NEWSLETTER OF THE FP7-PEOPLE-2012-ITN "PNMR"

pNMR news

Pushing the Envelope of Nuclear Magnetic Resonance Spectroscopy for Paramagnetic Systems

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Editor-in-chief: Erin Rossini

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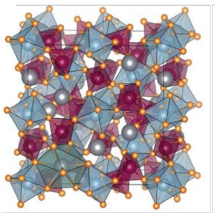
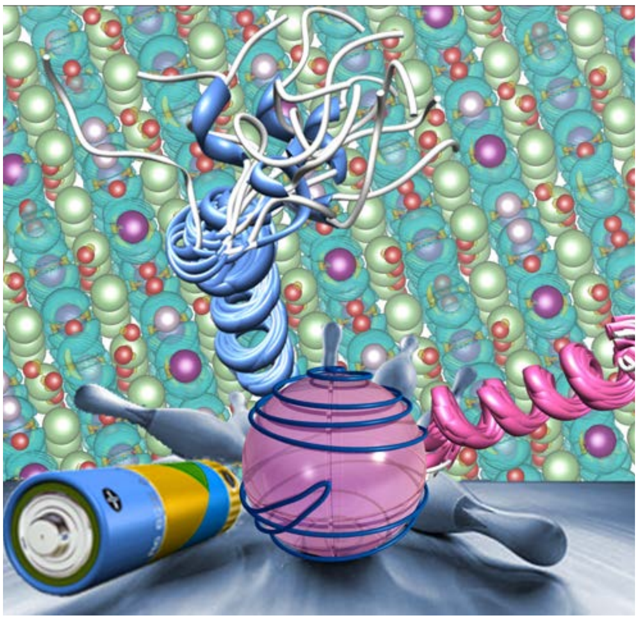


METAL IONS AND PARAMAGNETISM:
industry, energy, environment and life sciences

METAL IONS ARE PRESENT at the active sites of many catalytic processes that are at the core of modern chemistry. Whether they form defined organometallic molecular species or they are supported on surfaces, they are the principal actors in chemical processes such as olefin polymerisation, olefin and alkyne metathesis, hydrogenation, and nanostructure synthesis. They also are the key constituents of versatile materials, e.g., molecular magnets, nanodevices such as engines and magnetic resonance imaging contrast agents. As such, they have a tremendous impact on many fields within industry, energy, environment and life sciences. The paramagnetic materials that are found in electrodes in batteries, or in phosphors for solid-state lighting, play an important role in a range of devices that are instrumental in improving the efficiency of energy conversion, storage and use. Similarly, metals play a fundamental role in biology. Approximately one-third of all proteins and enzymes purified to apparent homogeneity require metal ions as cofactors for biological function. For a wide range of these metalloproteins, the metal ion and its environment determine the chemistry, comprising the active site in catalysis. In turn, protein structure and environment modulate the metal properties such as electronic structure, redox potential and detailed stereochemistry. A precise understanding of the role of the metal centres is an essential element for controlling these complex systems, modifying their behaviour, and allowing rational design of improved sites.



THE pNMR NETWORK:
a close match of theory and experiments

ONE OF THE INTRINSIC FEATURES of many transition and lanthanide metals ions is that they are paramagnetic. This means that the metal centres contain unpaired electrons. NMR of paramagnetic molecules ("paramagnetic NMR", pNMR) provides a direct probe of the electronic structures in such important compounds. However, to date the full exploitation of the NMR spectra of paramagnetic molecules have been hindered by a number of experimental issue, and by the lack of quantitative quantum-mechanical treatments of the parameters of paramagnetic NMR.

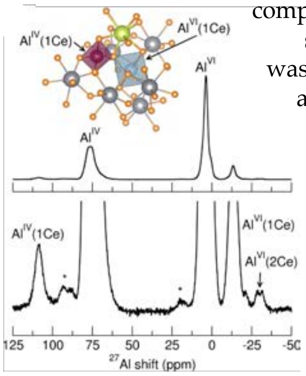
The Initial Training Network "pNMR" combines leading theory groups with the key leading experimental NMR groups in Europe, bridging the gap between the two fields through the joint training of PhD students and young researchers, so as to develop pNMR into a more powerful spectroscopic technique. The goal of the network is, therefore, to train young researchers in both the experimental and theoretical aspects of pNMR, so as to extend the fields of application, both through the exploration of the role of metal centres in key areas of science (e.g., in bioinorganic chemistry, catalysis and magnetic materials), and through the development of new efficient strategies for paramagnetic labelling of diamagnetic molecules. This will not only spread the essential know-how between academic groups but also extend it to those segments of industry that either supply NMR spectroscopy equipment or use pNMR, e.g., in the pharmaceutical industry.

LIVE FROM THE pNMR LABS

LIGHTING MATERIALS: Rational design of new luminescent Ce-doped YAG

GEORGE et al. CHEM. MAT. 2013, 25, 3979

THE OXIDE GARNET $Y_3Al_5O_{12}$ (YAG), when substituted with a few percent of the activator ion Ce^{3+} ($Y_{3-x}Ce_xAl_5O_{12}$), is a luminescent material that has nearly ideal properties for excitation by a blue solid-state light source. It is today the canonical phosphor with widespread use in solid-state lighting. In a collaboration between Brad Chmelka, Ran Seshadri (UCSB), and the Lyon lab, in combination with diffraction techniques and computational methods, high-resolution 1 GHz solid-state ^{27}Al and ^{89}Y NMR spectroscopy was used to determine the local environments and to correlate them with the macroscopic luminescent properties of Ce-substituted YAG, so **to provide critical information for the rational design of new phosphor materials**.

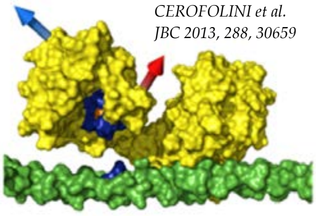


The garnet solid-state white lighting phosphor $Y_{3-x}Ce_xAl_5O_{12}$ has a interpenetrated double-gyroid structure that provides a highly rigid environment for Ce^{3+} activator ions.

MATRIX METALLOPROTEINANSES: proteins in action

MMP-1 in solution is poised to interact with collagen and proceed along the steps of collagenolysis.

CEROFOLINI et al. JBC 2013, 288, 30659



Matrix metalloproteinases (MMPs) are two-domain enzymes capable of catalysing the hydrolysis of highly structured substrates such as triple-helical, interstitial collagen. In collaboration with the Svergun (EMBL Hambourg) and Teixeira (Coimbra) groups, the Florence laboratories used paramagnetic NMR spectroscopy and small angle x-ray scattering (SAXS) to calculate the **interdomain flexibility** in a member of this family (MMP-1), an essential property for allowing **movement of the MMP along collagen fibrils** and for unwinding/perturbation of the collagen and accommodation of a single, otherwise inaccessible, peptide chain into the active site.

LEIDEN UNIVERSITY: Opening of the new facility for paramagnetic NMR

SEPTEMBER 2013: Congratulations to Professor Marcellus Ubbink and his research team on the recent opening of the Paramagnetic NMR Facility at Leiden University in The Netherlands. This state-of-the-art facility is home to a Bruker Ascend 850 MHz spectrometer. The facility is open to scientists interested in collaborations. Support is offered in the design and synthesis of paramagnetic probes, either for general application (such as lanthanide tags and spin labels) or a dedicated purpose (such as enzyme substrates modified with a paramagnetic group). Please visit: http://nmr.lic.leidenuniv.nl/paranmr for more details.

pNMR FELLOWS

pNMR ESRs AND ERs: the next generation of pNMR spectroscopists

WE ARE VERY PLEASED to welcome all of the new students (Early-state researchers, ESRs) and post-doctoral fellows (Experienced Researchers, ERs) to the pNMR Network. They had a chance to meet and briefly get to know one another at the Multidisciplinary Workshop held in Chamonix. Please check out the Student Profile section in each Newsletter to learn more about them.

CNRS Lyon, FR - Kevin Sanders (USA), Andrea Bertarello (IT)
TU Berlin, DE - Arobendo Mondal (IN)
Univ. of Oulu, FI - Syed Awais Rouf (PK)
Univ. of Cambridge, UK - Roberta Pigliapochi (IT)
Slovak Academy of Sciences, Bratislava SK - Peter Cherry (UK)
Stockholm University, SE - Sheryar Khan (PK)
Leiden University, NL - Mathilde Lescanne (FR)
CIRMMP Florence, IT - Witold Andralojc (PO)
ETH Zürich, SU - Florian Allouche (FR)
Giotto Biotech, Florence IT - Tobias Schubeis (DE)
Bruker BioSpin, Rheinstetten DE - David Bennett (UK).

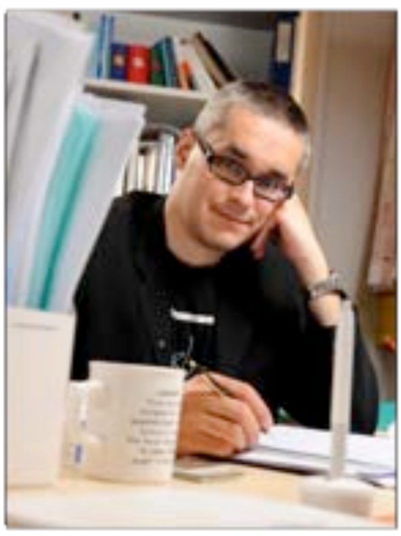
Student profile
MATHILDE LESCANNES
Leiden University (The Netherlands)

Q: Where are you from?
A: I am from Bordeaux (France) but spent 4 years in Grenoble (France) for my studies.
Q: Why did you decide to pursue a PhD in Science?
A: I did a Masters which naturally led to a PhD but I really realized that I wanted to pursue a PhD when I did my training in a laboratory of NMR. I then discovered the laboratory life, worked with people from different backgrounds and enjoyed the work of research.
Q: Do you have a Science Hero or Mentor?
A: I would not say that, but I know that my physics teacher in high school played a important role in my interest for physics science. He was able to go further and go out of the school program to embed our subject into a more general physics issue.
Q: What did you want to be when you were a child?
A: I wanted to be an astronomer because I had a passion for stars formation and for what happened in the sky in general.
Q: What are you looking forward to in the Netherlands?
A: Being abroad is a chance to meet new people and learn a new language. I had already gone to the Netherlands and I liked the country. So I really hope to enjoy the lifestyle (bikes, canals). It sounds very pleasant.
Q: What advice would you give to young women who are interested in Science?
A: Do not to be afraid of her insecurities, everyone has them, so don't be discouraged. Do not hesitate to ask questions and work with other people because it's always more easy to understand. However what is important is not to underestimate her knowledge but be able to share what she does know. Hard work is obviously a part of the equation (but not only in science!). And for sure not to be intimidated to see many more men in her field than women, it's changing.

Mathilde is working on a PhD on "Assignment of NMR spectra of large tagged proteins on the basis of pseudocontact shifts" under the direction of Pr. Ubbink.

Researcher Q & A
JUHA VAARA
Oulu University (Finland)

Q: Why did you choose to study science/physics?
A: I originally entered the university in order to get a somewhat more practical education and I in fact got my MSc degree in electrical engineering, although physics was my favourite topic at school. During the engineering studies I was disappointed about the lack of sufficient physical motivation of why/detail on how, e.g., certain electronic devices work in the way they do. I realized that my ambitions were more on the "why" side of matters instead of how to apply science in engineering. I went to graduate school in a physics program and, as I was in the field of molecular physics, later did post-docs and got my first junior faculty position in physical and theoretical chemistry, before becoming a full professor in physics.
Q: Who is your all-time scientific hero and why?
A: A stereotypical answer is Albert Einstein, among the many greats of the early 20th century. Many somewhat more mundane people that I have known personally have impressed and influenced me, and to name a single person among them I would like to mention Pekka Pyykkö, professor emeritus in chemistry of the University of Helsinki. He is a scientific Gesamtkunstwerk.
Q: What are you examining in your research?
A: My field is theory and computation of magnetic resonance. I like to work on the physical phenomenology of magnetic interactions with the electronic structure of atoms, molecules, and solids, and to use various electronic structure and molecular simulation techniques in demonstrating the phenomena. A most satisfying situation is when the phenomenological findings are confirmed experimentally. The single topic that I am currently mostly interested is the theory and predictions of the emerging field of nuclear magneto-optic spectroscopies, where the magnetization of an ensemble of nuclei is used to influence the polarization properties of a light beam.
Q: How does your work apply to pNMR?
A: The chemical shift of nuclei in an electronically open-shell molecule constitutes a relatively narrow but intriguing physical problem, due to the fact that the ground state of the system is a thermally populated ensemble of states. Add to that the fact that many of the interesting open-shell molecules have metal ions and low-lying electronically excited states, and the result is an interesting and challenging enough (for me) research project. The fact that solving this problem would have great practical potential, too, does not decrease my interest in it, either.
Q: What are the real-world applications of your research?
A: Our work aids in the analysis and understanding of the physics of magnetic interactions and the associated spectroscopic experiments and, in some cases, provides the basics of new and improved spectroscopic methods. These, in turn, are essential in developing new materials, medicine etc. for further scientific and industrial purposes. To give an example, the ultimate goal of nuclear magneto-optic spectroscopy, which I mentioned above, is to develop a more sensitive alternative with (in imaging applications) higher spatial resolution, to the traditional magnetically detected NMR.



Juha is a Professor in physics at the University of Oulu since 2009.

Q: If you weren't a chemist/physicist, what profession would you be interested in?
A: In retrospect, a realistic career alternative that would have been equally interesting would have been to become archaeologist --- as I did not end up in a practical profession anyway. Had I had sufficient talent and background, a career in music would have been interesting, too, but this would have been a rather unrealistic scenario.

PNMR NETWORK TRAINING

INTEGRAL TO the research-based training programme is the series of workshops, practical training courses, international conferences, and outreach actions, located at the different sites. These will i) train the young researchers of the network in the basics of pNMR and ii) disseminate the results of the network to the larger NMR community and to the general public.

Solid-state NMR of materials and proteins
Lyon, France - September 5-6 2013
(cosponsored by Bruker Biospin)

At the Centre de Résonance Magnétique Nucleaire à très hauts champs (CRMN) in Lyon, an applied training course was held that brought together 35 instructors and participants from over 11 countries. This course was organized by the pNMR Network but open to many external participants also. The two day program included lectures, instrument demonstrations and hands on exercises, and three parallel courses were designed with the intention of serving a larger group of participants. Topics included solid-state NMR of dia- and paramagnetic materials, as well as basic and advanced approaches in solid-state NMR of proteins. For everyone this event not only provided technical information but a chance to network with other students, professors and industry professionals.

First pNMR Workshop
Chamonix, France - September 7-8 2013
(cosponsored by Bruker Biospin)

SURROUNDED BY the French Alps, the network partners came together on this September weekend to introduce the new pNMR ITN Network students, exchange management ideas and discuss science. The weekend began with a private ITN meeting where the new students and post-doctoral fellow were welcomed. The supervising professors and lead researchers discussed matters pertaining to the management of the project, as well as upcoming training courses and workshop dates. During the afternoon external researchers joined the pNMR Network group to listen to the lead researchers describing the past, present and future problems to be tackled by the pNMR ITN. The day finished with a keynote lecture titled: "Structure and Dynamics of Large and Glycosylated Proteins Using Paramagnetic Tags" by James H. Prestegard of the University of Georgia's Complex Carbohydrate Research Center (www.ccrc.uga.edu/). Workshop participants were treated to a dinner at Maison Carrier courtesy of Bruker (one of the corporate pNMR network partners). Guests were treated to a menu based on traditional "Savoyard" recipes in a very charming ski lodge atmosphere.

The Sunday morning talks continued with speakers invited from outside of the pNMR Network (R.W. Schurko-U Windsor, U. Akbey-FMP Berlin, E. Brunner-TU Dresden, R.G. Griffin-MIT, B.F. Chmelka-UC Santa Barbara), and everything was wrapped up following a buffet lunch.

Electronic and Nuclear Relaxation, and Electronic Structure Calculation
Mariapfarr, Austria - 21-25 February 2014

The physical and quantum chemical background of NMR shifts of paramagnetic compounds will be discussed. One aim is to build improved bridges between the standard interpretation framework used traditionally in the pNMR field and more recent developments in physical formalism and quantum-chemical methodology. Additionally, a modern view of relaxation in pNMR spectroscopy will be given. This course is open to any interested, however there are a limited number of places available. Also, there are no registration fees, but the participants are responsible for their own travel and accommodation costs. Registration will be open until January 6th, 2014. For details and registration visit: http://www.ens-lyon.fr/crmn/pnmr/events/training-course-mariapfarr-2014/

UPCOMING EVENTS

Solution and solid-state NMR of Paramagnetic Molecules
Florence, Italy - 13-19 July 2014
cosponsored by EMBO

The course focuses on schemes for the acquisition of the NMR spectra of paramagnetic systems and on the analysis of the information that can be retrieved from the paramagnetic restraints. It will describe the main approaches used to characterise molecules and their complexes and on the characterisation of the relaxation profiles of paramagnetic systems through field dependent measurements. We aim to cover hyperpolarisation techniques, that are becoming increasingly important for improving the sensitivity of the NMR experiments, both in solution and in the solid state. For details and registration visit: http://events.embo.org/14-paramagnetism/index.html