RamanFest 2013 Symposium

Program

First Conference on Advanced Applied Raman Spectroscopy

RFS2013

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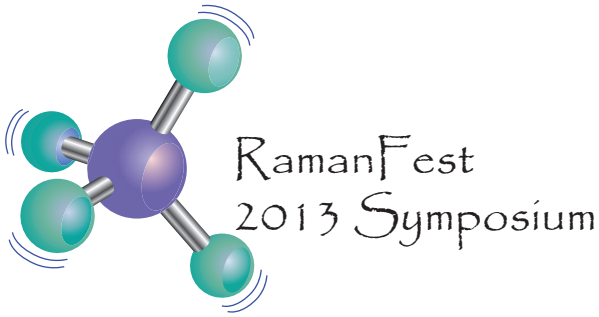


RamanFest 2013 Symposium

The RamanFest 2013 Symposium is a two day conference addressing cutting edge Raman techniques including life science applications, imaging and TERS (Tip Enhanced Raman Spectroscopy). It will encourage discussion on the latest capabilities of Raman spectroscopy, stimulated by key note lectures from internationally renowned scientists, and an accompanying poster session.

RamanFest 2013 Symposium is co-organized by LASIR (Laboratoire de Spectrochimie Infra-rouge et Raman, UMR8516, Université Lille 1, France) and HORIBA Scientific.

Book of abstracts

Gala Dinner

The gala Dinner will be held at 7pm at the restaurant
«Le Compostelle» in Lille,
4, rue Saint Etienne, 59000 LILLE

Visit of LASIR

The laboratories of LASIR can be visited on Friday 24th, at 15:30.

RamanFest 2013 Symposium

Thursday 23rd May 2013

10:00 **Welcome**

Posters will be on display the whole day. Poster presenters are asked to hang their posters for session 1.

10:15 *Chair: Myriam Moreau, LASIR, Université de Lille 1, Sciences et Technologies, France*

10:15 A meander through Raman spectroscopy developments and applications over the last 30-40 years
John Chalmers, VS Consulting, United Kingdom

11:00 New directions in Raman spectroscopy: wavelength modulation and shaping light
Prof. Kishan Dholakia, School of Physics and Astronomy, University of St Andrews, Scotland

11:45 Life science applications of Raman spectroscopy
Prof. Michel Manfait, MéDIAN, Biophotonique et Technologies pour la Santé, FRE CNRS 3481 MEDyC, Université de Reims Champagne Ardenne, Paris

12:30 **Lunch and first poster session**

14:00 Can Raman microspectroscopy solve the sperm conundrum?
Dr Con Mallidis, Centre for Reproductive Medicine and Andrology, University Clinic Münster, Germany

14:45 Probing single cell bacteria – the application of Raman to microbiology
Dr Wei Huang, Department of Civil and Structural Engineering, University of Sheffield, United Kingdom

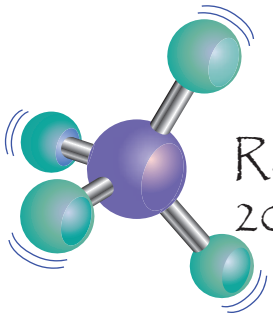
15:30 **Coffee and first poster session**

16:00 Exploring the world of polyconjugated molecules in biological systems
Prof. Giuseppe Zerbi, Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Milan, Italy

16:45 Exploring Raman spectral data using chemometrics
Prof. Ludovic Duponchel, Laboratoire de Spectrochimie Infrarouge et Raman (LASIR), CNRS UMR8516, Université Lille 1, France

17:30 **Open Discussion**

19:00 **Evening Gala Dinner**



RamanFest
2013 Symposium

Friday 24th May 2013

9:30 **Welcome**

Posters will be on display the whole day. Poster presenters are asked to hang their posters for session 2.

Chair: Simon FitzGerald, HORIBA Scientific

9:45 Fast imaging of ultralow frequency modes based on VBG technologies
Prof. Ping Heng Tan, State Key Lab of superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, P. R. China

10:30 **Coffee and second poster session**

11:00 Factors affecting image quality with 3D Raman mapping
Dr Neil Everall, Company Research Associate, Intertek-MSG, Wilton, United Kingdom

11:45 Tip-Enhanced Raman spectroscopy - surface analysis on the nanometer scale
Dr Volker Deckert, Friedrich-Schiller-Universität Jena, Germany

12:30 **Lunch and second poster session**

14:00 Far- and near-field Raman spectroscopy and polarization: selected case studies
Dr Razvigor Ossikovski, Laboratory of Physics of Interfaces and Thin Films, École Polytechnique, Palaiseau, France

14:45 **Open discussion**

15:15 **Concluding remarks**

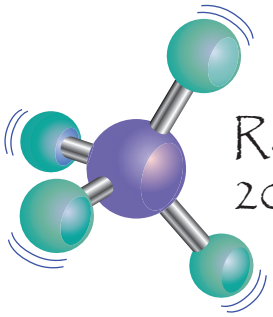
15:30 **End of the Symposium**

Visit to LASIR laboratories (Laboratoire de Spectrochimie Infrarouge et Raman, Lille)

RamanFest 2013 Symposium

Thursday 23rd May 2013: Posters

1. The applications of Raman spectroscopy to study structural phase transition at dynamic temperature regime
   A. Krylov
2. The advantages of the Raman scattering technique for studying the high pressure phase transitions in the single crystals
   A. Krylov, S. Krylova, A. Vtyurin, A. Oreshonkov, S. Goryainov
3. In-situ Raman spectroscopy characterization of polyhydroxyalkanoate (PHA, biodegrable polyester) synthesized by bacterial fermentation of sustainable resources
   M. Yerly, M. Zinn, P. Brodard
4. Raman Imaging of Sub-Micrometer Thin Layers
   B. S. Chernev, G. C. Eder, H. Schröttner, M. Dienstleder
5. Raman measurement of NiO
   C. Baratto
6. Off-line reaction monitoring of the oxidation of alkenes in water at low concentrations using DROP COATING DEPOSITION RAMAN Spectroscopy
   A. Shaghayegh
7. Probing substrate-catalyst-DNA interactions in DNA based asymmetric catalysis with UV and visible resonance Raman Spectroscopy
   A. Draksharapu, A. J. Boersma, G. Roelfes, W. R. Browne
8. Investigating electronic properties of Carbon based nanostructures by Raman spectroscopy
   F. Yaghobian, N. Paradiso, T. Korn, C. Strunk, C. Schüller
9. Multivariate image processing for Raman maps in plant sciences
   H. Hall, J. Felten, B. Sundberg, A. Gorzsás
10. Chemical composition in wood cell walls revealed by multivariate Raman imaging
    J. Felten, H. Hall, B. Sundberga, A. Gorzsás
11. Explanation of the spectra of surface enhanced optical phenomena, based on ideas of tip enhanced spectroscopy
    V.P. Chelibanov A.M. Polubotko
12. Reactivity studies on dinuclear manganese tmtacn complexes
    D. Angelone, J. W. de Boer, W. R. Browne
13. Real-time fluorescent-SERS (Dual modal) endomicroscopic imaging system for multiplexed diagnosis
    S. Jeong, H. Kang, G. Kim, H. Chang, M. Cha, Y. Lee, D. Hong Jeong
14. New possibilities for paper analysis by Raman chemical imaging
    E. Pigorsch, M. Finger, St. Thiele, E. Brunner
15. In situ Raman spectroscopy on Lithium-Oxygen batteries
    S. Lepper, D. Fenske, J. Neumann
16. Sub-spectral evaluation of Raman shifts that define strains and species within the genera *Staphylococci* and *Escherichia*
    J. F.M. Al-Marashi, N. Kapel, T. S. Wilkinson, H. H. Telle
17. Reliable Raman measurements in research, health and industry - New reference procedures supply traceability for SERS and conventional Raman spectrometry
    S. Zakel, B. Güttler, R. Stosch
18. Application of the Raman spectroscopy for the identification of bacteria in the field of Food science
    A. Assaf, G. Thouand
19. Single cell membrane analysis by TERS is reaching nanometer scale
    M. Richter, H. Haschke, M. Hedegaard, T. Deckert-Gaudig, P. Lampen, V. Deckert
20. Development of an environmental levitation cell coupled with Raman micro-spectrometry to probe *in-situ* physical-chemistry processes within atmospheric particles
    Y. Tobon, M. Moreau, S. Sobanska, J. Barbillat



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Friday 24th May 2013: Posters

21. Raman microspectrometry for environmental sample characterization - from individual particle analysis to vegetable leaf investigation.
    S. Sobanska, V. Dappe, M. Moreau, Y. Tobon, J. Barbillat
22. Development of a chemometric procedure for evaluating the quality of Raman spectra used in bacterial strains discrimination
    C. Cordella, A. Assaf, G. Thouand, P. Roger, N.D. Rutledge
23. Analysis of single nucleotide mutations in *Yersinia Pestis* bacteria by using SERS monitoring and electrochemical melting
    E. Papadopoulou, S. Goodchild, D. Cleary, S. Weller, NittayaGalea, T. Brown, P. N. Bartletta
24. Raman scattering based analysis of new kesterite photovoltaic materials: correlation with chemical analysis and device properties
    T. Jawhari, X. Fontané, A. Fairbrother, V. Izquierdo-Roca, E.Saucedo, L. Calvo-Barrio, A. Pérez-Rodríguez
25. Micro-Raman characterization of silicon carbide
    N. Piluso, R. Anzalone, M. Camarda, F. LaVia
26. Temperature dependent structural transformations of dimyristoylphosphatidylcholine (DMPC)-water systems investigated by micro-Raman spectroscopy
    A. Fasanella, K. Cosentino, A. Beneduci, G. Chidichimo, E. Cazzanelli, M. Castriota
27. Laser induced aggregation of gold nanorods for SERS biosensing in liquid environment
    B. Fazio, C. D'Andrea, E. Messina, V. Villari, N. Micali, O. M. Maragò, G. Calogero and P. G. Gucciardi
28. Raman imaging of copper ores
    S. Kostudis, M. Hof, S. Kutschke, K. Pollmann
29. Potential of Raman spectroscopy in the diagnosis of urinary tract infections
    F. Michel, I. Espagnon, F. Derepas, D. Leroux
30. Synthesis, FT-IR, FT-Raman and dispersive Raman spectroscopic study of a host molecule (=$C_{52}H_{72}N_4O_{12}Si_2$) which potential applications in sensor devices
    M. Kurt , M. Karabacak, S. Okur, S. Sayin, M. Yilmaz
31. Polymorphism and phase recognition of molecular crystals probes by lattice phonons Raman microscopy
    T. Salzillo, I. Bilotti, E. Venuti, R. Guido Della Valle, A. Brillante
32. Photon-counting Raman spectroscopy of chip-scale photonic devices
    M. J. Collins, C. Grillet, S. Shahnia, A. S. Clark, A. C. Judge, E. C. Magi, P. Grosse, B. Ben Bakir, S. Menezo, J. M. Fedeli, C. Xiong, M. J. Steel, D. J. Moss, B. J. Eggleton, C. Monat
33. The study of electronic exitations in the high critical temperature superconductors by Raman scattering
    S. Benhabib
34. Determination of the composition of cryolitic melts involved in the Hall-Héroult process by Raman spectroscopy
    C. Malherbe, G. Eppe, B. Gilbert
35. Development of a quantitative approach to measure phospholipids indried drops by Raman spectroscopy
    C. Malherbe, L. Jadoul, B. Gilbert, E. De Pauw, G. Eppe
36. The effect of zirconium doping on the thermal decomposition of hydrotalcites
    G. Weightman, E. Dvininov, H. Stephenson, A. Lepkin
37. Raman spectroscopy studies on pulsed laser deposited graphene
    Laura Ursu, Cristian Ursu and Mihaela Olaru

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A meander through Raman spectroscopy developments and applications over the last 30-40 years; from where we were then to where we are now

John Chalmers
VS Consulting, United Kingdom

When in the 1970s Raman spectrometers began slowly to appear, alongside the well-established mid-infrared spectrometers, in the research laboratories of large industrial chemical companies, it would have been inconceivable then to believe how widespread their presence is today. Also, one could not have foreseen the diversity of applications that now exist for the Raman spectroscopic technique and its off-shoots. The last 40+ years has inter alia seen wide industrial up-take, perhaps most notably within the pharmaceutical industry, of the Raman spectroscopic technique. In addition, as well as many and varied applications within the natural sciences field, there have been many exciting new applications within the life sciences arena. Conservation science has also benefited considerably through application of the new generation of Raman spectrometers. And so the story goes on…

This opening presentation (largely a personal perspective) will look back over some of these instrumental and applications developments and hopefully set the scene for the expert, exciting state-of-the-art presentations to follow in this RamanFest meeting.

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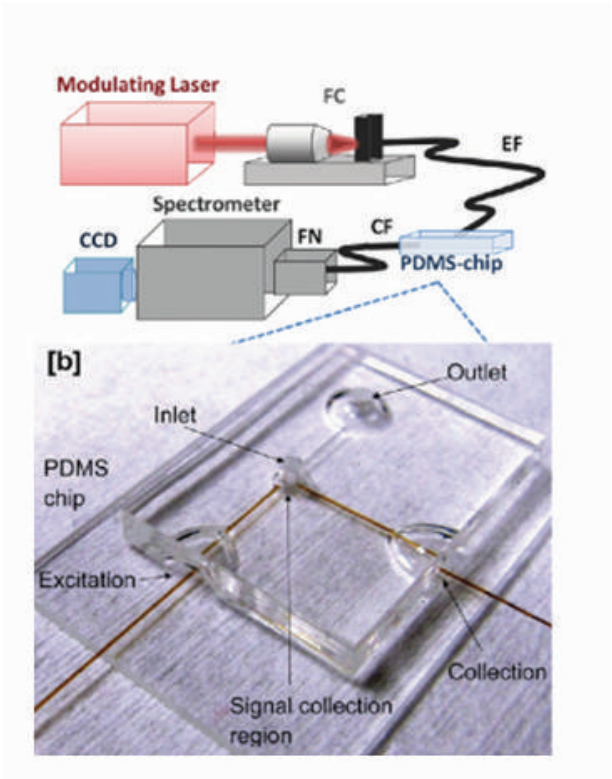
New directions in Raman spectroscopy: wavelength modulation and shaping light

Prof. Kishan Dholakia
School of Physics and Astronomy, University of St Andrews, Scotland

Label-free chemical characterization of single cells is an important aim for biomedical research. Standard Raman spectroscopy provides intrinsic biochemical markers for noninvasive analysis of biological samples but is often hindered by the presence of fluorescence background. In this paper, we present an innovative modulated Raman spectroscopy technique to filter out the Raman spectra from the fluorescence background. The method is based on the principle that the fluorescence background does not change whereas the Raman scattering is shifted by the periodical modulation of the laser wavelength. Exploiting this physical property and importantly the multichannel lock-in detection of the Raman signal, the modulation technique fulfills the requirements of an effective fluorescence subtraction method [1]. We have applied this method on chip and using fibre probes [2] and even applicability to surface enhanced Raman studies for background free detection [3].
The field of microfluidics aims to realise portable devices which can perform fast and sensitive bioanalyte detection with minimal sample preparation. Raman spectroscopy is a powerful analytical tool for analyte detection owing to its high specificity and its ability for multi component detection in an analyte. Combining microfluidics with Raman spectroscopy would help in achieving miniaturized analytical devices that can provide rich information about the analytes. However the low cross section of Raman process demands special geometries to achieve such a convergence. The majority of the previous embodiments were restricted to free space geometry, limiting portability. However recent stuides where fiber based Raman detection system, incorporated in microfluidics offers the opportunity to develop portable optofluidic bioanalyte detection devices [2] (see figure).
Indirect imaging scheme based on correlation measurements may retrieve both amplitude and phase and inherently accommodate issues relating to aberrations or imperfections within the optical system. We have recently realised such a scheme using the concept of optical eigenmodes. We split the laser light into two different beams. One beam does not interact with the target, but illuminates a high-resolution CCD camera (multipixel detector). The other one interrogates, in transmission, the target (or sample) and then illuminates a photodiode (single-pixel detector) providing no spatial resolution. The transmission wave front of this beam is decomposed, using an optical lock-in amplification technique, onto an orthogonal set of optical eigenmodes. [4] We will describe progress on using this approach for “wide-field” Raman imaging.



References:
[1] A DeLuca et al. Anal. Chem 82, 738 (2010)
[2] P. Ashok et al., J Biophotonics 4, 514 (2011); Lab Chip 11, 1262 1270 (2011); S. Dochow et al., Biomedical Imaging 1, 383 (2013)
[3] B. Praveen et al. Analyst, in press (2013)
[4] A DeLuca et al., Phys Rev A 84, 021803 (2011)

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Life science applications of Raman spectroscopy

Prof. Michel Manfait
MéDIAN, Biophotonique et Technologies pour la Santé, FRE CNRS 3481 MEDyC,
Université de Reims Champagne Ardenne
Plate-forme d'Imagerie Cellulaire et Tissulaire

Raman microspectroscopy is a promising tool for a range of biomedical applications: diagnosis of malignant tissues, analysis of the interaction between a drug and its cellular target, or investigation of molecular alterations associated with a pathological state. This technique can be performed at various scales from the cellular level to in vivo measurements. Combined with advanced statistical data processing, Raman microspectroscopy permits to identify new diagnostic biomarkers. In this presentation, examples of application at the cellular and tissular levels will be presented. The biomedical issues concern mainly the diagnosis of tumoral cells or lesions and the assessment of intrinsic skin ageing. The data processing as well as the employed instrumentation will be depicted.

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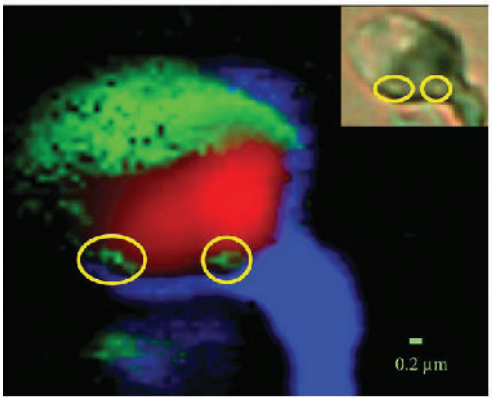
Can Raman microspectroscopy solve the sperm conundrum?

Dr Con Mallidis
Centre for Reproductive Medicine and Andrology, University Clinic Münster, Germany

Despite recent technological and analytical advances in the field of reproductive medicine, fertility clinics worldwide are still confronted with a large disparity between the high fertilization rates now achievable by modern artificial reproductive treatments and the concomitantly low pregnancy and/or take home baby rates. The introduction of the many and varied modern techniques has significantly increased the amount of information available to scientist and clinician alike, however the ability to non invasively and non destructively assess the integrity of sperm nuclear DNA (nDNA), and then select a homogeneous sperm population, all of which are capable of successfully achieving a pregnancy and a healthy baby remains elusive. In fact, the sperm nDNA tests currently available are of limited clinical use as they destroy the sample.
Raman microspectroscopy appears to fulfill the stated criteria. For a number of years it has successfully been used in the analysis and selection of living bacteria and stem cells without any apparent adverse reactions. We are an interdisciplinary collaboration of clinicians, researchers in male reproductive function, mathematicians and physicists who together with partners in industry have undertaken a systematic appraisal of the method's utility on sperm DNA assessment. During our initial studies we modified and optimized a confocal Raman microspectroscopic system which we then showed was able to detect the presence, extent and location of oxidative, UV induced and naturally occurring nDNA damage as well as intact DNA in air dried sperm. In follow up work, we found the assessments provided by the technique to be reproducible and accurate, findings that were commensurate to those of an independent spectroscopic method (FTIR) and the most validated sperm nDNA assay (Sperm Chromatin Structure Assay – SCSA).
Our aim is to research and develop an innovative automated system which can provide accurate information on a living sperm's DNA status that will be of use not only diagnostically but also therapeutically. In other words, provide the clinician and embryologist with the thus far unavailable means of selecting and catering the treatment options to suit the individual patient/couple.



Raman image based on colour coded individual spectra showing close resemblance to the features of the scanned sperm (inset). The discrimination of the image is such that small irregularities in the sperm head such as vacuoles (yellow circles) were distinguishable.

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Probing single cell bacteria – the application of Raman to microbiology

Dr Wei Huang
Department of Civil and Structural Engineering, University of Sheffield, United Kingdom

A single cell is the basic functional unit of life and all living organisms start from single cells. Learning how cells work by studying individual cell is an important interest of cell biology and single cell technology promotes a deep understanding of cell biology. Single cell Raman spectra (SCRS) provide intrinsic chemical 'fingerprints' of individual cells, containing rich information on nucleic acids, protein, carbohydrates and lipids. We employ Raman micro-spectroscopy to develop Raman single cell technology to characterise cell types, physiological states and phenotypic changes. A recent development is to develop Raman activated cell sorting (RACS), which combines SCRS for cell identification and isolating cells of interest. RACS technology has been applied to identify and sort uncultured bacteria for single cell genomics. RACS was also combined with stable isotope probing (SIP) to address the fundamental questions of microbiology 'who (bacteria) is doing what (biological roles), where and when?' RACS will revolutionise our ability to study the roles of single cells and uncultured bacteria in microbial population. It will be a powerful research tool to open a new frontier for isolation of individual live cells for attempted cultivation and for extension of '-omics' including genomics, transcriptomics and proteomics.

References:

- *Li, M., Huang, W.E., Gibson, C.M., Fowler, P.W. and Jousset, A. (2013) Stable isotope probing and Raman spectroscopy for monitoring carbon flow in a food chain and revealing metabolic pathway.* ***Analytical Chemistry 85****: 1642-1649.*
- *Li, M., Canniffe, D.P., Jackson, P.J., Davison, P.A., FitzGerald, S., Dickman, M.J., Burgess, J.G., Hunter, C.N., Huang, W.E.* (2012) Rapid Resonance Raman micro-spectroscopy to probe carbon dioxide fixation by single cells in microbial communities.* ***ISME Journal 6****:875-885*
- *Huang, W.E., Ferguson, A., Singer, A.C., Lawson, K., Thompson, I.P., Kalin, R.M. et al. (2009) Resolving Genetic Functions within Microbial Populations: In Situ Analyses Using rRNA and mRNA Stable Isotope Probing Coupled with Single-Cell Raman-Fluorescence In Situ Hybridization.* ***Applied and Environmental Microbiology 75****: 234-241.*
- *Huang, W.E., Stoecker, K., Griffiths, R., Newbold, L., Daims, H., Whiteley, A.S., and Wagner, M. (2007) Raman-FISH: Combining stable-isotope Raman spectroscopy and fluorescence in situ hybridization for the single cell analysis of identity and function.* ***Environmental Microbiology 9****: 1878-1889.*
- *Huang, W.E., Griffiths, R.I., Thompson, I.P., Bailey, M.J., and Whiteley, A.S. (2004) Raman microscopic analysis of single microbial cells.* ***Analytical Chemistry 76****: 4452-4458.*

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Exploring the world of polyconjugated molecules in biological systems

Prof. Giuseppe Zerbi
Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Milan, Italy

At present Material Scientists are, strongly and worldwide, engaged in the efforts to exploit the conversion of the energy of photons into electrical energy for innumerous applications (from solar cells to sensors, molecular motors etc). The basic concept is to be able to photoexcite the system from the HOMO to the LUMO level and then offer an environment where electrons and holes can travel through to carry the electrical signal to a suitably engineered collector.

In the biological world one finds that many basic biochemical processes are initiated by the absorption of light by a system of polyconjugated double bonds which act as photoreceptors. The chemistry and physics of polyconjugated molecules has quickly developed and attracted the interest not only of basic science, but also of technology and industry.

Starting from the early works by Rimai et al. resonance Raman spectroscopy of polyconjugated systems turns out to be a unique tool for the understanding of the chemistry and the structural properties of many natural and syntetic molecules containing conjugated C=C or C≡C bonds.

These systems can be considered low band-gap materials whose gap can be suitably modulated by the length of the conjugated chain. Vibrational spectroscopy of these systems requires to consider simultaneously the dynamical as well as the peculiar electronic properties which are generated by the existence of a vibronic interaction (expressed in the jargon of physics as electron-phonon coupling) which dominates the Raman spectrum and from which many information can be derived on the molecule.

The research has developed at an explosive rate after the discovery of the synthesis of polyacetylene (G. Natta et al. Atti Accademia Nazionale Lincei, Rend. Sci.Fis.Mat.Nat., **25**, 2 (1958)) and of many other oligomers and polymers (with well defined chemical structure) of unsaturated or aromatic monomers. The physics ,physical chemistry and molecular spectroscopy of polyconjugated systems have been (and are being) studied and the knowledge acquired has paved the way to a new wide field of organic syntheses and technological applications in photonics and molecular electronics.

We shall present a few basic aspects of Raman spectroscopy of polyconjugated systems considered as one-dimensional polyconjugated polymers (e.g. oligoenes and polyacetylene) or two-dimensional systems (e.g. polyaromatic hydrocarbons (PAH) and graphene/graphite) where electron-phonon coupling plays a dominant role. For a review see: G. Zerbi “Conducting Polymers, Theory and Perspectives” in Vibrational Spectroscopy of Polymers, N.J. Everall, M.Chalmers and P.R.Griffith, Wiley (2007), p. 487.

The basic concepts and a few worked out examples of systems recently studied will be presented.

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Exploring Raman spectral data using chemometrics

Prof. Ludovic Duponchel
Laboratoire de Spectrochimie Infrarouge et Raman (LASIR), CNRS UMR8516, Université Lille 1, France.

Chemometrics is the chemical discipline that uses mathematical and statistical methods, (a) to design or select optimal measurement procedures / experiments and (b) to provide maximum chemical information by analyzing chemical data. In a more general manner, it corresponds to the entire process whereby data (e.g., numbers in a table or spectra as rows in a matrix) are transformed into information used for decision making. There is therefore a huge potential to explore Raman spectral data in a multivariate way by exploiting simultaneously all variables in the considered spectral domain. This presentation will provide first a general overview of major chemometrics tools for the development of quantitative (multivariate regressions) or qualitative models (clustering and classification methods) capable of predicting a concentration or class membership from a spectrum. In the second part, more original algorithms such as multivariate curve resolution or super-resolution will be presented. The current craze for these concepts is explained by their great potential. Multivariate curve resolution is indeed capable of extracting simultaneously spectra and corresponding contributions of all pure compounds from mixture spectra with no a priori. For example, this is of particular importance for spectroscopic imaging for which a chemical image of an unknown compound can even be generated. For its part, the super-resolution approach uses several low resolution images of the same sample (observed in different ways) in order to retrieve a higher resolution chemical image. This issue is especially important because nanosciences force us to analyze always smaller structures or observe always more details on bulk samples.

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Fast imaging of ultralow frequency modes based on VBG technologies

Prof. Ping Heng Tan
State Key Lab of Superlattices and Microstructures,
Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, P. R. China

Probing ultra-low frequency modes is crucial for many important applications such as nanomaterials research, pharma, and semiconductor processing. The low frequency mode lower than 50 cm^{-1} is much lower than a traditional notch or an edge filter cut of most Raman spectrometers. Measurement of Raman bands with frequencies very close to the excitation line has traditionally been possible with the use of a triple monochromator system and its low in throughput is a bottleneck for many materials, for example, graphite and few layer graphenes. We show that detection of Raman modes down to 10 cm^{-1} is possible by combination of a single monochromator (e.g., HR800) and BragGrate notch filters (BNF)[1]. The BNF can be with optical density 3, and with a spectral bandwidth of 5-10 cm^{-1}. Three filters for each excitation are necessary to suppress the Rayleigh signal, which is typically 10^9-10^{12} stronger than the Raman signal.
The experimental setup and the advantage of using HR800 system in the combination system are discussed in detail. We apply this system to the shear and layer breathing modes of several layered materials, from few layers to bulk sample.
Fig. 1 depicts the Raman spectra of few layer and bulk graphite and MoS_2[1,2]. We show that the corresponding Raman peaks measure the interlayer coupling. A chain model can explain the results, with general applicability to any layered material, allowing a reliable diagnostic of their thickness. The application of this technique in fast mapping, stoichiometry and crystal orientation determination is discussed in detail.

References:
[1] P. H. Tan et al., Nature Materials 11, 294-300 (2012).
[2] X. Zhang et al., Phys. Rev. B 2013, in press.

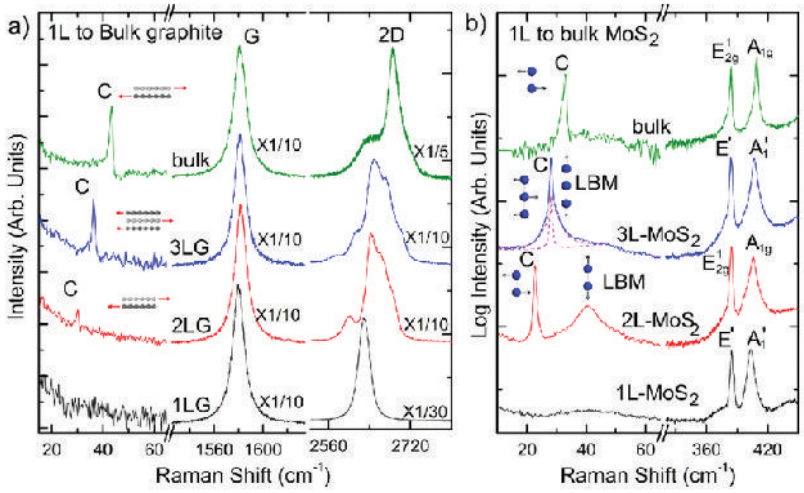


Fig. 1 (a) Raman spectra of 1LG, 2LG, 3LG and bulk graphite measured at 633 nm, and (b) those of 1L-MoS2, 2L-MoS2, 3L-

RamanFest 2013 Symposium

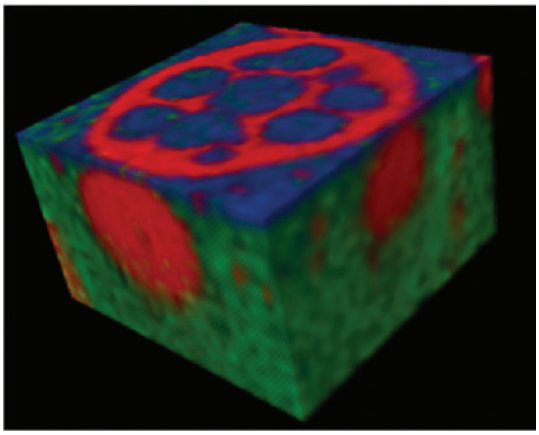
Factors affecting image quality with 3D Raman mapping

Dr Neil Everall
Company Research Associate, Intertek-MSG, Wilton, United Kingdom

Confocal Raman microscopy is an established technology for analysing complex materials on the micron scale. It is particularly useful when investigating the internal structure of transparent or semi-transparent samples, for example by non-destructive optical depth profiling, and it is widely used in industry and academe for this purpose. Furthermore, modern confocal Raman microscopes can image structures in three dimensions on relatively short timescales, so it is becoming increasingly important to know how to optimise and interpret the resultant volumetric images.

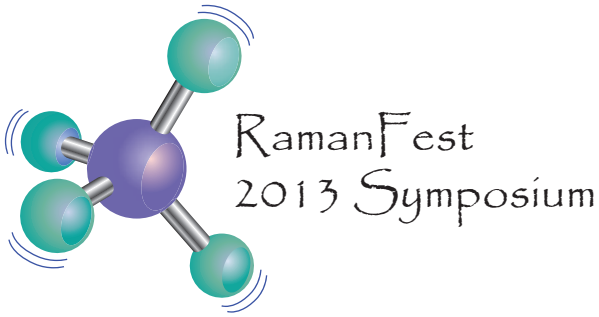
It is now well known that the choice of microscope objective strongly influences the depth resolution and spatial accuracy of confocal Raman data; in particular, the standard metallurgical objectives that are routinely supplied with commercial instruments yield compressed depth scales, poor depth resolution and degraded spectral S/N (compared with a properly corrected objective [1,2]). When depth profiling planar-layered structures one can estimate the true structure from the distorted data using fairly simple numerical treatments, but this is harder to do with more complicated samples, and the degradation in S/N inevitably decreases the image quality.

This presentation will discuss the accuracy and quality of 2D and 3D Raman images of complex structures including polymer laminates, coated fibres and dissolving beads. It will show how a properly corrected objective reveals the true internal structure of the sample, while a metallurgical objective gives badly distorted images where the size and shape of objects is incorrect and it is difficult to resolve structural features. Furthermore, the decreased spectral S/N unnecessarily lengthens the data acquisition time compared with a corrected objective, which negates some of the benefits accrued from the technological advances that have produced ultra-fast mapping systems.



3D confocal Raman image of partially dissolved particle (red) in resin (green), obtained with 100X oil immersion objective. The image dimensions are ~60x60x40 µm and the blue layer is the immersion oil.

References
[1] N Everall, Analyst, 2010, 135, 2512
[2] N Everall, J Lapham, F Adar, A Whitley, E Lee and S Mamedov, Appl. Spectrosc. 2007, 61, 251



Tip-Enhanced Raman Spectroscopy - Surface Analysis on the Nanometer Scale

Dr Volker Deckert
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Raman spectroscopy especially in combination with microscopy is a well established analytical tool. Minimum requirements on sample preparation and the ability to measure in aqueous conditions renders it in particular useful for the exploration of bio samples. The main drawback was the lack of sensitivity, however this has been addressed by the introduction of plasmonic technologies (surface enhanced Raman scattering - SERS). SERS allows to detect minute amounts of sample, even down to the single molecule level. The electromagnetic field enhancement that is achieved by the illumination of nanometer sized silver or gold particles (e.g. colloids, silver islands, or structured systems) is not isotropically distributed over each particle, but strong variations in the field strength relate to an even higher localization of the associated field compared to the size of the particle. This localization can reach dimensions down to a few tens of nanometers. As the intensity of the Raman signals scales roughly with the fourth power of the field, a localization of the Raman enhancement below 10 nm can be expected. To make use of this localization in an extreme form of SERS, only one nano particle is chosen as an enhancing probe and moved in a controlled way over the sample of interest. This so-called tip-enhanced Raman scattering (TERS) allows lateral resolutions well below the diffraction limit of normal optical experiments and still preserves the specificity and sensitivity of SERS. The high spatial resolution of TERS opens new possibilities for label free surface analysis. As the investigated volume is extremely small $< 10^3$ nm^3 naturally so is the number of probed molecules. Depending on the size this refers to only 10^2 - 10^5 molecules. Consequently, the effect of impurities and molecular orientations is quite different from larger sample volumes. For example the composition of a single cell measured with micro-Raman as a whole and the same cell measured with TERS must be the same, however, the appearance of the spectra will be quite different. The single spectra of the latter should show features of single or small protein aggregations, whereas the micro-Raman spectrum will show the average of all compounds present in that cell.

We will show examples of TERS on bio surfaces that demonstrate that the resolution can even reach a single molecule level. Beyond the resolution and sensitivity a next step will be the time resolved investigation of nano scale phenomena. Results regarding the investigation of photo catalytic reactions indicate that also reaction dynamics can be investigated with nanometer resolution.

RamanFest 2013 Symposium

Far- and near-field Raman spectroscopy and polarization: selected case studies

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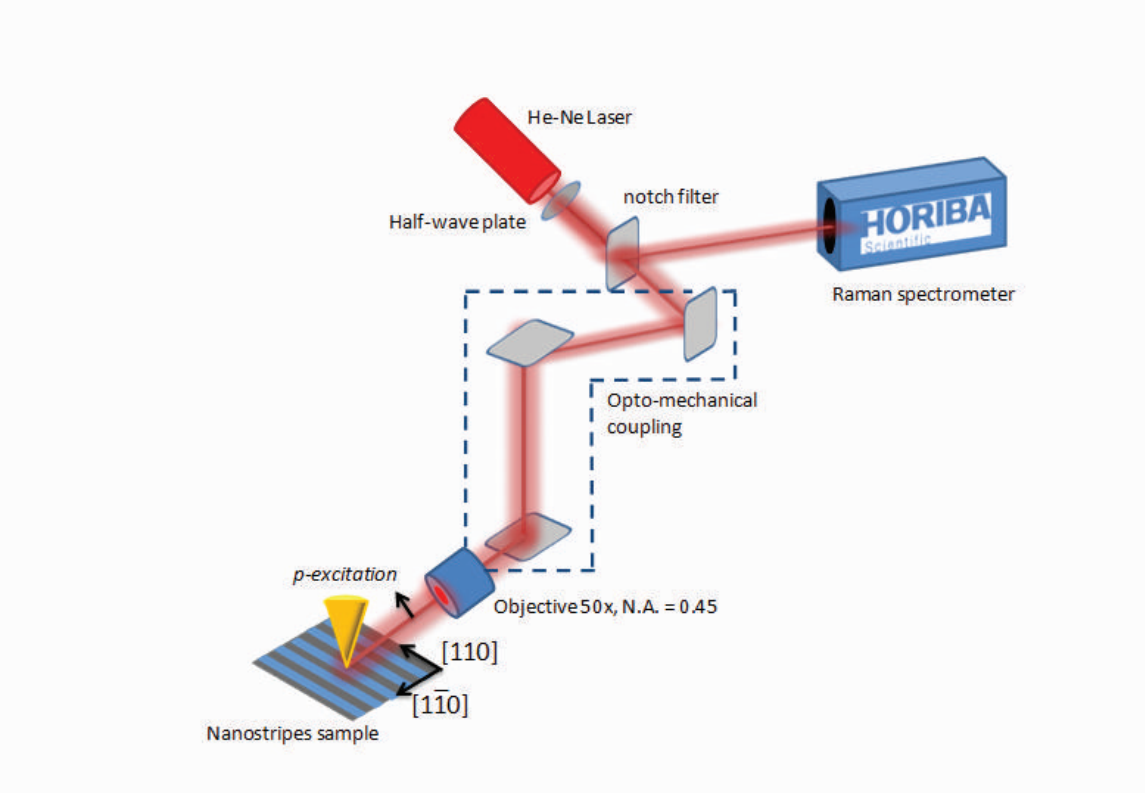
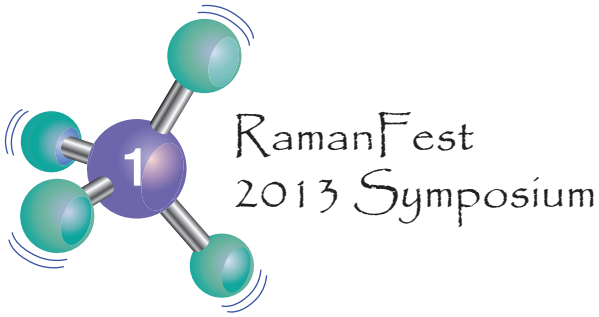
The potential benefits that can be obtained by controlling the polarization states of the exciting and scattered radiations in a Raman scattering experiment are presented through several selected case studies. When coupled with light polarization control, Raman spectroscopy is thus capable of providing extra information on the structural properties of the materials under investigation. The experimental examples shown are taken from the area of both conventional i.e., far-field, as well as from near-field (or TERS) Raman spectroscopy. They cover topics such as the stress tensor measurement in strained, both full-sheet and nano-patterned, semiconductor structures, the Raman scattering tensor determination from near-field measurements on azobenzene thiol self-assembled monolayers, as well as sub-wavelength spatially resolved strain mapping of embedded semiconductor nano-stripes.



Principle schematics of the sub-wavelength spatially resolved strain measurement experiment



The applications of Raman spectroscopy to study structural phase transition at dynamic temperature regime

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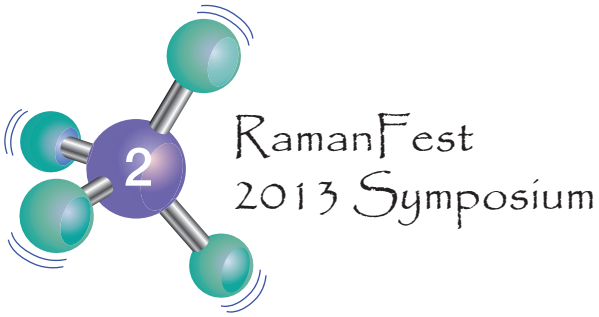
The present investigation demonstrates advantages of dynamic temperature regime by study phase transition of $Rb_2KMoO_3F_3$ single crystal. Dynamic temperature regime means that sample temperature is changing during spectra record with a specified rate. Rb_2KMoO_3F belongs to a family with the cubic symmetry in its high temperature phase. However, due to the presence of two types of anions F and O in the anionic octahedra, their local symmetry is less than cubic and it can be correspond to *fac*- or *mer*- isomers. Owing to the difference in partial electron charges of two anions, F and O, both isomers possess dipole moments. At the same time the space symmetry group of compounds remains to be Fm-3m (Z=4) due to disordering of F and O positions and the octahedra disordering in crystal lattice. Upon cooling, after passing the phase transition temperature the crystal symmetry is reduced and disorder in the structure is to decrease in a whole or in a part. The Raman scattering study of the $Rb_2KMoO_3F_3$ structure as well as the investigation of linewidth anomalies is presented. Anomalous increase of the linewidth of the fully symmetric vibrations of octahedron groups has been observed, which is connected with the crystal lattice disorder. Wide temperature area is found below structural phase transition where different lattice disorder can be obtained at a given temperature by varying the rate of sample cooling. It is possible to control the disorder degree of the octahedral groups by varying cooling rate when passing through the point of phase transition. The anomalous linewidth, range of metastable states, control over the degree of ordering, all these phenomena are rarely seen in crystalline compounds.



The advantages of the Raman scattering technique for studying the high pressure phase transitions in the single crystals

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The report covers problems connected with the study of structural phase transitions in crystals under hydrostatic pressure by Raman spectroscopy. A number of problems solved by this method are outlined. For example the crystal twinning after the phase transition complicates the investigation of structural transformations by X-ray structural analysis. It is noted that this method is sufficiently informative. It is shown that the study of pressure dependence of Raman spectra even at room temperature makes a significant contribution into understanding phase transition nature. Raman spectroscopy experiment usually consists in measuring the parameters of lines observed in a single crystal spectrum at different pressures. Traditionally, the line parameters in spectra are mode position, intensity, damping constant and polarization. The experiment shows that the location of ion vibrations and molecular groups are sensitive to pressure. Anomalous phonon wavenumber decrease with the pressure increase evidences a special role of the phonon in the crystal dynamics. This phenomenon can be due to the existing phase transition. Raman spectroscopy can be also used to determine internal mode splitting caused by the changes of the lattice symmetry at phase transition. The polarization of the observed spectra is usually violated under pressure. However, some polarization observations are presented in this work. Special attention is paid to the families of perovskite and perovskite-like crystals since the temperature and pressure changes cause a number of anomalies in their properties, including structural phase transitions. Experimental studies of the phase transition in ScF_3, $RbMnCl_3$, Rb_2KScF_6, Rb_2KInF_6, Rb_2NaYF_6, Rb_2KTiOF_5, $(NH_4)_2WO_2F_4$, $(NH_4)_2MoO_2F_4$ crystals are presented in the report.

In-situ Raman spectroscopy characterization of polyhydroxyalkanoate (PHA, biodegradable polyester) synthesized by bacterial fermentation of sustainable resources

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Polyhydroxyalkanoate (PHA) is a large class of biodegradable polyesters synthesized by bacteria as an intracellular carbon storage compound. Besides, PHA presents interesting material properties, ranging fromadhesives to elastomers and thermoplasts. By using carbon sources from agricultural waste materials, such as waste from fruit processing and wine production, a sustainable synthesis of PHA can be developed.
In this context, Raman spectroscopy has the potential of monitoring the production of PHA directly during the fermentation, which cannot be measured otherwise. As seen on Fig. 1, the first tested samples were isolated poly(3-hydroxynonanoate) (PHN), freeze-dried biomass (*Pseudomonas putidaGPo1*) without PHN, and freeze-dried biomass (*P. putidaGPo1*) with 41.8% (w/w) PHN (stained with Nile Red for microscopy purposes). Three different methods for the preparation of the samples were tested: biomass in water solution, freeze-dried biomass directly on microscope glass slides, and drop of water solution of biomass air-dried on microscope glass slides.

Figure 1: Purified poly(3-hydroxynonanoate) (PHN, left), freeze-dried biomass without PHN (center), and freeze-dried biomass with 41.8 % (w/w) PHN (stained with Nile Red, right).

The measurements in solution are problematic, because the cells stay in suspension and therefore prevent a reliable Raman signal to be measured. Measuring freeze-dried biomass directly is possible, but the fluorescence of the Nile Red stain is a problem. We found that a laser pre-exposure reduces the fluorescence without affecting the Raman spectrum, but the procedure is time-consuming. Finally, preparing dried drops of biomass on glass greatly reduces the fluorescence, and an efficient Raman identification of PHA inside the biomass can be achieved.

RamanFest 2013 Symposium

Raman Imaging of Sub-Micrometer Thin Layers

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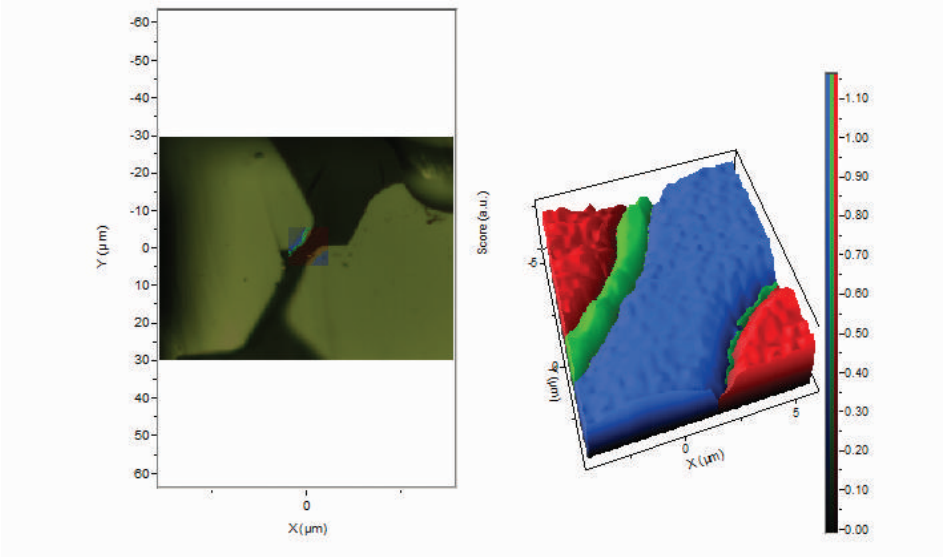
Thin layers of functional materials are widely present in material composites in various fields of technology, either as thin barrier layers in packaging films, as adhesive layers in multi material laminates, as corrosive protection in various metallic composite components or conductive layers in semiconductors. As the functionality of the whole multi material composites is often critically dependent on the reliable and efficient operation of these thin layers, the knowledge of their structure, chemical identity, thickness or compactness is important for product development, quality control and for the assessment of the ageing behaviour or failure analysis.
One particular system we investigated consisted of copper-zinc-tin sulfide, commonly referred to as CZTS, covered with a submicrometer buffer layer of CdS. The task was to visualize those thin layers in the virgin and degraded state by means of Raman imaging. The samples were embedded in a quick curing matrix and the subjected to ion milling (Ilion Slope Cutter) in order to obtain a perfectly flat surface for the Raman measurements. Raman images were collected on a HORIBA Jobin Yvon LabRam 800 HR, equipped with DuoScan®; the latter was driven in scanning mode. The resulting Raman images were compared to high resolution electron micrographs and EDXS-mappings (Zeiss Ultra 55 scanning electron microscope).



White light micrograph and Raman image of two neighbouring CZTS crystals (red), showing clearly the CdS layers (green). The blue colour represents the embedding medium.

RamanFest 2013 Symposium

Raman Measurement of NiO

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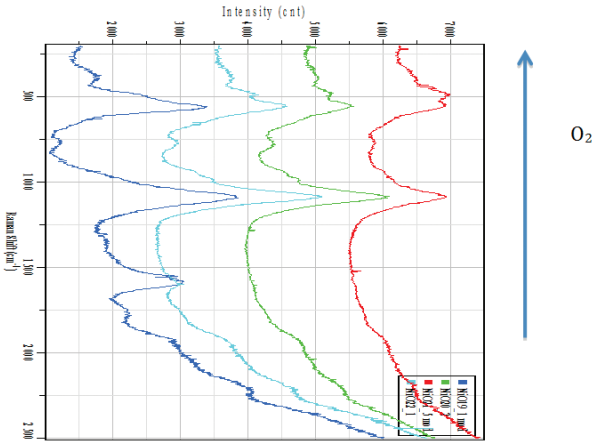
NiO for gas sensing

NiO_19 200°C 0 % (blue)
NiO_22 200°C 10 % (light blue)
NiO_20 200°C 25 % (green)
NiO_21 200°C 50 % (for XRD)



The band up to 1200 have vibrational origin:
The shoulder at ~375cm^{-1} is indicative of the high nickel vacancy concentration and the non-stoichiometry of the samples
- one-phonon (1P) TO (500 cm^{-1}) and LO modes (570 cm^{-1})
- disorder induced band at 570
- two-phonon (2P)
- 2TO modes (730 cm^{-1})
- TO+LO (906 cm^{-1})
- 2LO (1090 cm^{-1})

the band at 1490 cm^{-1} is due to a two-magnon scattering (2M)

Thin films were deposited at 200°C by varying the O_2 / Ar ratio during the deposition. All thin films showed distinctive peaks from NiO. Film deposited in inert atmosphere showed 2M peak, that progressively disappear when O_2 is inserted. The 2M peak is still visible in thin film at 10 % and no more visible at higher O_2 concentrations.
1p LO mode at 570 cm^{-1} and 2LO mode at 1090 cm^{-1} are the most prominent peaks, but as the oxygen increases to 50 % the TO peak at 500 cm^{-1} increase its intensity and the 2LO peak gradually decrease its intensity.

RamanFest 2013 Symposium

Off-line reaction monitoring of the oxidation of alkenes in water at low concentrations using DROP COATING DEPOSITION RAMAN Spectroscopy

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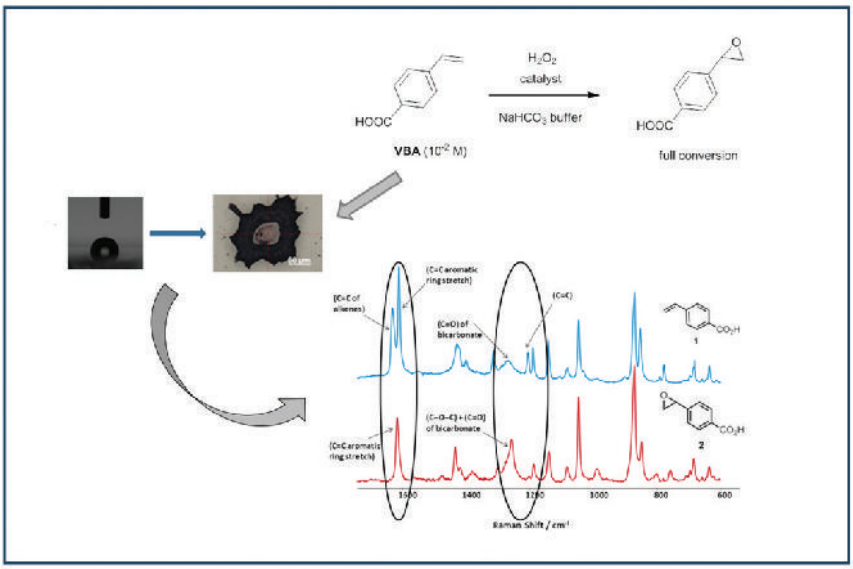
The application of drop coating deposition Raman (DCDR) spectroscopy to the field of reaction progressmonitoring is addressed in this contribution. Although, DCDR spectroscopy has seen recent application in the study of biological fluids, its application in other areas has not yet been explored. Here we apply the technique to the catalysed oxidation of alkenes to epoxides in aqueous solutions at concentrations < 10 mM. The effect of surface characteristics, background interferences, homogeneity of distributionof analytes, drying time, as well as instrumental limits of detection and calibration are discussed. We demonstrate that reproducible spectra can be obtained routinely, with relatively little variance, withshort acquisition times and samples volumes of 2-10 µl and as little as 1 µg of analyte. The utility of the technique compared with online reaction monitoring by 1H NMR and Raman spectroscopy is demonstrated in the excellent correlation between data obtained off and on-line.



RamanFest 2013 Symposium

Probing substrate-catalyst-DNA interactions in DNA based asymmetric catalysis with UV and visible resonance Raman spectroscopy

Apparao Draksharapu[a], Arnold J. Boersma[b], Gerard Roelfes[a,*], Wesley R. Browne[a,*]

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[b]Department of Biochemistry, Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands.

In DNA based asymmetric catalysis[1] the second coordination sphere provided by DNA is the source of chirality that is harnessed to render Cu(II) catalyzed reactions enantioselective.[2,3] A hybrid catalyst is generated by non-covalent binding of a Cu(II) complex to DNA.[1][Cu(dmbpy)(NO_3)$_2$] **(1)** catalyzes enantioselective C-C, C-N and C-O bond forming reactions in water with DNA as the source of chirality. A central question is the precise mechanism by which the chirality of the DNA double-helix is transferred to the product of Lewis acid (Cu(II)) catalyzed reactions. In this presentation the application of UV/Vis absorption and Raman spectroscopy to study the interactions between the Cu(II) catalyst, the azachalcone substrate and salmon testes (st-)DNAwill be discussed.

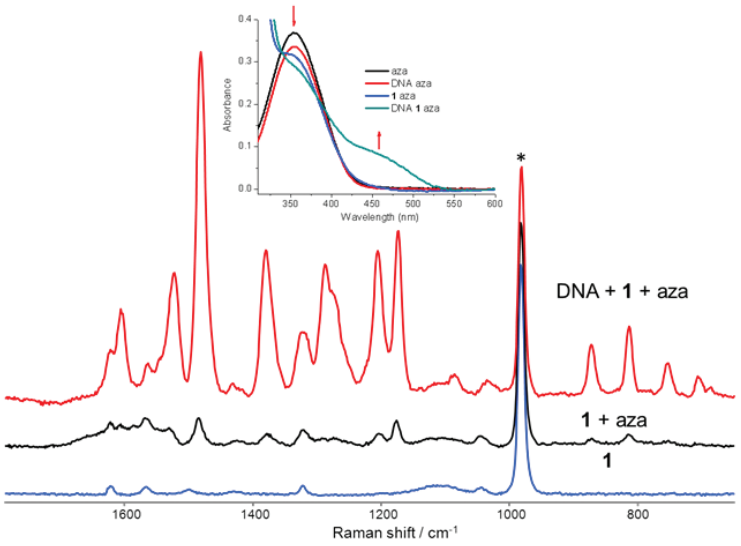

Figure 1: UV/Vis absorption and resonance Raman spectra at λ_{ex} 473 nm in MOPS buffer. * SO_4^{2-} as internal standard

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RamanFest 2013 Symposium

Investigating electronic properties of carbon based nanostructures by Raman spectroscopy

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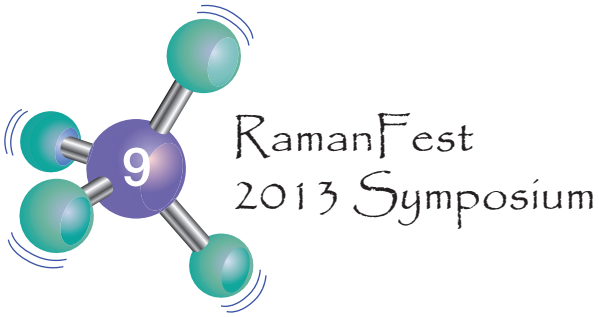
Raman spectroscopy plays the key role in the experimental investigation of electronic properties of carbon based nanostructures, i.e., devices based on graphene, carbon nanotubes, aromatic molecules or hybrids of those. It is a practical and non-invasive technique that can provide detailed information on the electronic and vibrational properties of the sample, down to the single molecule level (e.g. for carbon nanotubes). When applied to nanodevices, this technique allows crossing optical information and data acquired from transport measurement. Nanodevices based on «novel materials» as single and multi-layer graphene, on suspended or functionalized carbon nanotubes and on single aromatic molecules are studied with the Raman spectroscopy. Electronic properties of two-dimensional graphene are still largely unknown and under experimental investigation. Furthermore, graphene with great chemical inertness along with its extreme physical strength and high electron mobility sustains particularly large enhanced Raman signals for molecules at its surface and it is potential to be investigated for graphene-enhanced Raman scattering.



Multivariate image processing for Raman maps in plant sciences

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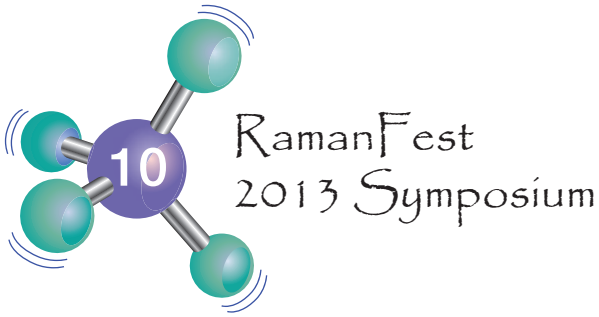
Raman microspectroscopy is an excellent tool for cost effective, non-destructive in situ investigation of plant materials, allowing sub-cellular spatial resolution and providing a complete fingerprint of the chemical composition of cell walls, while maintaining tissue context and anatomical features. However, interpretation of spectra in terms of specific cell wall biopolymers (lignin, cellulose, pectins, hemicelluloses, etc.) is often problematic. These problems include suboptimal spectral quality (due to the optical-physical properties of sections, among other factors) and the close chemical similarity of many cell wall biopolymers, resulting in overlapping, unspecific bands that are seldom diagnostic individually. With the exception of Raman image processing of plant materials, different multivariate methods are frequently applied to spectroscopic data in order to enhance input data quality and to decipher qualitative and quantitative information from the spectra. Our aim is to develop a multivariate approach that is specifically tailored to process Raman spectroscopic maps of plant materials. The method handles data pre-treatment (noise-filtering, cosmic ray removal, baseline correction, smoothing and normalization) as well as analysis (multivariate curve resolution) in an efficient way, maximizing resolving power, reproducibility and automation (i.e. minimizing the need of user supervision). The ultimate goal is to employ multivariate imaging to visualize qualitative and quantitative variation (spatial distribution) of any user-defined property, such as individual biopolymers (e.g. cellulose distribution), tissue, cell type or cell layer specific chemical compositional changes (e.g. the composition of wood fibers in different developmental zones in tree stems), and the effects and extent of perturbations (e.g. wounding, fungal infections, transgenic modifications), or any combination of these. One example is the investigation of compositional changes in poplar fibers in connection with tension wood formation (see the poster “Chemical composition in wood cell walls revealed by multivariate Raman imaging” by Judith Felten et al, for more information).



Chemical composition in wood cell walls revealed by multivariate Raman imaging

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Fiber cells are responsible for the mechanical support in stems and branches of angiosperm (leaf) trees. These cells have layered cell walls, consisting of the middlel amella, primary cell wall and a lignified secondary cell wall with sub-layers. Secondary cell walls develop last during fiber differentiation and make up the major part of woody biomass. Fiber cell development can be impacted by environmental stimuli. When a stem or branch is displaced by e.g. wind, snow-load or asymmetric crown shape, a cellulose-rich layer with gelatinous structure (G-layer) forms within the fiber cells. This special type of wood is called tension wood (TW). The presence of TW puts a strain on the stem to reorient growth towards a more favorable (upright) position. The gaseous plant hormone ethylene is involved in TW formation and ethylene biosynthesis is induced in displaced stems. However, even transgenic, ethylene-insensitive trees are able to form fibers with G-layers (G-fibers). Using Fourier-transform infrared microspectroscopy, we detected that the overall chemical composition of G-fibers in ethylene insensitive trees is different compared to G-fibers in wild type trees. The question arose whether this chemical difference resides in all cell wall layers, or is mostly attributed to the G-layer itself. We are using Raman-imaging, which provides high enough spatial resolution, combined with a newly developed multivariate approach (see poster Multivariate image processing for Raman maps in plant sciences by András Gorzsás) to classify spectroscopic data of fibers according to cell wall layers and to compare data from these layers to reveal chemical differences between a) cell wall layers in normal fibers and G-fibers and b) G-fibers of ethylene insensitive and wild type trees. This approach allows us to discover how TW formation alters the composition of the respective cell wall layers and whether this depends on ethylene signaling.

Explanation of the Spectra of Surface Enhanced Optical Phenomena, Based on Ideas of Tip Enhanced Spectroscopy

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Investigation of surface enhanced optical phenomena is of great interest. In [1] it was demonstrated that the reason of their enhancement, of SERS in particular are strong dipole and quadrupole light-molecule interactions arising in surface electromagnetic field near rough metal surfaces. The enhancement coefficients for the dipole and quadrupole mechanisms of SEIRA, SERS and SEHRS can be described by the approximate formulae

and can be very strong. Here n = 1 for SEIRA, n = 2 for SERS and n = 3 for SEHRS, $C_0 \sim 1$ is a numerical coefficient, l_1 is a characteristic size of the roughness of a tip, or cone type, $0 < \beta < 1$, $B_{\alpha\alpha} >> 1$, is a numerical coefficient, associated with some features of the quadrupole interaction, is the distance from the top of the tip and the molecule, a is a size of the molecule. The most enhancement in symmetrical molecules arises due to the quadrupole light-molecule interaction with the Q_{main} quadrupole moments, which are linear combinations of the quadrupole moments Q_{xx}, Q_{yy}, Q_{zz} with a constant sign, transforming after the unit irreducible representation of the molecule symmetry group. The scattering via the quadrupole moments causes appearance of forbidden lines in the pointed processes in molecules with sufficiently high symmetry and explains strong forbidden lines, caused by vibrations with the unit irreducible representation in the SEIRA and SEHRS spectra. In addition it explains appearance of forbidden lines in SERS and all other features in all these spectra. Analysis of a large number of the spectra of specific symmetrical molecules demonstrates the validity of the above theory.

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RamanFest 2013 Symposium

Reactivity studies on dinuclear manganese tmtacn complexes

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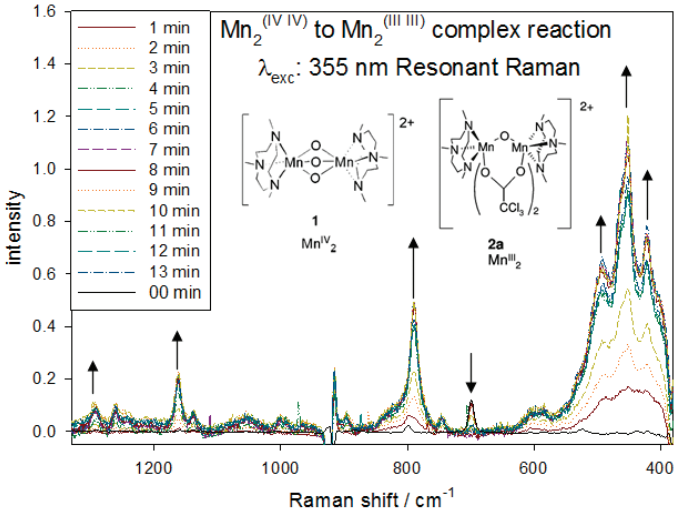
The $[Mn^{IV}_2(\mu\text{-}O)_3(tmtacn)_2]^{2+}$ complex [1] (where tmtacn = N,N',N"-trimethyl-1,4,7-triazacyclononane) was found by our group to be a highly efficient catalyst for epoxidation and cis-dihydroxylation of alkenes with H_2O_2 in presence of carboxylic acids[1]. The high activity (2000 turnovers) is achieved as a result of the autocatalytic formation of a bis(μ-carboxylato)-bridged dinuclear manganese (III,III) complex [2]. In this contribution the efforts to elucidate the autocatalytic transformation of complex [1] into the bis(μ-carboxylato)-bridged complex [2] are reported (in figure). UV-vis, Raman and Resonance Raman spectroscopy are employed to monitor the kinetics and the formation of intermediates and the product.



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RamanFest 2013 Symposium

Real-time fluorescent-SERS (Dual modal) endomicroscopic imaging system for multiplexed diagnosis

Sinyoung Jeong[1], Homan Kang[2], Gunsung Kim[1],Hyejin Chang[1], MyeongGeun Cha[1], Yoon-Sik Lee[2], and Dae Hong Jeong[1*]

Thus far, optical imaging techniques using nanoprobes have been intensively studied for an accurate, early, and rapid diagnosis in biomedical research fields, since it has significant advantages for in vivo diagnosis, such as non-invasive process, harmless of non-radioactivity, and high sensitivity. Especially, for accurate diagnosis of a specific disease, multiplex approach in bio-imaging is essential, because not a single biomarker is expressed but multiple biomarkers are expressed by a specific disease simultaneously. In this regard, although fluorescence has been successfully used to track the distribution and localization of bio-molecules due to highly intense signal, it has limitations in multiplex diagnosis due to broad emission band, multiple excitation source and photo-bleaching. On the other hand, surface enhanced Raman scattering (SERS) has great advantages in multiplex detection owing to a narrow bandwidth of less than 1 nm, high photo-stability, and high sensitivity. However, SERS has also obstacles for *in vivo* multiplex bio-imaging such as low penetration depth. To overcome the problems, we designed the fluorescence and Raman endomicroscopic imaging system (FREIS) with fluorescence-SERS active nanoprobes (F-SERS dots) in order to utilize advantages of intense signal of fluorescence, multiplex capacity of Raman scattering, and accessibility of endomicroscope. It was designed to be able to detect the fluorescence and Raman signal simultaneously. Furthermore, FREIS provided the fluorescence images and SERS spectra with real-time. It means this system can be applied for real-time in vivo diagnosis of cancer during clinical endoscopic examinations. Herein, to demonstrate the possibility of *in vivo* detection, we investigated the F-SERS dots on the slide glass and the surface of phantom tissue.

RamanFest 2013 Symposium

New possibilities for paper analysis by Raman chemical imaging

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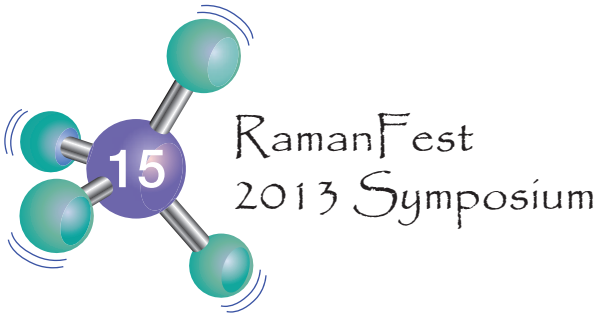
With a few exceptions, paper is a product with a highly complex structure. Apart from fibrous materials, it contains a multitude of different components such as fillers, pigments, sizing and wet strength agents in addition to other chemical additives. The resulting paper properties depend strongly on the penetration and its consequent cross-sectional distribution (z-direction) of the additives in the paper sheet. Therefore, it is important to know the z-distribution of these substances in paper and paper board. However, analytical methods investigating the structure and composition of paper in z-direction have been lagging behind surface-analytical methods (x-y direction) to this day. Measurements in z-direction continue to present a major challenge regarding both local resolution and material specificity.
Raman spectroscopy offers new opportunities to analyse the z-distribution of substances in paper. It is capable of effectively detecting chemical compounds selectively and with a high spatial resolution of a few micrometers. In addition, Raman spectroscopy is particularly suitable for the spectroscopic analysis of paper because the numerous OH groups present in cellulose give no signals in the Raman spectra. Therefore, unlike infrared and near infrared spectra, the Raman spectrum shows many characteristic vibration bands of the other paper components which can then be evaluated.
Despite the great potentials of Raman spectroscopy for spatially high-resolution chemical analysis, so far, only few Raman studies have been reported on paper cross sections [1]. The poster presents Raman spectroscopic studies of the z-distribution of chemical substances in the paper cross section. Results obtained from model and industrial papers demonstrate the new possibilities for paper analysis by Raman imaging.

Reference:
[1] E. Pigorsch, M. Finger, St. Thiele and E. Brunner, Analysis of Starch Distribution in the Paper Cross Section by Raman Microscopy, Appl. Spectrosc. 67(1) (2013) 59-65



In situ Raman spectroscopy on lithium-oxygen batteries

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Lithium-oxygen batteries are prospective next generation systems for storing electrical energy, since theoretical energy densities exceed those of Li-ion batteries by nearly one order of magnitude. However, the nature of electrochemical reactions during cycling is still under debate. For the analysis of emerging reaction products Raman spectroscopy is a powerful tool. Especially when used for in situ measurements it helps to gain insight into the chemical reactions and the nature of reaction products directly during charge and discharge. For this purpose we have constructed an electrochemical cell that serves multiple requirements like electrical feedthroughs, optical window, gas flow and minimized film of electrolyte. Since there is not yet a suitable electrolyte that serves all demands in the lithium-oxygen cell system we have investigated various ionic liquids and DMSO-based electrolytes that are prospective candidates to be applied in lithium-oxygen system. For reaction mechanism during charge in DMSO-based electrolyte the obtained Raman data suggest a direct dissolution of Li_2O_2 into Lithium and oxygen without any intermediate. Conclusions are supported by mass spectroscopy of the gaseous species evolving from the Raman cell during the charging cycle.

RamanFest 2013 Symposium

Sub-spectral evaluation of Raman shifts that define strains and species within the genera *Staphylococci* and *Escherichia*

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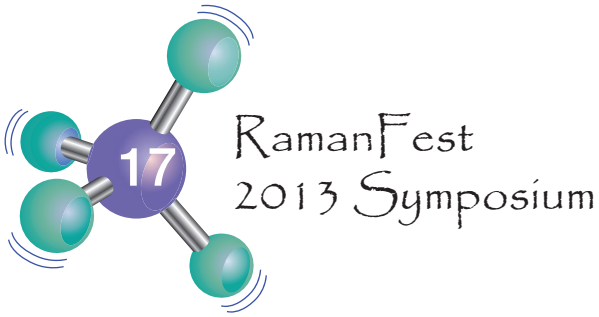
Robust and reproducible discrimination is a major goal of cutting edge microbiology. Current methods of discrimination involve biochemical, protein and DNA techniques and automated versions of them but are not so amenable to rapid diagnostics because of the need to prepare biological molecules for analysis. Raman spectroscopy has gained wide acceptance as a next-generation tool due to its ability to analyse intact micro-organisms in the forms of colonies, micro-colonies, biomass smears or single cells.

The spectra of bacterial specimen are complex with well over 100 Raman signatures which have been used to discriminate at species and strain level. For chemometric processing key information on the discrimination between micro-organisms is by and large found within the «spectral fingerprint region» 600-1600 cm^{-1} on which we restricted our analysis. In particular, we tried to identify major discriminatory «hot spots» for given micro-organisms, related to biological molecules including amino acids, DNA/RNA, sugars and fats.

The aim of our (and other groups') current efforts is to gauge the potential of micro-Raman spectro¬scopy for identifying bacteria at both the species and strain level, and further to discriminate between strains that may reveal different profiles of antibiotic resistance. Here we present some results from systematic studies on a selection of clinically relevant bacteria, namely *Staphylococcus epidermidis* (strains 1457, 1457-M10 and 9142), *Escherichia coli* including wild-types (strains B, K12 and Top10) and specimen expressing ampicillin and kanamycin resistance (Top 10^{Amp} and Top 10^{Kan}).

The bio-informatics processing and analysis reveal that the replicate spectra for each individual strain exhibited very high reproducibility, and showed that bacterial species, strain and isogenic mutant strains with defined resistance could be separated into discrete clusters. As expected, the degree of separation decreased in the order «species» → «strain» → «isogenic strain».



Reliable Raman measurements in research, health and industry - New reference procedures supply traceability for SERS and conventional Raman spectrometry

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Raman spectrometry is widely applied for the identification and quantification of chemical compounds. However, one major obstacle preventing quantitative Raman measurements from being reliable and comparable comes from the limited availability of reference materials and procedures. To underpin industrial and bio-medical applications of Raman spectrometry is one objective of the *European Metrology Research Programme* (EMRP).

Joint Research Projects (JRPs) implemented within this framework support collaborative metrological research and development. In particular, current JRPs cover metrological needs for 2D/3D dimensional traceability of spatial mapping and depth-profiling as well as for amount-of substance measurements of biomolecules (*"Thin Films", "Raman Metrology", "Metallomics"*).[1-3]

Quantitative (micro) Raman spectrometry places itself at the borderline between analytical chemistry and dimensional metrology. While traceability of the chemical composition of a sample is achieved via high purity reference compounds, reference standards and methodologies qualified to provide traceability to spatial resolution and area measurements are not yet available. Since existing optics standards have proved inadequate for lateral Raman mapping, PTB has designed and fabricated new reference samples. The link to the SI unit of length was accomplished by scanning force microscopy being itself traceable to the metre.

Traceability of amount-of-substance measurements to the mole has been achieved at PTB by the adaption of the isotope-dilution (ID) technique from mass spectrometry. In the so-called IDSERS approach, an isotopologue of the target analyte is added to the sample prior to the analysis to act as internal standard. The method has been validated by successful participation in two international ring trials on clinical chemistry. Recently, IDSERS was accepted as a higher order reference procedure for the determination of biomarkers in human serum and admitted to a publicly accessible database maintained by the International Bureau of Weights and Measures (BIPM)[4].

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Application of the Raman spectroscopy for the identification of bacteria in the field of food science

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The detection of microorganisms is required in all field of health particularly in the food safety chain. The regulation requires systematic controls to check the innocuousness of products by standard microbiological methods that are tedious, yet time-consuming and need highly qualified staff.
Our project aims to evaluate the applicability of the Raman spectroscopy in the identification of microbiological contamination following the instructions and the requirements of a typical identification scheme. Thanks to Raman spectroscopy, the fingerprint of the main components of the bacterial cell is compared with a pre-established database of pathogens spectra in order to identify the strain.
To cope with the low reproducibility of analyses, several bacterial strains were analyzed by Raman spectroscopy according to their growth phases in the purpose to identify the best phase for identification. The classification of spectra by Principal Component Analysis and Hierarchical Ascendant Classification shows that the exponential growth phase is the optimal stage for the discrimination because bacteria are more homogeneous and consequently the identification is more secure. A rigorous protocol was designed and validated with many samples from food industry. A good correlation was obtained by comparing the spectrum of isolated bacteria with the database already established.
The final goal is to introduce this procedure in the control system of food production chain thanks to a reliable database for various microorganisms.

Thanks to all financial partners of this project, special thanks to Conseil Général de la Vendée for his financial support

RamanFest 2013 Symposium

Single cell membrane analysis by TERS is reaching nanometer scale

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It is known that cell surface glycoproteins are acting as cell specific identifiers for cell-cell interactions. Those macromolecules are often important integral membrane proteins, where they play a role as a receptor for active ingredients and second messengers.
A common method to identify membrane proteins is antibody labeling. Depending on the nature of the markers it is possible to use fluorescence or Raman spectroscopy as an analytical method. Especially silver and gold-labeled antibodies turned out to be very interesting as they can be used to increase the sensitivity of Raman labels via a plasmon enhancement[1]. However, the lateral resolution capability with respect to the location of specific protein arrangements of this method is limited. Another disadvantage of labeling with antibodies is the selectivity of the marker. Different and specific markers must be chosen for each protein of interest.
To provide spectroscopic information with high spatial resolution tip-enhanced Raman scattering (TERS) is the technique of choice[2]. The combination of an atomic force microscope (AFM) with a Raman microscope provides information on the topography and the molecular structure of a sample with high sensitivity.
We present results of TERS mapping measurements on colon cancer cells. In particular, an area of 90 x 90 nm was analyzed. Within this area spectra were recorded on a square grid with a spacing of 10 nm.
Based on hyperspectral unmixing algorithm (N-FINDR), a band assignment of the spectrum of each endmember was done. As expected, all the TERS bands can be attributed to proteins or lipids, the known components of the cell membrane. Correlating the band assignment and the N-FINDR results, a label-free localization of membrane components could be achieved. We demonstrate that the combination of high lateral resolution and specificity of TERS potentially allows a direct differentiation of membrane protein and lipid regions[3].

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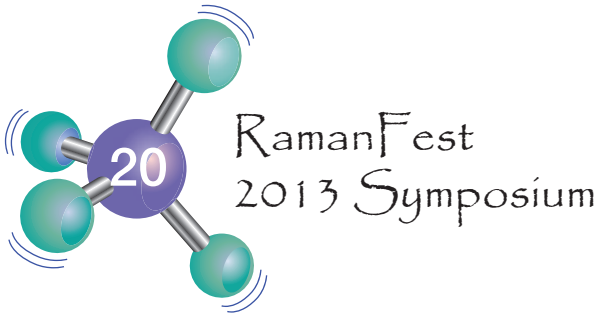

Development of an environmental levitation cell coupled with Raman micro-spectrometry to probe in-situ physico-chemical processes within atmospheric particles

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Raman spectroscopy is a non-destructive technique that provides detailed molecular and structural information with a spatial resolution of about 1 μm^3, and it is a valuable tool to follow real-time evolutions of volume or surface structures under controlled conditions. Micro-Raman spectroscopy, coupled to an environmental levitation cell, is especially useful for studying, at micrometric scale, the in-situ modifications of aerosol when exposed to reactive environments or humidity without the influence of a contacting surface. Moreover, photochemical transformation can be followed by irradiation of the particles.
Here, we present an environmental acoustic levitation cell coupled to the micro-Raman spectroscopy to monitor the physical and chemical processes occurring in particles of atmospheric interest when exposed both, to humidity and UV-Vis light. Physical and chemical changes can be followed at the interface or deeper depending on the optical properties of the particle.
The levitation system consists of a modified ultrasonic levitator (APOS BA 10, Tec5, Germany), installed within a small dimension environmental cell. The cell comprises 4 optics accesses, and transparent quartz windows allowing the exposure to UV radiation. Two inlet/outlet valves are used for gas supplies to modify the environment inside the cell. The relative humidity and the temperature are also measured within the cell by using an adapted sensor. The levitator was horizontally coupled to a Raman microspectrometer HORIBA Scientific LabRam HR, equipped with a CW 473, 532 and 633 nm lasers and a Liquid Nitrogen-cooled CCD camera. We used the micro arrangement in backscattering mode.
This work is supported by funds from the «Laboratoire d'Excellence (LABEX) - CaPPA project (Chemical and Physical Properties of the Atmosphere)» through the PIA (Programme d'Investissement d'Avenir) under contract «ANR-11-LABX-0005-01- and IRENI (Institut de Recherche en ENvironnement Industriel) program.

RamanFest 2013 Symposium

Raman microspectrometry for environmental sample characterization From individual particle analysis to vegetable leaf investigation

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The analysis of metals in environmental solid samples (aerosols, soils, sediments, plants…) is required to determine the contamination level in the environment. However, the total concentration of elements measured in bulk samples is not sufficient to predict the impact of metals in term of toxicity and/or bioaccessibility. It's now well established that characterizing the speciation of metals i.e. molecular forms within such samples is much more important to understand the metal accumulation and transfer in the ecosystems. Determining the spatially resolved speciation is of prime importance to understand the physical and chemical processes involved in the accumulation and compartmentalization of metals which in term determine their toxicity.
Raman spectroscopy is a non-destructive technique that provides detailed molecular and structural information with a spatial resolution of about 1 μm^3 without sample preparation. The Raman mapping enables to record a huge spectral data set from a defined area of the sample. The treatment of the spectral data set by using chemometric methods such as multicurve resolution (MCR) is powerful to extract pure spectra which are attributed to a unique molecular species and to image the distribution of species within samples.
Here we present the application of Raman microspectrometry to characterize the spatially resolved metal speciation in environmental solid samples. We investigated the speciation of lead within industrial particles and plants contaminated by atmospheric fallouts from industrial emissions. The study is focused on the foliar transfer of particles. Analyses of individual particles collected in the atmosphere give information about the molecular species within particles and the mixing state of particles before their deposition. The molecular analysis of particles combined with image analysis performed on optical images provides a size-resolved distribution of lead-rich species within particle samples. Raman analyses (in the UV range) of plant leaves contaminated with lead-rich particles were unique to characterize the speciation and distribution of lead within leave samples. Then, we were able to propose, for the first time, an internalization mechanism of particles by plant leaves which occurs during the foliar transfer of industrial particles.

RamanFest 2013 Symposium

Development of a chemometric procedure for evaluating the quality of Raman spectra used in bacterial strains discrimination

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Usually, mass spectrometry and related techniques are widely used to control the microbiological quality of food. Optical spectroscopies such as Raman spectroscopy complete this set of techniques efficiently. The proposed communication shows a new Raman-based methodology to produce good spectra usable in a chemometric procedure allowing the identification of the microbiological contamination following the instructions of ISO 2002:6579 standard method. This procedure was setup on 272 Raman spectra acquired on a selected microbiological strain (*Escherichia coli*). Discriminant PLS models (PLS-DA) and stepwise factorial discriminant analysis (FDA) were applied to found the best models for separating GOOD and BAD spectra. The same procedure was repeated and applied with success on spectra issued from new bacterial strains for both extracting the best Raman spectra and for classifying 98 samples from 5 different strains. The best discriminant model gives 100 % good classification for calibration and validation sets with a minimum number of components. The discrimination of two serotypes of Bacillus strain was also possible with this procedure. The performances of the calculated models are compatible with their use in quality control context via an automatic and on-line acquisition procedure.

RamanFest 2013 Symposium

Analysis of single nucleotide mutations in *Yersinia Pestis* bacteria by using SERS monitoring and electrochemical melting

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There is an increasing demand for low cost, rapid and sensitive methods for the detection of mutations in the post-genomic era. Here we demonstrate the effective discrimination of Single Nucleotide Polymorphisms (SNPs) from the genome of *Yersinia Pestis*, which is the causative agent of plague and closely related Yersinia species.

Previously we showed that we can exploit SERS together with electrochemical melting to discriminate mutations in short DNA strands[1,2]. In this study, discrimination of SNPs within unpurified long PCR products from Y.pestis utilising both applied potential and temperature was achieved.

For the analysis, Raman active gold sigmoidal segment void (SSV) surfaces were prepared according to a previously published method.[1]Dithiol-modified 24-mer probes were immobilised on the gold surface and then hybridised with the PCR products that were labelled with Texas Red.The PCR product was 251 bases long with the A to G mutation at position 110 bp. When hybridised to the probe sequence on the surface, it had long overhanging sequences at both ends. Applying acathodic potential cause the spectral intensities of the Texas Red bands to decrease as the dsDNA on the surface denatures. Plotting the SERS intensities against potential yields the SERS melting profiles of the wild type and the mutant. At room temperature, both strands display broad melting profiles and discrimination of DNA strands carrying only one mismatch is not very clear.

Interestingly repeating the experiment at lower temperature (10°C), improves the discrimination. The sigmoidal melting transition of the wild type becomes sharper while the one of the mutant remains broad.

Those results illustrate the discriminating power of this technique.

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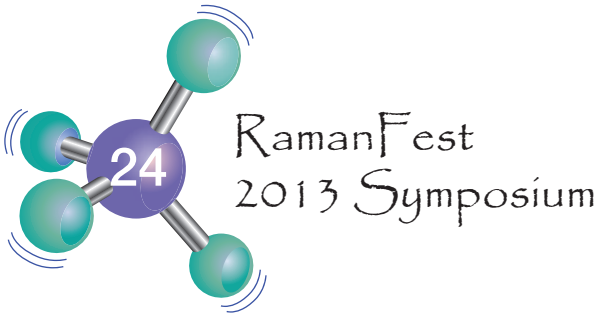

Raman scattering based analysis of new kesterite photovoltaic materials: correlation with chemical analysis and device properties

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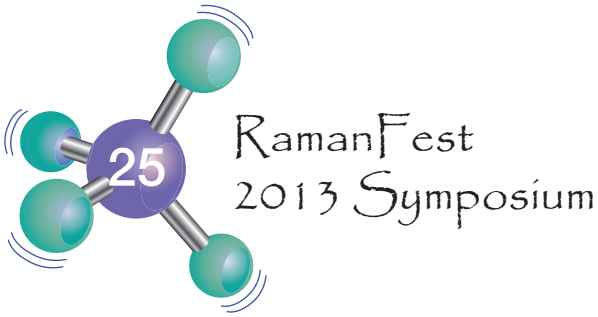
The numerous advantages which Cu_2ZnSnS_4 (CZTS) kesterite compounds offer for thin-film photovoltaic (PV) solar cells have recently increased the interest of the scientific community in these materials. CZTS compounds are only composed of non-toxic and earth abundant elements, which make these materials especially suited for the development of new sustainable PV technologies. As a result, several new processes for kesterite film formation have been proposed, which require new characterization methodologies. During the processing of the solar cell absorbers, different types of secondary phases are often formed. Presence of these phases should be well controlled and characterized precisely since they can lead to deterioration of the solar cell efficiency. X-ray based characterization methods have a limited application for this material, because several secondary phases have almost the same structure and in consequence, very similar x-ray diffraction patterns. In this work we present a methodology based on classical and pre-resonant Raman scattering strategies for the selective high sensitivity detection of secondary phases in the Cu_2ZnSnS_4 system, by using several excitation wavelengths, from infrared to ultraviolet. This method allows detecting different phases such as ZnS, Cu-S and Sn-S. Detection of these phases has been used for the optimization of the processes for production of kesterite-based device-grade absorbers. This has led to the development of specific chemical surface treatments for the selective removal of ZnS secondary phases, as well as the characterization of the mechanisms involved in films synthesis, investigating the role of intermediate binary phases such as Cu_xS, Sn_xS_y and ZnS in the reaction pathway leading to the formation of CZTS device-grade films using a two-step PVD deposition and sulfurization process. The detailed characterization of these processes by depth-resolved Raman scattering combined with Auger Electron Spectroscopy was used to optimize the technological process conditions in order to improve optoelectronic devices properties.



Micro-Raman characterization of 3C-SiC microstructures

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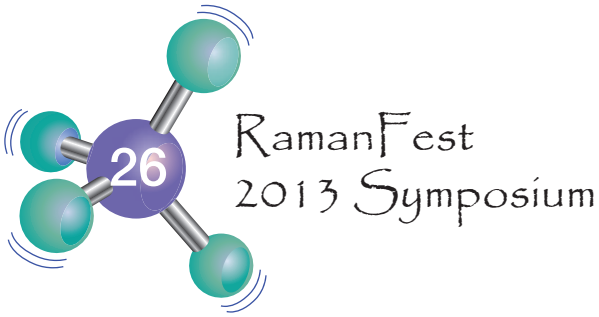
The high spectral and spatial resolutions of micro-Raman tools allow to characterize micro- and nano-electromechanical systems (MEMS and NEMS) fabricated in single crystal 3C-SiC. Such micro-structures (cantilever, bridge and planar rotating point) are receiving particular attention thanks to the material physical properties: its wide band gap (2.3 eV), its ability to operate at high temperatures, its mechanical strength and its inertness to the exposure in corrosive environments. The stress characterization performed through the use of microstructures allows to analyze the relaxation of the epilayer after removing the substrate (001)Si. The analysis of the stress distribution within a small critical region has been performed by probing the transverse optical mode (TO). An intense stress field has been revealed around the anchorage point of the 3C-SiC structure, that is the zone where the microstructure starts to be released. Such a region (called undercut) experiences an intense stress field that consists of a simple planar stress plus shear stress terms. TO Raman mode undergoes an intense shift (more the 2 cm^{-1}) within small region (about 20 micron). These variations can be ascribed to a deep modification of the stress tensor where the role of the shear component cannot be neglected leading to a failure of the standard interpretation of the measurements based on the validity of the generalized axial regime.
Furthermore, micro-structures have been analyzed by Raman spectroscopy to determine the Raman stress free value of the material. Micro-Raman analysis of 3C-SiC membrane square (1x1mm), deflected by an applied pressure, has been performed. Through the development of a dedicated theory for the large deflection a linear relationship between the shift of the Raman modes and the total in-plain stress has been found. The calculated stress free value of the TO Raman mode is 796.71 ± 0.04 cm^{-1}.



Temperature dependent structural transformations of dimyristoylphosphatidylcholine (DMPC)-water systems investigated by micro-Raman Spectroscopy

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Cells of living organisms can be thought as phospholipids membranes, sometime functionalized by proteins, which are immersed into water environment. The physical-chemical interactions at the interface membranes/water are responsible of the stabilization of the membranes. In addition, the drug efficiency, the pharmaceutical mechanism and the improvement of the drug design can be addressed to the interactions between the interface membranes-water with the drug and to the membrane-drug. In this framework, it is important to find membranes models able to simulate and simultaneously simplify the biological systems to better understand the physical chemistry interactions at the interface level. Dimyristoylphosphatidylcholine (DMPC) is a synthetic phospholipid used in order to make Large Unilamellar Vesicle (LUV), Giant Unilamellar Vesicle (GUV) and Multilamellar Vesicle (MLV). In this work, in order to understand the formation mechanisms of the vesicles, mixtures of DMPC and water with different weight ratios have been made and analyzed by micro-Raman spectroscopy at different temperatures in the range between 10 to 35°C. These investigations, beyond the determination of phospholipid hydrocarbon chains order, provide information about the composition and the conformation of the lipid membranes. The spectra were collected by a Raman microprobe HORIBA Jobin Yvon LabRAM (spectral resolution ~ 2 cm^{-1}) equipped with a CCD detector and a He-Ne laser (λ = 632.8 nm).
The Raman evidences of the vesicle formation has been proposed and the mixture with better ratio DMPC/water, to be used as in-vitro model for biological systems, has been identified.

RamanFest 2013 Symposium

Laser induced aggregation of gold nanorods for SERS biosensing in liquid environment

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The discovery of Surface-Enhanced Raman Scattering (SERS) opened the doors to promising applications in optical biosensing for proteins detection [1,2]. A controlled creation of hot spots in liquid, the natural habitat of biomolecules, is a challenge in which optical forces play an important role [3].

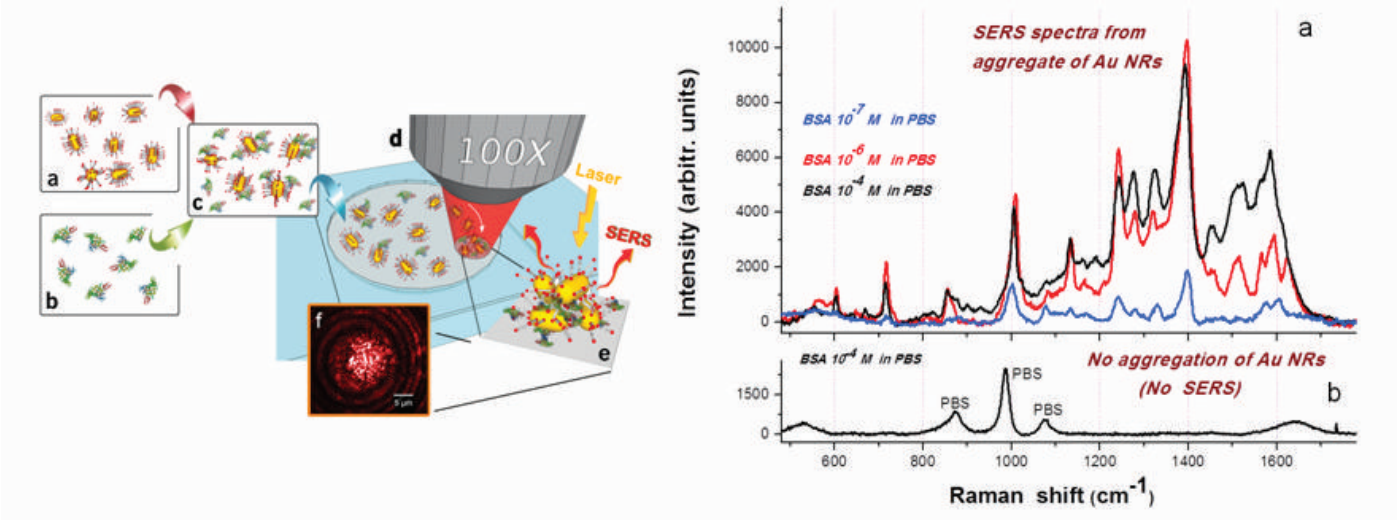

Fig. 1: **Left**. *(a-e) Sketch of the experiment and (f) picture of the BSA-NRs aggregate.* **Right** *(a) SERS spectra of BSA at different concentrations (10^{-4} M black, 10^{-6} M red, 10^{-7} M blue). (b) Solution phase Raman of BSA at 10^{-4} M.*

Here we report [4] on a novel concept of label-free, all-optical SERS biosensor for proteins detection in liquid, based on the laser-induced aggregation of gold nanorods (NRs) in proteins buffered solution (Fig.1, left). Commercial gold NRs dispersed in deionized water and capped with CTAB molecules are mixed with the target proteins dissolved in PBS in a glass microcell. A laser beam is then focused on a micron scale spot inside the liquid solution. Due to repulsive optical interaction, NRs-protein complexes thermally drifting through the laser spot pushed towards the bottom of the glass microcell. Here they stick and accumulate, forming SERS-active aggregates. BSA has been used as a model protein to test the sensor performances (Fig 1, right). We reach sensitivities down to 10^{-7} M (blue line), whereas solution phase Raman spectroscopy of BSA is already impossible at concentrations of 10^{-4} M (black line). This methodology can pave the way to a new generation lab-on-chip sensors that implies user-friendly experimental set up allowing for highly sensitive vibrational spectroscopy of biomolecules in their natural habitat [4].

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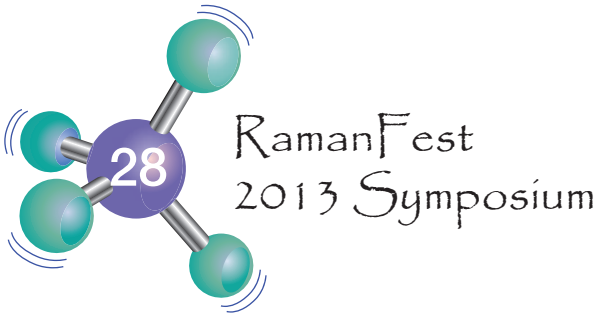

Raman imaging of copper ores

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In Middle Europe large deposits of Kupferschiefer involve the Upper Lusatia, the northeastern part of Saxony. The regional Kupferschiefer raised again interest of both industry and science because in this region its copper content constitutes the most important natural copper resource. There is no efficient biotechnological approach applied yet due to the fact that Kupferschiefer is complexly composed comprising different sulfidic minerals, carbonates and organic compounds. Bioleaching, which means the use of microorganisms and their metabolites to extract metals from their ores, reduces costs of high energy input and avoids the usage of toxic chemicals thus benefitting environment (Narayan 2009) and employees. Raman spectroscopy enables a fast and specific chemical identification of minerals and ores (Hope 2001) as well as the detection of changes e.g. that are caused by oxidation (García-Meza 2012). Also Raman spectroscopic imaging of biotic components such as biofilms has already been performed (Virdis 2012).
We aim to use Raman spectroscopy to investigate the interactions of microorganisms and ore surface: Different polished sections of bornite, chalcopyrite (both from Henderson Mine, Namagualand, South Africa), chalcosite (Ashio, Japan) and copper shale (Polkovice, Poland) were analysed by polarising microscopy to ensure correct spectra assignment. Subsequently identical areas were analysed by Raman imaging using 2D scanning function. After incubation with microorganisms the sections will be investigated again in order to evaluate chemical changes of the ore surfaces, biofilm formation and to monitor bioleaching processes.

Acknowledgments:
Best thanks to Axel Renno, Michaela Rossner and Andreas Bartzsch for their constant support.

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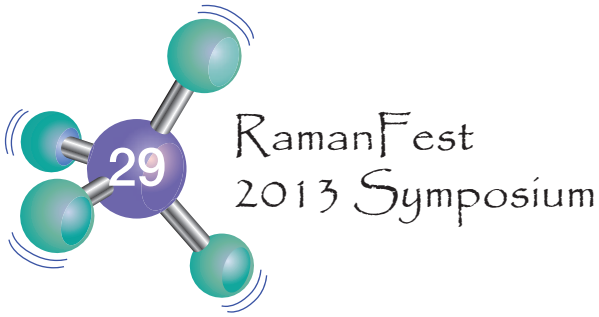

Potential of Raman spectroscopy in the diagnosis of Urinary Tract Infections.

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The potential of Raman spectroscopy to discriminate between 12 pathogens responsible for Urinary Tract Infections was evaluated from colonies cultivated on a growth medium. This clinical application seemed well suited for Raman analysis due to the relatively low number of species commonly observed in this type of infection (20 at most), due to the low probability to observe multiple species per sample and the high biomass present in positive urines. Different sample preparation techniques (smeared or washed after dispersion in a buffer or in synthetic urine) and conditions of spectral acquisition (photo-bleaching and accumulation times) were investigated in order to maximize the Signal-to-Noise Ratio (SNR) hoping to increase the level of correct classification. We are reporting here that despite a significant increase in SNR, the classification performance was not improved. The similarity between acquired spectra was estimated running Pearson correlation analysis. Although the compared spectra were acquired with different acquisition parameters, average classification levels approaching 90 % in a leave-one-strain-out analysis were measured: an indication that micro-Raman analysis seems relatively robust to variations in the acquisition protocol.

Synthesis, FT-IR, FT-Raman and dispersive Raman spectroscopic study of a host molecule (=$C_{52}H_{72}N_4O_{12}Si_2$) which potential applications in sensor devices

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The solid phase FT-IR, FT–Raman and dispersive Raman spectra of the host molecule (=$C_{52}H_{72}N_4O_{12}Si_2$) which potential applications in sensor devices have been recorded in the region 400–4000 and 50–3500 cm^{-1}, respectively. The spectra were interpreted in terms of fundamentals modes, combination and overtone bands. The structure of the molecule was optimized and the structural characteristics were determined by density functional theory (DFT) using B3LYP method with 6–31G(d) basis set. The vibrational frequencies were calculated for the studied molecule by DFT method, and compared with the experimental frequencies, which yield good agreement between observed and calculated frequencies. Finally the calculation results were applied to simulate infrared and Raman spectra of the compound. Obtained these spectra also showed good agreement with observed spectra. The dipole moment, linear polarizability and first hyperpolarizability values were also computed. The linear polarizability and first hyperpolarizability of the studied molecule indicate that the compound is a good candidate of nonlinear optical materials.

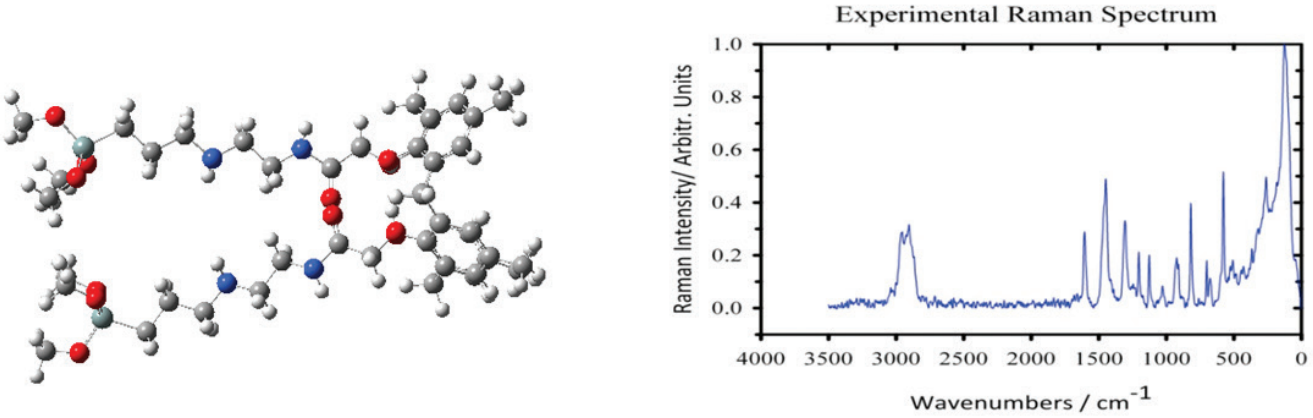

Figure: Studied molecule ($C_{52}H_{72}N_4O_{12}Si_2$) and its spectrum

Polymorphism and phase recognition of molecular crystals probes by lattice phonons Raman microscopy

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Polymorphism occurs when the same chemical compound exhibits two or more crystalline modifications and is quite common in organic molecular materials, where molecules are held together by non-directional, weak Van der Waals forces. The increasing interest of material engineering for the development of new electronic devices based on organic semiconductors has raised the attention on this subject for this class of materials. The careful phase control of polymorphic materials is indeed of paramount importance whenever phase purity is a strict requirement in sample preparation, as, for instance, in organic electronics devices. In fact, in these systems, charge carrier mobility, being dependent on the purity and the method of preparation of the material, ultimately will strongly depend on their crystal structure.
Raman spectroscopy is a valuable tool for non invasive, in situ recognition of molecular identity and conformation. However, when polymorphism occurs in molecular crystals, the chemical identity in the different crystal phases implies very similar or identical spectra for the intra-molecular vibrational modes of different polymorphs. One should then focus the attention on inter-molecular modes, i.e., collective translational or rotational motions of the molecules in the unit cell. These modes produce dynamical deformations of the crystal lattice called lattice vibrations or lattice phonons, whose frequencies, involving Raman shifts in the range ~10-150 cm^{-1}, probe the intermolecular interactions and hence are very sensitive to different molecular packings [1]. Because each crystal structure has its own dynamics, in organic molecular crystals lattice phonons are the fingerprints of the individual crystal structure.
The method illustrated here, lattice phonon confocal Raman mapping, is a powerful technique to probe the crystal structure of organic materials, being fast, reliable and capable to monitor in situ physical modifications and phase inhomogeneities in crystal domains at the micrometer scale. Comparison of optical images and Raman maps conclusively show that no relationship exists between morphology and crystal phase: structural information can be drawn only from Raman images. It is then crucial to perform a spectroscopic test in order to verify the phase purity in all crystals treated, especially for those cases in which crystal morphology cannot assist phase recognition.

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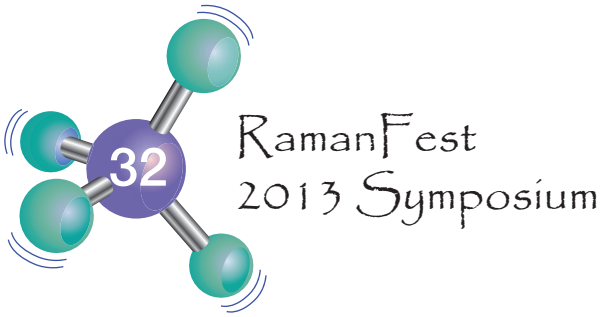

Photon-counting Raman spectroscopy of chip-scale photonic devices

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Nano-photonic integrated circuits monolithically fabricated on-chip have applications in sensing [1], lab-on-a-chip spectroscopy [2], all-optical signal processing [3] and photonic single photon generators [4]. In many applications it is vital that the characteristic Raman spectrum of the device be known. The spectral distribution of spontaneous Raman scattering (SpRS) can be measured in bulk samples with free-space optics [5], often requiring laser power level incompatible with the damage threshold of many chip-scale devices. Measurements of stimulated Raman scattering have been performed using nonlinear pump-probe techniques [6], requiring the addition of either a highly tunable or ultra-broad bandwidth probe. Recently photon-counting techniques have been demonstrated to measure weak SpRS signals in long optical fibers [7,8], however no direct measurements of the SpRS spectra of nano-photonic devices over a broad bandwidth had been performed.

We present a method for directly measuring the spontaneous Raman scattering in nano-photonic devices using an integrated and alignment-free setup. Using a pulsed fiber laser, liquid-crystal-on-silicon spatial light modulator and single-photon detector, we create a broadband photon-counting Raman spectrometer [9,10]. Our current setup provides a fixed measurement bandwidth of 10 THz, with the measured detuning range set by the choice of the pump laser line. We measured experimentally the Raman spectrum of several photonic integrated circuits fabrication from materials including amorphous and crystalline silicon as well as chalcogenide (As_2S_3) and compared this to free-space measurements of bulk samples and observed excellent agreement.

In conclusion, we have demonstrated direct broadband photon-counting Raman spectroscopy with the sensitivity required for characterization of chip-scale nanophotonic devices. Our method uses narrowband single photon sensitivity tuned over a broad spectrum to measure low SpRS signals.

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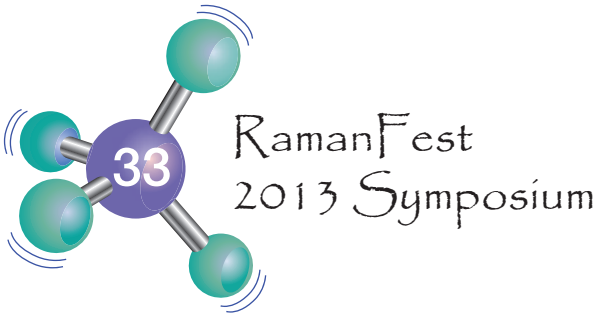

The study of electronic exitations in the high critical temperature superconductors by Raman Scattering

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The Raman responce in cuprates is related to the gap superconductor which represents the parameter of ordre. This parameter shown the electronic dynamic in the nodal and the antinodal regions.

Determination of the Composition of Cryolitic Melts Involved in the Hall-Héroult Process by Raman Spectroscopy

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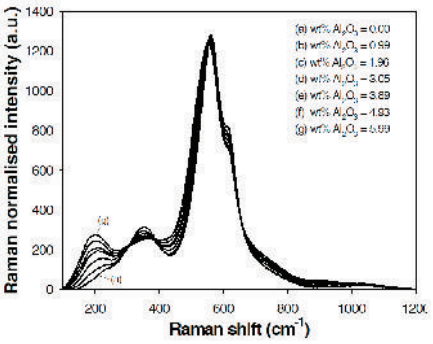
Worldwide metallic aluminium production involves the Hall-Héroult process. The metal is electro-deposited from aluminium oxide solubilised in a molten salts mixture at around 950°C. The main components of the industrial melts are cryolite (Na_3AlF_6), aluminium fluoride and alumina (Al_2O_3) to which additives such as CaF_2 are added. The cryolitic melt is conveniently characterised by both the molar NaF/AlF_3 ratio and the Al_2O_3 content. Nowadays the Hall-Héroult process remains the more economically efficient process even if it still suffers from a high consumption of energy[1]. In particular the overvoltage required by the electrolysis is drastically dependent on the melt composition, especially regarding the Al_2O_3 content. Controlling the industrial bath composition during the process is therefore critical to reduce the energy loss. Unfortunately there is, up to now, no in situ analytical method to do so.

Considering our experience in the study of such highly corrosive media by Raman spectroscopy and since the bath spectrum is function of the molar NaF/AlF_3 ratio and the Al_2O_3 content, we have proposed in the past to apply that technique to the direct determination of the melt composition[2]. However, if the method was successful at the lab scale, it could not be extended on the field for practical reasons, among them the too long time needed by spectra recording.

Very recent instrumental developments on CCD based spectrometers have made the proposed method more feasible and this presentation will first demonstrate that, employing an updated instrument, better quality spectra are obtained and in shorter times. Secondly, new results relevant to the development of our analytical method for the direct determination of the molar NaF/AlF_3 ratio and the Al_2O_3 content in cryolitic melt will be discussed. For instance, various important aspects of the calculation procedure assisted by home-made software will be illustrated:

- The estimation and subtraction method of the Rayleigh decay from melt spectra.
- The development of an internal normalisation procedure based on equilibria in the melt.
- The calibration curves for the determination of the molar ratio NaF/AlF_3 in the melt.
- The calibration curves for the determination of oxide content in the melt.

Finally, the overall procedure for the composition determination which is now directly applicable on the industrial field will be presented, together with a comparison of the results obtained on samples of known composition.



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RamanFest 2013 Symposium

Development of a quantitative approach to measure phospholipids indried drops by Raman spectroscopy

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Raman spectroscopy is an uprising analytical technique to study biomolecules. Not only it is a molecular spectroscopic method that gives information about the structure of the molecules but it is also a very valuable tool for quantitative analyses. Amazingly, mainly for experimental reasons, applications of Raman spectroscopy to quantitative analyses are scare even if there is often no fancy sample preparation and no sample destruction.

Phospholipids, as part of the lipidic molecules, are interesting biomolecules to analyse within biological samples. They play a role in the structure of live cells and are also suspected to be part of the development of some diseases like cancers. Raman spectroscopy, as a non invasive and non destructive method, is a potential candidate to quantify and to visualize the spatial distribution of phospholipids by molecular imaging. Unfortunately, the lack of specific phospholipid bonds (they are composed of mainly carbon-carbon and carbon-hydrogen chains) limits the use of Raman spectroscopy in the identification process of those phospholipids in complex biological samples. In addition, phospholipids are not likely to give intense Raman signals. Mass Spectrometry, as a complementary technique, enables the structural analysis of biomolecules in complex biological media but imaging mass spectrometry by MALDI-MS is rather limited for quantification purposes. The idea proposed here is to develop an independent and reliable quantitative approach by Raman spectroscopy for molecular imaging with an ultimate goal to make the link with MALDI-MS data.

We present here the results obtained during our tentative to analyse quantitatively dried drops of phospholipidic solutions by Raman spectroscopy. Drops of different solutions of phospholipid were deposed onto different material supports. The spots were then analyses by confocal Raman microspectroscopy. Experimental settings have been optimised and the analysis of the intensity profile of the Raman signal inside the spot allows the establishment of a calibration curve for the determination of the phospholipids amount within a 1 µL solution.

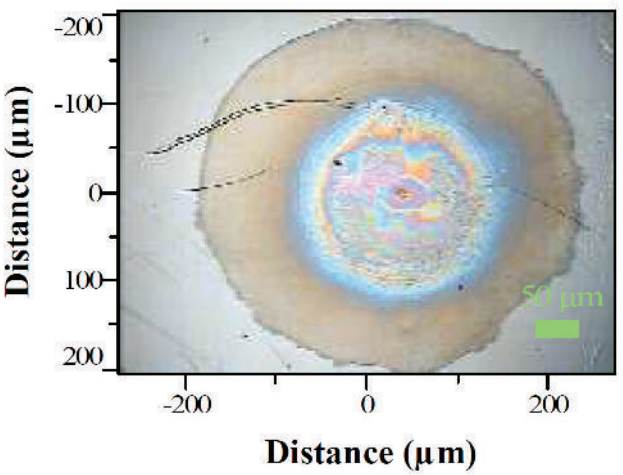
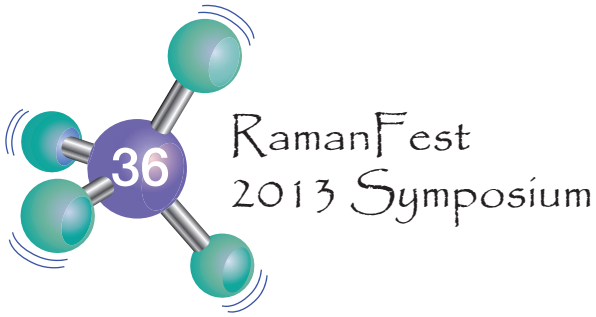


Figure.1 : Spot of a dry drop of phospholipid solution onto an inox plate.



The effect of zirconium doping on the thermal decomposition of hydrotalcites

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Hydrotalcites, a class of layered hydroxides with a general formulae $Mg_6Al_2(CO_3)(OH)_{16}•4(H_2O)$, have found diverse applications as catalysts, e.g., in the reaction of polymerisation, aldol condensation or Michael addition, in medicine as an antacid, and have been investigated as alternatives to basic oxide high-temperature sorbents for CO_2 sequestration. Before being used in these applications hydrotalcites must be first «activated» by calcination to obtain the required high-energy sites or remove interlayer anions to produce highly dispersed basic metal and metal oxide sites. When calcined, the hydrotalcites form a mixture of metal oxides. A similar composition and structure of the mixed oxides cannot be achieved by simple mechanical mixing of the pure metal oxides; the gain in activity justifies the indirect route towards the final catalyst or adsorbent with hydrotalcites being a sacrificial intermediate material.

Hydrotalcites may be doped with additional metals. This can be done to improve a catalytic effect or to improve the materials thermal stability. In this study the effect of zirconium doping was investigated. While the thermal decomposition of doped hydrotalcites have been extensively studied before, the comparisons have always been made between materials of different metal lattice structures. The effect of doping a hydrotalcite on the thermal decomposition has not been compared to the thermal decomposition of undoped hydrotalcites with the same metal lattice structure. Knowledge of thermal decomposition process is essential to standardise calcination procedure to produce the optimal performing mixed oxide.

To determine the effects of doping on thermal decomposition, two sets of hydrotalcites were made. The first (HTC1) was made with an undoped Mg-Al lattice, while the other (HTC2) was made with an Mg-Al-Zr lattice. The structure and thermal decomposition of these materials was studied under transmission electron microscopy (TEM), thermo-gravimetric analysis (TGA), in situ x-ray diffraction (XRD) and in situ Raman.

RamanFest 2013 Symposium

Raman spectroscopy studies on pulsed laser deposited graphene

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In the last years graphene has attracted considerable interest due to the huge potential for improvement of the current technologies [1]. There is still need to develop a method of forming uniform single-layer film and the precise control of the number of layers.

For graphene synthesis we propose to use Pulsed Laser Deposition (PLD) technique. There is only few articles that have been reported the deposition of graphene using PLD [2,3]. We obtain monolayer and few layers graphene using the catalytic growth of carbon laser produced plasma species on a predeposited nickel thin film. The influences of different nickel film characteristics (growth orientation and thickness) and deposition parameters (substrate temperature and cooling rate) on the graphene properties investigated through Raman spectroscopy. By means of Raman analyses in different region of the sample defects in sp2 honeycomb lattice and the number of layers are evaluated. Attempts are made to estimate the covering order of monolayer/few layers graphene by Raman mapping.

Acknowledgments
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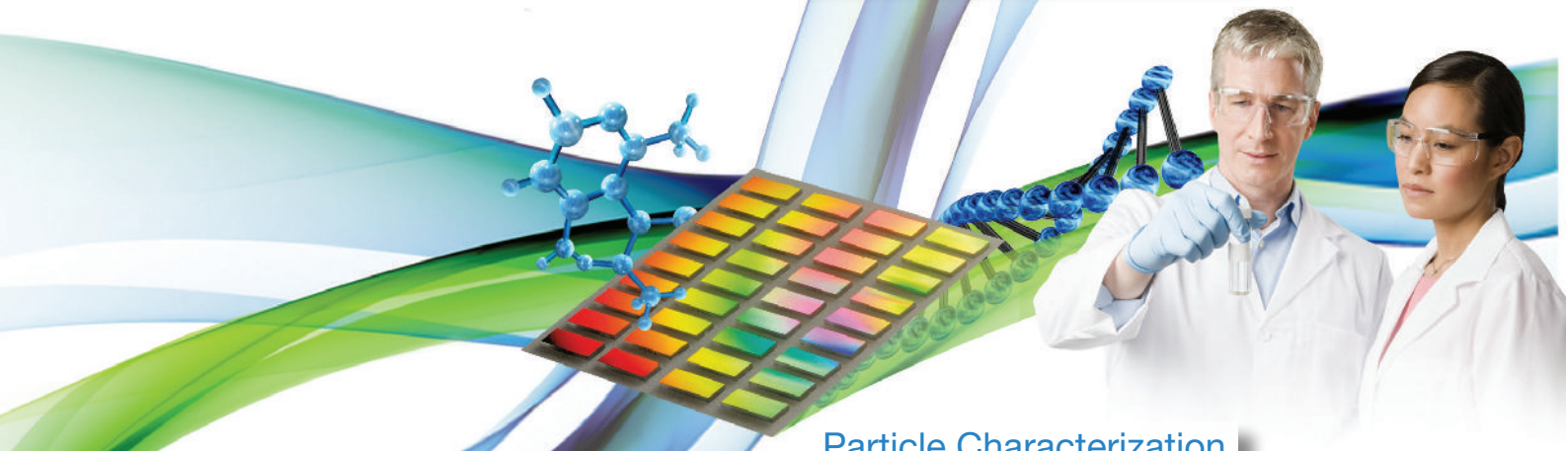

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