. The CRS method has the potential to determine epidermal compound accumulation, ultimately, providing a powerful alternative to in identifying toxic compounds early on.

2 Abstracts – Oral presentations

Raman microscopy mapping at the NNNC

Andrew J. Davies,[1,2,3] Graham A. Rance,[2,3] Sergei V. Novikov,[1] Andrei N. Khlobytstov[2,3]

[1] *School of Physics and Astronomy, University of Nottingham, Nottingham, NG7 2RD, UK*
[2] *School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK*
[3] *Nottingham Nanotechnology and Nanoscience Centre, University of Nottingham, Nottingham, NG7 2RD, UK*

By obtaining a Raman spectrum at a single point on the sample an array of spectra can be built up to obtain a point-by-point map of a sample. Thus, Raman microscopy affords the ability to map the distribution of components of a sample in one-, two- or three-dimensions. This talk investigates some of the ways this powerful technique can be used to yield information on samples illustrated with two examples. In the first example, a flake of graphene was mapped in two-dimensions. The differences in the spectra revealed different regions formed from one, two, three or four layers of graphene. The second example examines how confocal Raman microscopy can be used to obtain a depth map through a sample, in this instance a polymer formed of two layers.

3 Abstracts – Poster presentations

High temperature molecular beam epitaxial growth of graphene on sapphire substrates

A.J. Davies,[1,2] T.S. Cheung,[1] A. Summer,[1] I. Cebula,[1] A.N. Khlobystov,[2] P.H. Beton,[1] C.T. Foxon,[1] L. Eaves,[1] S.V. Novikov[1]

[1] *School of Physics and Astronomy, University of Nottingham, Nottingham, NG7 2RD, UK*
[2] *School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK*

Here we report the growth of graphene using a custom-designed dual chamber molecular beam epitaxy (MBE) system, based on the GENxplor from Veeco. The standard GENxplor has been specially modied by Veeco to reach growth temperatures of up to 1850^{o}C in high vacuum conditions and is capable of growth on substrates up to 3 inches in diameter. Our estimate of the growth temperature is based on a thermocouple reading. In order to calibrate the temperature we have formed graphene on the Si-face of SiC by heating wafers to temperatures above 1400^{o}C. To demonstrate the scalability of the developed process, we have grown graphene on SiC substrate sizes ranging from 10x10 mm^2 up to 3-inch diameter.

We have also grown graphene layers on sapphire substrates using a SUKO-63 carbon sublimation source. Growth at substrate temperatures between 1000 and 1650^{o}C have been investigated. We report the results of a range of techniques Raman spectroscopy, atomic force microscopy, scanning tunnelling microscopy that we have used to characterise these layers.

3 Abstracts – Poster presentations

Development of the R152a as a new electrochemical bath and the use of Raman spectroscopy for speciation

Xue Han, Michael W. George

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

Supercritical Fluid Electrodeposition (SCFED) is a relatively new development in the area of electrodeposition and this approach tries to exploit some of the advantages of these fluids such as the lack of surface tension enable them to penetrate to the bottom of the nano pores with enhanced mass transport rates.[1,2] It requires an appropriately designed precursor and a carefully chosen supporting electrolyte needed to be dissolved in the SCF and provide appropriate conductivity which is particularly important because of the need to pass larger currents. The conditions of this fluid will greatly affect the quality of the final deposit and it is crucial to understand the physical chemical properties of these mixtures giving an understanding of the conditions that are required to operate in one phase and resulting conductivity of the electrochemical bath. In order to have a full understanding of electrodeposition, we also need to be able to monitor and probe the process, i.e. species in the electrochemical bath during the deposition. Furthermore, it is important to study the effect of trace impurities, such as water, on the stability of the precursors and the electrochemical process (**Figure 1**).

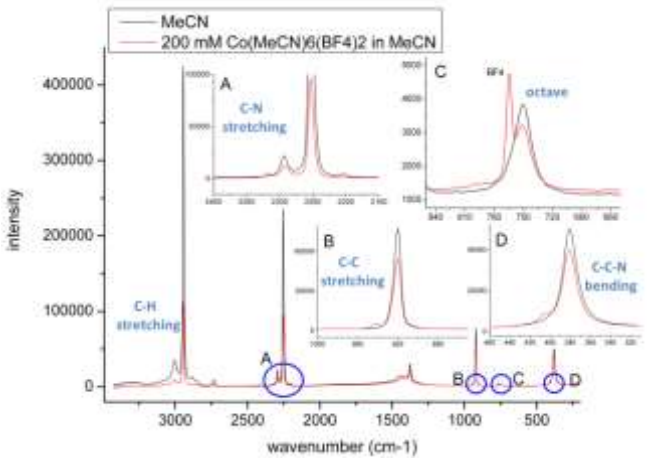

Figure 1. Raman spectra of $Co(MeCN)_6(BF_4)_2$ in MeCN.

[1] Dhepe et al. (2003), Phys. Chem. Chem. Phys., 5, 5565.
[2] Hasan and Farouk (2013), J. Supercrit. Fluids, 80, 60.

3 Abstracts – Poster presentations

A spectroscopic study of hexabenzacoronene-functionalised Re(I) complexes

Raphael Horvath,[1] Anastasia B. S. Elliott,[2] Xue-Zhong Sun,[1] Michael G. Gardiner,[3] Nigel T. Lucas,[2] Keith C. Gordon,[2] Michael W. George[1]

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[3] *School of Chemistry, University of Tasmania, Private Bag 75, Hobart, Australia*

Polycyclic aromatic hydrocarbons are of interest due to their abilities to act as charge-acceptors and to self-assemble into supermolecular structures, making them potential active components in electronic devices.[1] Transition metal complexes, such as substituted $Re(CO)_3Cl(bpy)$ (bpy = 2,2'-bipyridine), have also attracted attention due to their light-harvesting and emissive properties.[2]

Here, we investigate the photophysical properties of $Re(CO)_3Cl(bpy)$ substituted by hexabenzacoronene (HBC). The general structure is shown in **Figure 1**; different R groups were chosen to influence the aggregation behaviour of the complexes.

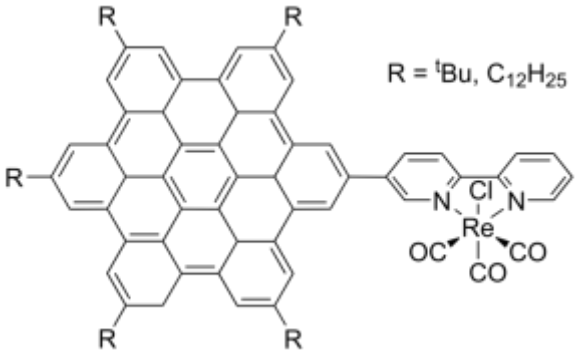

Figure 1. General structure of the complexes investigated.

Resonance Raman is used in concert with density functional theory calculations to characterise the initially formed excited state as a metal/HBC to bpy charge transfer transition. Using time resolved infrared, this can be shown to cascade to two further excited states, a charge-separated HBC to bpy state and a $\pi \rightarrow \pi^*$ state on the bpy moiety. This indicates that the attached HBC unit plays a significant part in the photophysics of this type of complex.

[1] Kastler et al. (2005), J. Am. Chem. Soc., 127, 4286.
[2] Takeda et al. (2011), Inorganic Photochemistry (Academic Press), 63, 137.

3 Abstracts – Poster presentations

Can Raman microscopy help understand infectious diseases?

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Bacterial infections cause 3x more deaths than road accidents each year. They are becoming increasingly difficult to treat as our battery of antimicrobials becomes compromised by the ability of the bacteria to develop resistance against them. Soon, routine surgical interventions will be too risky to perform unless novel antimicrobials are developed.

We study bacterial pathogenicity with the aim of understanding the molecular basis of virulence to identify novel antimicrobial targets. Autotransporter proteins are the largest family of proteins secreted from bacteria, and most of them are virulence factors. One that we study, produced by the opportunistic skin wound and lung pathogen *Pseudomonas aeruginosa* (AaaA) is a peptidase that releases arginine from an unknown substrate.[1] We would like to use Raman to monitor arginine metabolism in the bacteria and host cells during a skin wound infection to track where and when AaaA influences it. We hypothesize that the precariously balanced arginine levels in infected wounds are modulated by the bacterium for its advantage, and we would like to understand this on a single cell, real-time level (**Figure 1**).

The other autotransporter that we study (EspC) is released from Enteropathogenic *Escherichia coli* (EPEC) which is a leading cause of diarrhoea in children. EspC enters host cells where it proteolytically degrades host cell components. EspC uses a molecular machine (the T3SS needle) to gain entry to host cells and other effector proteins injected through the T3SS cause changes in actin within the host cell. We would like to use Raman Microscopy to monitor the molecular rearrangements occurring in host cells[2] as EspC and other effectors subvert its intracellular machines. We have a range of fluorescently tagged versions of both autotransporters to monitor in parallel with Raman as well as defined deficient mutants to use as controls.

Figure 1. Panel A. Actin (red) of host cell rearranged by proteins secreted in through T3SS needle (green) from EPEC. Panel B. AaaA (green) on surface of *P. aeruginosa*.

[1] Luckett et al. (2012), PLOS Pathogens., 8, e1002854.
[2] Saar et al. (2010), Science, 330, 1368.

3 Abstracts – Poster presentations

Micro-Raman analysis of minerals

Tamara Monti,[1] Ilia N Ivanov[2]

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The extreme complexity of the chemical and elemental composition of natural rocks requires high-resolution characterization techniques for a comprehensive study. In particular, natural rocks embed different types of minerals. Each family of minerals has its own range of chemical and crystallographic properties, which are associated to electrical, mechanical, and thermal characteristics.

In practical scenarios, the bulk characterization of these properties is hampered by several factors; for example, the pre-treatment process of rocks through microwaves is essentially ruled by selective heating of minerals inclusions.[1] It is therefore crucial to characterize the chemical composition of rock samples at micrometric scale.

In this work, Raman spectra are collected in backscattering geometry using a Renishaw inVia Raman Microscope with a 50 objective (Leica, NA = 0.75) using 532 nm probing light. Raman maps of different minerals are collected with sub-micrometric spatial resolution. In order to univocally recognize the minerals, comparisons with the spectra of pure elements is performed. In **Figure 1** we report the analysis on a pyrite inclusion.

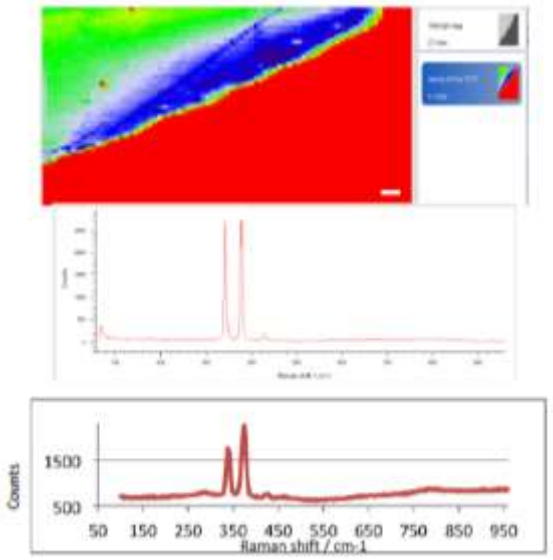

Figure 1. Raman map (top) with a pyrite inclusion edge. The green and blue tones are referred to different levels of a typical shift (377/cm-1). The red tone is mainly fluorescence of the gangue materials. The white bar is 1µm. Raman spectra of the inclusion (center) and of the pure pyrite mineral (bottom)

[1] Kingman et al. (2006), Int. Mater. Rev., 51, 1.

3 Abstracts – Poster presentations

Carbon nanotubes as templates for the controlled formation of sulphur terminated graphitised nanoribbons

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Graphitised carbon nanoribbons (GNRs) have received significant attention due to their unique electronic properties and are promising candidates for applications such as molecular electronics.

Although assembly of GNRs has been widely reported, the current methods suffer from limited control of their atomic structure or require the careful organisation of precursors on atomically flat surfaces under ultra-high vacuum conditions.

Carbon nanotubes can be used as effective one-dimensional templates for the controlled self-assembly of GNRs within the internal channel of the nanotube.[1]

[1] Chuvilin et al. (2011), Nature Mater., 10, 687.

3 Abstracts – Poster presentations

Raman Characterization of Liquid-Phase Exfoliated Graphene and Composite Membranes

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Graphene, a single layer of graphene, shows outstanding properties, which make this material attractive for several applications.[1,2] Amongst several methods of graphene production, liquid-phase exfoliation (LPE) shows a great potential as a mass-scalable and low-cost approach for industrial production of graphene.[2-4] For example, graphene dispersions can be used for producing graphene/polymer composites with superior properties.

However, in order to establish a technology based on LPE graphene, it is essential to be able to characterize the quality of the material, e.g., the yield of single-layers, the amount of defects, the amount of re-stacked flakes and so on, under different experimental conditions. In this work we show that Raman spectroscopy can be used as a metrology tool to qualitatively track the changes in composition of a graphene dispersion obtained by mixing n-octylbenzene at varying ratio with N-methyl-2-pyrrolidinone (NMP) or ortho-dichlorobenzene, (o-DCB).[5] Furthermore, we will show that Raman spectroscopy can be applied also to the study of composites, such as the ones obtained by mixing graphene with a polymer of intrinsic microporosity, such as PIM-1.[6,7]

[1] Geim and Novoselov (2007), Nature Mater., 6, 183.
[2] Novoselov et al. (2012), Nature, 490, 192.
[3] Hernandez et al. (2008), Nature Nanotech., 3, 563.
[4] Ciesielski and Samori (2014), Chem. Soc. Rev., 43, 381.
[5] Haar et al. (2015), Carbon, submitted.
[6] McKeown and Budd (2006), Chem, Soc. Rev., 35, 675.
[7] Y. Shin et al. (2015), in preparation.

3 Abstracts – Poster presentations

Understanding the changes in the mechanical behaviour of hair with humidity using Raman spectroscopy

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Water is a fundamental component of hair and affects its physical and mechanical properties.[1] Changes in humidity cause changes in the hair water content, which has a strong influence on the mechanical behaviour [2] and can consequently cause a drop out of style. There are a number of different models that attempt to explain this behaviour that imply different changes to the hair structure during mechanical change.[3] Here we use a confocal Raman spectrometer with a microscope stress-strain cell within which the humidity can be controlled to investigate and probe changes within hair.

Raman spectra were successfully collected from white virgin hairs at 5% strain intervals and at low (35%) and high (80%) humidity (RH). Changes were clearly seen in the keratin structure while the fibre was strained. As has been shown with complex molecular systems undergoing changes [4, 5], using 2D methods can give much clearer insights from the data. Detailed analysis has been carried out here using 2DCOS (2D Correlation analysis) and PCMW (perturbation-correlation moving windows).

The PCMW plots (**Figure 1**) at low and high humidity shows a global picture of the transitions occurring as the hair is strained. Two main transitions (one at low and one at high strain) can clearly be seen where α-helix changes into β-sheet. The first transition shifts to a higher strain at the higher humidity. From the 2DCOS analysis, it's implied that all transitions go via a disordered state (i.e. α → disordered → β). Disulphide bond breakages are observed only at high strains and are found to be independent of humidity.

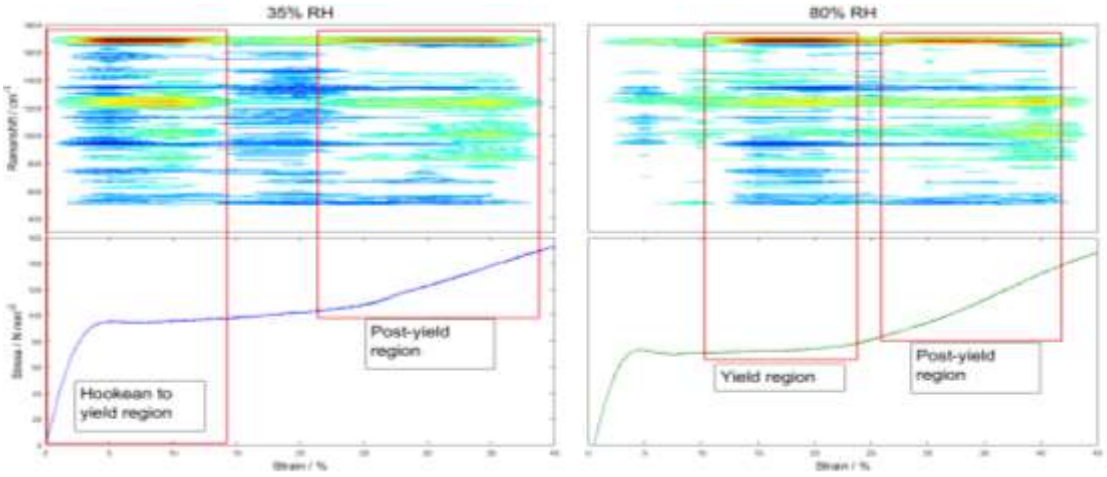

Figure 1. PCMW plot of Raman data from hair alongside the stress-strain curves at 35% and 80% humidity respectively.

[1] Pudney et al. (2013), Appl. Spectrosc. 67, 1408.
[2] Bell et al. (2004), J Cosmet. Sci. 55 (supplement), S19.
[3] Hearle (2000), Int. J. Biol. Macromol., 27, 123.
[4] Paquin et al. (2007), J. Raman Spectrosc. 38, 504.
[5] Ashton et al. (2013), Adv. Colloid Interface Sci., 199-200, 66.