NEUTRONS MATTER



VII International Workshop on Electron-volt Neutron Spectroscopy

Villa Wolkonsky and Centro Fermi, Rome, Italy 7th - 8th November 2017

BOOK OF POSTER ABSTRACTS





POSTER ABSTRACTS

Number	Presenter	Institution	Title
P.1	L. Arcidiacono	University College London UCL	Byzantine gold coins analysed using time – resolved prompt gamma activation analysis
P.2	L. Arcidiacono	University College London UCL	Time - resolved prompt gamma activation analysis at ISIS Spallation Neutron Source
P.3	J. Armstrong	Science and Technology Facilities Council	How do rotations alter the local potential of nanoscopic molecules? A C60 case study
P.4	E. Budennaia	Nottingham Trent University	Using Vesuvio to gain better understanding of self – cross- linking behaviour of smectite clays
P.5	C. Corsaro	CNR-IPCF	The similarities between Neutron Compton Scattering and NMR spectroscopy applied to investigate the degradation of cellulosic materials
P.6	A. Di Giulio	University of Rome Tor Vergata	A McStas simulation of the incident beam in the VESUVIO spectrometer
P.7	K. Drużbicki	University Adam Mickewicz	Hydrogen Dynamics in Molecular Solids: Insight from Simulations with Quantum Colored-Noise Thermostat
P.8	E. Gousseva	Queen Mary University of London	Resolving interfacial structures and dynamics in hybrid organic - inorganic cements
P.9	B. Hewer	Science and Technology Facilities Council	Advances in the reduction and analysis of data from epithermal neutron experiments using MANTID
P.10	V. Kapil	École Polytechnique Fédérale de Lausanne	Probing the momentum distribution of protons in ab inito water

P.11	S. Khazaei	Martin Luther University	Rotation tunnelling of coupled methyl quantum rotors in 4 methylpyridine : single rotor potential versus coupling interaction
P.12	M. Mahmoud	Queen Mary University of London	Graphene Nanoflake Reinforced Cements
P.13	D. Mallamace	Center for Colloids and Surface Science (CSGI)	The local structure of hydrogen bond in water studied in a wide temperature range by Neutron Compton scattering and NMR spectroscopy
P.14	A. Mamede	Molecular Physical-Chemistry, R&D Group, University of Coimbra	Shining the beam on bones Human Burned Skeletal Remains Probed by Neutron Spectroscopy
P.15	M. P. Marques	Molecular Physical-Chemistry, R&D Group, University of Coimbra	Intracellular water a secondary target in chemotherapy? Impact of Pt/Pd Anticancer Drugs in Breast Cancer Cells Probed by Neutron Techniques
P.16	M. Nardini	University of Rome Tor Vergata	Neutron Diffraction and Resonance Capture Analysis from Sumerian pottery from the citystate of Abu Tbeirah
P.17	D. Onorati	University of Rome Tor Vergata	Optimization of gamma detection methods for neutron energy analysis on eV neutron spectrometers
P.18	S. Parker	Science and Technology Facilities Council	Observation of the stretch mode in H2 and D2 by INS spectroscopy
P.19	A. Parmentier	University of Rome Tor Vergata	Hydrogen mean force and anharmonicity in polycrystalline and amorphous ice
P.20	J. Rawlings	Nottingham Trent University	Towards a better understanding of the self-cross-linking behaviour of smectite clays

P.21	G. Romanelli	Science and Technology Facilities Council	Recent Upgrades on the VESUVIO Spectrometer
P.22	A. Rosu–Finsen	University College London UCL	Benchmarking acidic and basic dopants with respect to facilitating the ice V to XIII and ice VI to XV hydrogen-ordering phase transitions
P.23	M. Salha	Queen Mary University of London	Supreme toughness in Aluminium enriched cements
P.24	V. Scacco	University of Rome Tor Vergata	Analysis of Neutron Activation Decay on the VESUVIO beam line at ISIS
P.25	Z. Sharif	University College London UCL	Exploring new areas of the ice phase diagram for metastable ice V with varying degrees of hydrogen-order
P.26	F. Song	Queen Mary University of London	Neutron scattering on atomic structure, stabilities and dynamics of cement
P.27	M.B. Umarji	Queen Mary University of London	Water gelation as a structural scaffold in cementitious materials
P.28	P. Ulpiani	University of Rome Tor Vergata	Enhancing the YAP detector's discrimination threshold installed in the VESUVIO spectrometer at the ISIS spallation neutron source

Byzantine gold coins analysed using time-resolved prompt gamma activation analysis

L. Arcidiacono,^{1,2,6} G. Festa,^{1,2,3} G.Romanelli,⁴ R.Senesi,^{1,2,5} M. Martinon-Torres,⁶ C. Andreani^{1,2,7}

¹University of Rome Tor Vergata, Department of Physics and NAST Center, Rome, Italy
² Museo Storico della Fisica e Centro Studi e Ricerche Enrico Fermi
³ CNR-IC Istituto di Cristallografia
⁴STFC, ISIS Spallation Neutron Source
⁵CNR-IPCF Istituto per i Processi Chimico-Fisici
⁶UCL, Institute of Archaeology
⁷CNR-IPCF Sezione di Messina, Messina, Italy

This work presents the first study of gold standards and coins minted in Carthage during the 7th century AD for which a Western African source of gold are suggested based on historical information and XRF analyses. The samples have been analysed using newly developed Time Resolved Prompt Gamma Activation Analysis (T-PGAA) for quantitative elemental analysis. The presented results show the potential of the technique, identifying the isotopes in both the standards and coins and attempting a first approach to a quantitative analysis. Using this innovative technique, we also show an increase in the sensitivity to detect trace elements in coins through which it will be possible to characterize and identify the provenance of the gold used to forge them. T-PGAA consists in the measurement of gamma energy spectrum induced by the radioactive capture as a function of incident neutron Time of Flight, directly related with the energy of incident neutrons. The campaign of measurements has been conducted in VESUVIO beamline at ISIS Spallation Neutron Source.

Time - resolved prompt gamma activation analysis at ISIS Spallation Neutron Source

L. Arcidiacono,^{1,4} G. Festa,^{1,2,3} R. Senesi,^{1,2,3} C. Andreani^{1,2,3}

¹Department of Physics and Center NAST, University of Rome Tor Vergata, Rome, Italy ²CNR-IPCF, Messina, Italy

³Museo Storico della Fisica e Centro Studi e Ricerche Enrico Fermi, Roma, Italy

⁴University College of London, UK

This work presents the development of a recent neutron technique coming from the merging of Prompt Gamma Activation Analysis (PGAA) and Neutron Resonance Capture Analysis (NRCA). These two methods are widely used for material characterisation and by their combination, exploiting the resonances in the neutron epithermal range of energy; we obtained a more powerful method called Time -resolved Prompt Gamma Activation Analysis (T-PGAA). It measures the gamma energy spectrum induced by radiative capture as a function of the incident neutron Time of Flight, which is directly related to the energy of the incident neutron.

The dual TOF-photon energy resolved acquisition aims to increase the capacity of elemental/isotopic identification and quantification for different applications, such as characterisation of ancient valuable artefacts, beamline environment investigations, new material analysis. The technique exploits the high resolutions and the fast response in time of a High Purity Germanium Detector, coupled with its cooling chain and the readout electronics is composed by a digitizer CAEN and NIM modules to shape the signal from the detector. Results on recent measurements on standard samples are presented and discussed.

Keywords: high purity germanium detector; epithermal neutrons; elemental analysis; quantitative analysis

References

[1] G. Festa, L. Arcidiacono, A. Pappalardo, T. Minniti, C. Cazzaniga, A. Scherillo, C. Andreani, R. Senesi, "Isotope identification capabilities using time resolved prompt gamma emission from epithermal neutrons", JINST 2016

[2] G. Festa, C. Andreani, L. Arcidiacono, G. Burca, W. Kockelmann, T. Minniti, R. Senesi "Characterization of gamma ray background at IMAT beamline of ISIS Spallation", JINST

[3] Y. Toh, M. Ebihara, A. Kimura, S. Nakamura, H. Harada, K. Hara, M. Koizumi, F. Kitatani, K. Furutaka, Senesi, "Synergistic effect of combining two non destructive analytical methods for multielemental analysis"

How do rotations alter the local potential of nanoscopic molecules? A C60 case study

J. Armstrong¹ and G. Romanelli¹

¹ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX – United Kingdom

The discovery of fullerene was hailed as the birth of nanoscopic chemistry, whereby the scientific community had the first example of artificial synthesis of a complex and highly geometric molecule. With this new novel structure came the question of what unique/unusual properties such an entity might possess. The extremely high symmetry of C60 begs one to consider the molecule as a single spherical particle, with however two provisos. Firstly, unlike a typical Lennard-Jones-style particle, C60 has a very small ratio of interaction distance to diameter. Secondly, all of its mass is located on the surface of this hypothetical pseudo particle, and the molecule as a whole has the possibility of rotations in addition to translations. Indeed one might also consider that the structure and dynamics could be heavily dictated by the tessellation of the pentagonal and hexagonal interactions of neighbouring molecules. To answer all these questions, much experimental work was performed on C60, probing its dynamic and thermodynamic behaviour. Indeed, through neutron scattering it was shown to possess exotic properties including a static, to discrete hopping rotor phase at 90K, with a first order phase transition from BCC to FCC at 270K and a now continuous rotor phase.

We present results of Inelastic and Deep-Inelastic Neutron Scattering experiments performed on the Tosca and VESUVIO instruments at ISIS on a C60 powder sample in the temperature range 5 K – 300 K. We have studied the change in shape of the carbon Nuclear Momentum Distribution as a function of temperature, and across the two phase transitions at 90 K and 260 K.

Inelastic Neutron Scattering results show that in going from the static-to-rotor phase, the introduction of rotational modes does not significantly perturb the vibrational spectra, with only an increasing population of low energy modes according to Boltzmann statistic being observed. On the other hand, Deep Inelastic Neutron Scattering results suggest changes of the carbon Nuclear Momentum Distribution across 90 K and 260 K, where the static-to-rotor and BCC-to-FCC transitions are located.

Keywords: Deep Inelastic Neutron Scattering; Fullerene; Nuclear Momentum Distributions

References

[1] W. I. F. David et al, Europhys. Lett. 18 (3) 219-225 1992

- [2] D. Chen, A. Nakahara, D. Wei, D. Nordlund and T. Russell, Nano Lett., 2011, 11, 561–567.
- [3] E.Verploegen, R.Mondal, C.J.Bettinger, S.Sok, M.F.Toney and Z. Bao, Adv. Funct. Mater., 2010, 20, 3519–3529.

[4] J. Armstrong, S. Mukhapadhyay, F. Bresme & F. Fernandez-Alonso, Phys. Chem. Chem. Phys., 2016

[5] G. Romanelli and M. Krzystyniak, Nucl. Instr. Meth. Phys. Res. A, 2016, 819, 84-88

Using Vesuvio to gain better understanding of self – cross- linking behaviour of smectite clays

F. Gao¹, J. Rawlings¹, <u>E. Budennaia</u>¹, C. Brown¹, M. Loughlin¹, M. Krzystyniak²

¹School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham, NG11 8NS, UK ²ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK

Layered structured smectite clays are one of the important fillers which initiated filler enhanced nanocomposite science and technology. Over the past two decades, they have been widely used to enhance many engineering properties such as mechanical properties, barrier resistance, fire retardancy and dielectric performance etc. The recent work at Nottingham Trent University has widened the application of smectite clays into ultra-light weight thermal oxidation resistant materials, bacteria cellulose hydrated gels and bubble foam stability. It was interesting to find that two smectite clays, with commercial names SWN and Cloisite Na+ respectively, have similar crystal structure but very different behaviour in these widened applications. SWN clay exhibits self-cross-linking behaviour at concentration as low as 1.5wt% in aqueous suspension whilst Cloisite Na+ clay does not show such behaviour at low clay concentration range. This behaviour is concerned with if the ultralight weight structure could be formed and the ability to integrate layered structured nano-fillers into bacteria cellulose hydrated gel structure. In this study, Vesuvio neutron spectrometry together with other characterisation techniques were applied to gain better understanding of the mechanism behind these differences. The investigation of layered structured smectite clay in aqueous suspension is a complicated matter. As soon as the clay added into water, three states of clay structure can be generated, i.e., micro-sized clay particle aggregated state, individual nano-sized silicate sheet in exfoliated state and separated micro-sized individual clay particles in water suspension. In order to simplify the investigation, high extent of layer-exfoliated state through mechanical shear has been created for this investigation. The state of exfoliation has been evidenced by dynamic laser light scattering data. Different states of clay in aqueous suspension show significant different profiles in number and volume frequencies distribution of particle size. Samples of two type of clay in 3wt% clay aqueous suspension were investigated in this study. The results obtained show that SWN clay has much higher particle aggregation rate coefficient than Cloisite Na+ clay. The gelling state is quickly formed in SWN in the clay concentration studied whist Cloisite Na+ clay in the same concentration has no cross-point in frequency sweep storage and loss modulus curves measured by oscillation rheometer. The Vesuvio data show that the width of momentum distribution of both hydrogen and oxygen for two types of clay is higher in their aqueous suspension compared with their dried state without water. The anisotropy of hydrogen binding is higher in Cloisite Na+ clay aqueous suspension than in the case of SWN clay suspension. The hydrogen in Cloisite Na+ suspension is more bonded. This indicates that SWN clay has less interaction with hydrogen in water due to rapid self-crosslinking in particle themselves whilst Cloisite Na+ clay has strong interaction with water molecules rather than linking themselves together. Such a situation is likely associated with lower aspect ratio of SWN particles creates more numbers of exfoliated silicate sheets in the same mass concentration than Cloisite Na+ particles leading to reduced diffusion distance for particle collision. As a consequence the chance for self-cross-linking would be enhanced.

The similarities between Neutron Compton Scattering and NMR spectroscopy applied to investigate the degradation of cellulosic materials

<u>C. Corsaro</u>^{1,2}, D. Mallamace³, M. Missori⁴, R. Senesi^{1,5}, G. Romanelli^{5,6}, F. Mallamace^{2,7} and C. Andreani^{1,5}

¹CNR-IPCF Sezione di Messina, Viale F. Stagno D'Alcontres 37, 98158 Messina, Italy

²Dipartimento MIFT, Sezione di Fisica, Università di Messina, Viale F. Stagno D'Alcontres 31 I-98166, Messina, Italy

³Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase - CSGI, 50019 Firenze, Italy

⁴Istituto dei Sistemi Complessi, Consiglio Nazionale delle Ricerche, UOS Sapienza, Piazzale Aldo Moro 5, 00185 Roma, Italy

⁵Dipartimento di Fisica and NAST Center, Università degli Studi di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Roma, Italy

⁶ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK, Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215 USA

The local structure of cellulose fibers within paper is highly perturbed by humid environment. In order to understand microscopic variations at structural level, the choice of proper experimental techniques is mandatory. Both Neutron Compton Scattering (NCS) and NMR spectroscopy are very sensitive to the local environment of the studied nucleus (mainly hydrogen) [1, 2].

The hydrolytic and oxidative processes that provoke the progressive degradation of cellulosic materials are mediated by water. In fact, water molecules contribute to the consumption of the amorphous regions and the swelling of cellulose fibers [3]. Indeed, during the degradation process there is a dramatic change of the structure of the system that can be studied by NCS and NMR techniques.

Here we show the results of NMR experiments and propose new NCS investigations on paper samples as a function of hydration and aging. In particular, we consider modern paper as reference, artificially aged modern paper and ancient paper (naturally aged from Milan in 1430 and Perpignan 1413).

In such a way, we enter into the details of the local variations in the structure of the cellulose fibers due to aging and hydration processes. Our aim is to provide new insights into the correlations between these two phenomena in order to gain a control over them and to foresee an eventual restoration strategy.

Keywords: DINS; chemical shift; hydrogen bond

References

[1] Andreani, C., Krzystyniak, M., Romanelli, G., Senesi, R. & Fernandez-Alonzo, F. Electron-volt neutron spectroscopy: beyond fundamental systems. Adv. Phys. 66, 1–73 (2017)

[2] Mallamace, F. et al. NMR evidence of a sharp change in a measure of local order in deeply supercooled confined water. Proc. Natl. Acad. Sci. USA 105, 12725–12729 (2008).

[3] Corsaro, C., Mallamace, D., Vasi, S., Pietronero, L., Mallamace, F. & Missori M. The role of water in the degradation process of paper using 1H HR-MAS NMR spectroscopy. Physical Chemistry Chemical Physics **18** 33335-33343 (2016).

A McStas simulation of the incident beam in the VESUVIO spectrometer

A. Di Giulio¹, M. Zanetti², G. Romanelli³, R. Senesi¹ and F. Fernandez-Alonso³

¹University of Rome Tor Vergata, Department of Physics and NAST Center, Rome, Italy

³ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK

We present a Monte Carlo simulation of the incident neutron beam on the VESUVIO spectrometer at ISIS [1] using the McStas [2] code. As VESUVIO allows for concurrent measurements of neutron diffraction, transmission, and deep inelastic neutron scattering (DINS), both incident and transmitted beams are characterised by a broad energy range, spanning over several orders of magnitude from fractions of meV to hundreds of keV. Therefore, a transport simulation in the case of the VESUVIO spectrometer is a challenging task as the McStas code has been optimised for cold and thermal neutrons and rarely used for epithermal neutrons.

In this simulation study, we discuss the modelling of the collimation stages along the primary flight path so to reproduce the absolute intensity of the incident beam and its shape, both recently characterised experimentally [3]. Moreover, we included incoherent scattering samples so to compare the epithermal component of the simulated backscattering spectra to experimental results from Al, V, and Pb. Finally, we discuss strategies to complement the modelling of VESUVIO by including components for the final neutron energy selection based on epithermal neutron resonances and the emission of prompt gamma rays. The final goal is to reproduce DINS spectra obtained by a resonant Au foil cycling in and out the scattered neutron beam [4].

Keywords: McStas; Deep Inelastic Neutron Scattering

References

- [1] http://www.isis.stfc.ac.uk/instruments/vesuvio/
- [2] http://www.mcstas.org/
- [3] Romanelli et al, Measurement Science and Technology (2017)

[4] Mayers, J., and G. Reiter. "The VESUVIO Electron Volt Neutron Spectrometer". Measurement Science and Technology 23, no. 4 (2012): 045902. doi:10.1088/0957-0233/23/4/045902.

²Università degli Studi di Milano-Bicocca, Piazza della Scienza 3, 20126, Italy

Hydrogen Dynamics in Molecular Solids: Insight from Simulations with Quantum Colored-Noise Thermostat

<u>K. Drużbicki,</u>^{1,2} M. Krzystyniak,^{3,4} D. Hollas,⁵ P. Slavíček,⁵ G. Romanelli,³ F. Fernandez-Alonso^{3,6}

¹Faculty of Physics, Adam Mickiewicz University, Poznan, Poland

²Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia

³ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, United Kingdom

⁴School of Science and Technology, Nottingham Trent University, Clifton Campus, Nottingham, UK

⁵Department of Physical Chemistry, University of Chemistry and Technology, Prague, Czech Republic

⁶Department of Physics and Astronomy, University College London, Gower Street, London, UK

The microscopic origin and the temperature dependence of nuclear quantum effects (NQEs) remain the subject of ongoing discussion, both from experimental (neutron and photon spectroscopy) and theoretical (static and dynamic) perspectives. Molecular dynamics (MD) is a powerful numerical method to investigate properties of condensed matter systems. While, standard MD simulations are generally only valid in the classical limit and so for high temperatures, it is necessary to include NQE, e.g. zero-point energy contribution, to study the low temperature regime, the dynamics of light atoms (such as hydrogen) or the isotope effects. The method commonly used to simulate quantum dynamics is path integral molecular dynamics (PIMD), which is, however, particularly time consuming and becomes extremely expensive when high accuracy methods are used for calculating forces. In its standard formulation PIMD does not give access to the real time correlation functions. A new semiclassical approach to account for NQEs has been recently proposed, introducing an approximate treatment of the NOEs by imposing Ouantum Colored-Noise Thermostat (OT).[1-3] The main advantage of QT is its computational simplicity. The computational saving as compared with full PIMD simulation is substantial, especially for *ab initio* simulations. The semi-classical approach extends the range of applicability of real-time correlation functions towards the low-temperature limit and provides some approximate treatment of nuclear momentum distributions.[4] This may be of great importance for augmenting the functionality of inelastic neutron scattering experiments. In this communication we present an implementation of quantum-colored noise thermostat, which has been interfaced with CASTEP through the ABIN code.[5-6] The implementation has been tested against the internal CP2K implementation (PBE-D3/DZVP). The range of applicability of the semi-quantum NVT-MD simulations for interpretation of neutron scattering data was examined and compared to classical DFT-MD (Born Oppenheimer MD) and lattice-dynamics simulations (Density Functional Perturbation Theory).

Keywords: Inelastic Neutron Scattering; TOSCA; Momentum Distribution; VESUVIO; ab inito MD

References

[1] M. Ceriotti, G. Bussi and M. Parinello, Phys. Rev. Lett. 102, 020601 (2009)

- [2] M. Ceriotti, G. Bussi and M. Parinello, Phys. Rev. Lett. 103, 030603 (2009)
- [3] M. Ceriotti, G. Bussi and M. Parinello, J. Chem. Theory Comput. 6, 1170 (2010)
- [4] http://gle4md.org/data/lugano10.pdf Accessed: 21 Sept. 2017.

[5] S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert, K. Refson, M. C. Payne, Z. Kristallog. 220, 567 (2005)

[6] https://github.com/ PHOTOX/ABIN Accessed: 21 Sept. 2017

Resolving interfacial structures and dynamics in hybrid organic - inorganic cements

E. Gousseva,¹ F. Song,¹ K. V. Tian,² and G. A. Chass,^{1,*}

¹ School of Biological and Chemical Sciences, Queen Mary University of London, London, UK

²Department of Chemical Science and Technologies, University of Rome Tor Vergata, Rome, Italy

* Correspondence: g.chass@qmul.ac.uk

Hybrid inorganic-organic cements show increased fracture toughness with respect to their modern counterparts [1]. Construction and related applications have been dominated in the past 50 years by Portland cements, yet fall short of the requisite fracture toughness for their uses and are thus extrinsically toughened with metal reinforcing bars (rebar); themselves prone to oxidation (rusting) and eventual failure [2]. Hybrid cements, formed from addition of a small fraction of agriculturally based starches from rice or wheat effect sufficient elevation of the cements' intrinsic fracture toughness that no extrinsic toughening is required [3]. The bases for this raised ductility is still unknown, although preliminary works show the starches to limit Ca-nanoparticle growth to ~20-50nm and reduce particle dispersity, while amorphising the matrix $[4]^1$. We therefore initiated computational investigations of hybrid inorganic-organic cements cluster models, of 2-4nm³ size, employing electronic structure computations (semi-empirical, HF and DFT). Overall, results indicate an increased flexibility at particle interfaces and an elevated free volume (Vf) for the matrix. Further, branched starches show a dichotomous propensity to assist particle-particle binding, whilst simultaneously limiting particle growth size; an ideal cementation mechanism generating a porous, amorphous inorganic structure, inter-laced and agglomerated by organic polymers of high ductility. Future endeavours include carrying out neutron-compton scattering experiments on differing hybrid-cements to resolve their constituent atomic-cohesions, pre- and post-setting.

Keywords: cement; amylopectin; inorganic-organic hybrid; fracture toughness; atomic cohesion

References

[1] M. D. Jackson, S. R. Chae, S. R. Mulcahy, C. Meral, R. Taylor, P. Li, A.-H. Emwas, J. Moon, S. Yoon, G.

- Vola, H.-R. Wenk and P. J. M. Monteiro, Am. Mineral., 2013, 98, 1669–1687.
- [2] P. K. Mehta, Spec. Publ., 1991, 126, 1–32.
- [3] Yang, B. Zhang and Q. Ma, Acc. Chem. Res., 2010, 43, 936–944.
- [4] Y. Zeng, B. Zhang and X. Liang, Thermochim. Acta, 2008, 473, 1-6.

Advances in reduction and analysis of data from epithermal neutron experiments using MANTID

B. Hewer¹, L McCann¹, M Gigg¹, M Krzystyniak¹, and G Romanelli¹

¹ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK

We present the latest tools for the reduction and analysis of data from epithermal neutron experiments on the VESUVIO spectrometer using MANTID.

Since the last updates [1, 2], the analysis of Deep Inelastic Neutron Scattering experiments has evolved. We discuss recent updates in the user script to correct the data for multiple scattering and gamma background, including the handling of multiple scattering from hydrogen atoms in backscattering experiments. Corrected neutron Compton profiles can now be analysed using global fitting over bank of detectors. Also, Bayesian analysis can now be performed on neutron Compton profiles to evaluate the best model for the nuclear momentum distribution. Finally, a new algorithm has been created to predict and generate the shape of a neutron Compton profile using the Einstein nodel.

In addition to the routines for data analysis of data from Deep Inelastic Neutron Scattering data, new algorithms have been developed for the analysis of diffraction spectra obtained from backscattering banks [3], and transmission experiments.

Keywords: MANTID; data analysis; epithermal neutrons; neutron Compton profiles

References

 S Jackson, M Krzystyniak, A G Seel, M Gigg, S E Richards, and F Fernandez-Alonso, VESUVIO Data Analysis Goes MANTID, Journal of Physics: Conference Series **571** (2014) 012009
 E. Oram, An Overview of the development of Indirect Inelastic Data Reduction and Analysis in

[2] E. Oram, An Overview of the development of Indirect Inelastic Data Reduction and Analysis in MANTID between July 2015 - July 2016, RAL-TR-2016-011 ,2016, RAL Technical Report

[3] L McCann, Overview of developments in MANTID relating to indirect inelastic spectroscopy July 2016 - July 2017, RAL Technical Reports RAL-TR-2017-012. STFC, 2017.

Probing the momentum distribution of protons in ab inito water

V. Kapil,¹ A. Cuzzocrea² and M. Ceriotti¹

¹Department of Material Science and Engineering, École polytechnique fédérale de Lausanne, Lausanne, Switzerland

²Department of .Physics, Università degli studi di Trieste, Trieste, Italy

One of the most peculiar examples of nuclear quantum effects is the deviation of the proton momentum distribution in water from the Maxwell-Boltzmann distribution. This effect has been measured experimentally by Deep Inealstic Neutron Scattering [1] (also known as Neutron Compton Scattering) at temperatures ranging from 269 K to 400K with strong devations from classical behaviour at all temperatures. These experiments also show that the momentum distribution is very sensitive to the local environment of the proton but in an indirect way which makes it important to make validations with theory and first principle simulations.

In this work, we use the state of the art path integral molecular dynamics technique to calculate thermodynamic averages of room temperature liquid water. The momentum distribution is computed in terms of the off-diagonal elements of the density matrix by calculating open path integrals[2] in imaginary time. In order to study the

effect of the local potential energy landscape on the proton momentum distribution, we select three water potentials: 1) q-TIP4Pf [3], a simple flexible water model described by a harmonic bending term and an anharmonic but non-dissociable stretching term 2) MBPOL [4], a polarisable water model containing many body terms evaluated at the CCSD(T) level of electronic structure theory 3) B3LYP-NN [5] a fully dissociable neural network potential fitted to reproduce the energetics of water computed at the hybrid density functions level of theory B3LYP with D3 dispersion corrections. We present an in depth comparison of the momentum

distribution garnished by the three water models and discuss the agreements and disagreements with the experimental result.

Keywords: Statistical mechanics; quantum nuclear effects; ab initio; protons

References

[1] REITER, G. et al. Braz. J. Phys., São Paulo , 34, 1, 142147 2004

[2] MORRONE, J. et al. J. Chem. Phys. 126, 234504 2007

[3] HABERSHON, S. et al. J. Chem. Phys. 131,024501 2009

[4] BABIN, V. et al. J. Chem. Theory Comput. 128, 154519 2008

[5] KAPIL et al. J. Chem. Phys. 145, 234103 2016

Rotation tunnelling of coupled methyl quantum rotors in 4 – methylpyridine : single rotor potential versus coupling interaction

S. Khazaei and D. Sebastiani

Institute of Chemistry, Martin-Luther-University Halle-Wittenberg, Von-Danckelmann-Platz 4, 06120 Halle (Saale), Germany

At low temperature, methyl groups act as quantum rotors with quantized rotational states. Especially the large energy difference between the ground and first excited rotational states in 4-methlpyridine has been subject of experimental studies in inelastic neutron scattering (INS) [1] and in the context of hyperpolarization techniques in NMR spectroscopy [2-4]. Here, we present a theoretical explanation for the multiple structure of the rotational tunneling peaks [1]

observed in INS experiment of 4-methylpyridine within a coupled-pair model [5]. The focus is on the effect of chemical environment (molecular packing) on the rotational states. In particular, we study the influence of coupled motion of methyl rotators on the tunneling spectrum. In this regard, the potential energy surface (PES) of methyl rotations is obtained through a set of combined first principles and nudged elastic band calculations [6]. The quantum rotational energy levels are obtained by the numerical solution of two-dimensional time independent Schrödinger equation for the calculated PES. Our computed energy levels reproduce the observed tunnelling transitions in 4-methylpyridine in well agreement with experiments. Furthermore, we have simulated the interaction of two adjacent methyl groups within an analytical form for the coupled methyl groups composed of single rotor potential and coupling interaction terms. It is found that the main determinant factor controlling the splitting energy levels is the ratio of strengths of coupling and single rotor potential terms. By mapping the calculated PES profile of 4-methylpyridine on the analytical model, it turns out that the large tunnel splitting observed in 4-methylpyridine results from its weakly hindering potential with proportionally shallow single potential to coupling interaction.

Keywords: tunnel splitting; rotational coupling; single rotor potential; coupling interaction

References

[1] F. Fillaux, C. J. Carlile, and G. J. Kearley, "Inelastic-neutron scattering study of the sine-Gordon breather interactions in isotopic mixtures of 4-methylpyridine" *Phys. Rev. B.* **58**, 11416 (1998).

[2] M. Icker, S. Berger, "Unexpected multiplet patterns induced by the Haupt-effect" *J. Magn. Reson.* **219**, 1-3 (2012).

[3] B. Meier, J. –N. Dumez, G. Stevanato, J. T. Hill-Cousins, S. S. Roy, P.Hakansson, S. Mamone, R. C. D. Brown, G. Pileio, and M. H. Levitt, "Long-Lived Nuclear Spin States in Methyl Groups and Quantum-Rotor-Induced Polarization" *J.Am. Chem. Soc.* **135**, 18746 (2013).

[4] J. –N. Dumez, B. Vuichoud, D. Mammoli, A. Bornet, A. C. Pinon, G. Stevanato, B. Meier, G. Bodenhausen, S. Jannin, and M. H. Levitt, "Dynamic Nuclear Polarization of Long-Lived Nuclear Spin States in Methyl Groups" *J. Phys. Chem. Lett.* **8**, 3549 (2017).

[5] S. Khazaei and D. Sebastiani, "Tunneling of coupled methyl rotors in 4-methylpyridine: single rotor potential versus coupling interaction" *submitted in J. Chem. Phys.* (2017).

[6] S. Khazaei and D. Sebastiani, "Methyl rotor quantum states and the effect of chemical environment in organic crystals: γ - picoline and toluene" *J. Chem. Phys.* **145**, 234506 (2016).

Graphene Nanoflake Reinforced Cements

M. Z. Mahmoud,¹ F. Song,¹ K. V. Tian,² and G. A. Chass^{1,3*}

¹School of Biological and Chemical Science, Queen Mary University of London, London, UK

²Department of Chemical Science and Technologies and centro NAST, Università degli Studi di Roma TorVergata, Roma, Italy

³Department of Chemistry, The University of Hong Kong, Hong Kong SAR, China <u>*g.chass@qmul.ac.uk</u>

Structure reinforcement of cementitious material at the mesoscopic level has been trialled with additives of various composition and sizes; one of the most promising being nano-flakes of graphene and graphene oxide.1 These aid in the inhibition of crack formation and fracture propagation, effectively raising the compressive and flexural strength of the reinforced systems, relative to those of conventional cements.2,3 The atomic-level bases of these improvements remain poorly understood. We therefore initiated synergistic experimental-computational investigations using a molecular cluster approach to model small and large composite models. Results showed the identity of the constitutional isomer of the graphene/graphene-oxide nano-flakes as the dominating modulator of stability in the nano-composites engineered, and indirectly their bulk mechanical properties. Notably, the interfacial arrangements of the nano-flakes relative to Ca-silicate clusters played a near-negligible role. This opens the door to rational control of composite stability, and eventually mechanical properties, through the isomeric design of nano-flake additives to the cements. These trends are presently driving the rational design of empirical determinations employing coherent-THz and neutron scattering/diffraction to quantitatively resolve the phenomena in real cement systems.

Keywords: Cement; C2S; C3S; molecular cluster; graphene nanoflake; cement reinforcement

References

[1] K. Sobolev and M.F. Gutierrez, Am. Ceram. Soc. Bull, 2005, 84, 16-19.

[2] B. Wng, R. Jiang and Z. Wu, Nanomaterials, 2016, 6, 200.

[3] K. Gong, Z. Pan, A.H. Korayem, L. Qiu, D. Li, F. Collins, C.H. Wang and W.H. Duan, J. Mater. Civ. Eng., 2015, 27, A4014010.

The local structure of hydrogen bond in water studied in a wide temperature range by Neutron Compton scattering and NMR spectroscopy

D. Mallamace¹, R. Senesi^{2,3}, C. Corsaro^{3,4}, G. Romanelli^{3,5}, F. Mallamace^{4,6} and C. Andreani^{2,3}

¹Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase - CSGI, 50019, Firenze, Italy ²Dipartimento di Fisica and NAST Center, Università degli Studi di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Roma, Italy

³CNR-IPCF Sezione di Messina, Viale F. Stagno D'Alcontres 37, 98158 Messina, Italy

⁴Dipartimento MIFT, Sezione di Fisica, Università di Messina, Viale F. Stagno D'Alcontres 31 I-98166, Messina, Italy

⁵ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom

⁶Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215 USA

Water is certainly the most important and ubiquitous substance that we have on Earth. It is a small and simple molecule but shows many thermodynamical anomalous properties with respect to the other substances. These anomalies arise from variations in the structure and dynamics of the characteristic bonds that water molecules form with each other: the hydrogen bonds (HBs). The thermodynamic conditions strongly alter the properties of the HBs. For example, the lowering of the temperature favours the formation of an HB network by increasing both HBs strength and lifetime. The achievement of information on the transient evolution of the local structure of water would provide fundamental insight but is still a challenge.

Here we report the results of a combined NMR and neutron scattering study in liquid, ices and amorphous states of water, in a very wide temperature range from the superheated to the supercooled regime. In particular, we perform experiments by looking at the Neutron Compton Profile and at the magnetic shielding tensor [1, 2]. Our main finding concerns the identification of $T^* \simeq 315$ K [3] with the temperature that marks the onset of water tetrahedral structure. Moreover, we find that below T^* water is constituted by two coexisting liquids with different structure and thus different symmetry and density.

Our results provide a clear picture of the changes with temperature in the local order of the system and how this is related with the anomalies of water.

Keywords: DINS; Symmetry; hydrogen bond

References

[1] Andreani, C., Krzystyniak, M., Romanelli, G., Senesi, R. & Fernandez-Alonzo, F. *Electron-volt neutron* spectroscopy: beyond fundamental systems. Adv. Phys. **66**, 1–73 (2017)

[2] Mallamace, F. et al. *NMR evidence of a sharp change in a measure of local order in deeply supercooled confined water.* Proc. Natl. Acad. Sci. USA **105**, 12725–12729 (2008).

[3] Mallamace, F., Corsaro, C. & Stanley, H. E. A singular thermodynamically consistent temperature at the origin of the anomalous behavior of liquid water. Sci. Rep. **2**, 993 (2012)

Shining the beam on bones Human Burned Skeletal Remains Probed by Neutron Spectroscopy

<u>A.P. Mamede</u>,¹ L.A.E. Batista de Carvalho,¹ D. Gonçalves,² A. A. R. Vassalo,² C.I. Makhoul² S.F. Parker,³ G. Festa,^{4,5} C. Andreani⁴ and M.P.M. Marques^{1,6}

¹"Molecular Physical Chemistry" R&D Unit, Univ. Coimbra, Portugal

²Lab. Forensic Anthropology, Centre of Functional Ecology, Univ. Coimbra, Portugal

³ISIS Facility, STFC Rutherford Appleton Laboratory, Didcot, OX 11 0QX, UK

⁴Physics Department and Centro NAST- University of Rome Tor Vergata, Italy

⁵Museo Storico della Fisica e Centro Studi e Ricerche Enrico Fermi, Italy

⁶Dep. Life Sciences, Fac. Science and Technology, Univ. Coimbra, Portugal



Fig. 1 – INS spectra (at MAPS, with 5240 cm⁻¹ incident energy) of HAp (SMR2910b) and human femur burned at 500, 700 and 900 $^{\circ}$ C.

Burned human skeletal remains were probed by combined optical and neutron vibrational spectroscopy - FTIR, Raman and INS (inelastic neutron scattering). This is an innovative way of tackling heat-induced changes in human bone tissue, aimed at relating burned to pre-burned parameters which will have a significant impact on crime scene investigations, bioanthropology positive and archaeology. At present. identification of skeletal human remains found in archaeological or forensic settingsot be carried out when the bones have been subject to high temperatures (e.g. cremation, explosions), since heat induces significant variations in the skeleton, namely dimensional changes due to an impact on hydroxyapatite's (HAp) crystal structure [1,2]. Although previous studies have attempted to tackle this problem [2], this is the

first experimental approach based on the intrinsic properties of bone (*e.g.* microcrystallinity) and the first INS study on burned human bones [3]. Human femur and humerus (burned under controlled conditions), as well as pre-historic and medieval bones (Central Italy) were probed. Several unsettled issues have been clarified, such as HAp hydroxylation and the H-bonding pattern within the bone's microcrystalline framework. The HAp OH libration and stretching bands were simultaneously detected by INS (at MAPS). A crystallinity enhancement was clearly observed upon increasing temperatures [3,4]. Additionally, defined temperature-dependent variations were found for particular vibrational bands, allowing to build reliable quantitative relationships (varying with the type of bone). For the archaeological samples, INS allowed access to the complete vibrational pattern (despite their high fluorescence that severely undermines analysis by Raman), leading to a reliable estimate of the temperature to which these bones were subject to prior to their discovery.

References

[1] T.J.U. Thompson, Forensic Sci.Int., 146S (2004) S203-S205.

^[2] T.J.U. Thompson, J.Forensic Sci., **50** (2005)1-8.

^[3] M.P.M. Marques et al., RSC Adv., 6 (2016) 68638-68641.

^[4] M.G. Taylor et al., Phys. Chem. Chem. Phys., 3 (2001) 1514-151

Intracellular water a secondary target in chemotherapy? Impact of Pt/Pd Anticancer Drugs in Breast Cancer Cells Probed by Neutron Techniques

<u>M.P.M. Marques^{1,2}</u>, A.L.M. Batista de Carvalho¹, V. Garcia Sakai³, L. Hatter⁴ and L.A.E. Batista de Carvalho¹

¹"Molecular Physical Chemistry" R&D Unit, Univ. Coimbra, Portugal
 ²Dep. Life Sciences, Fac. Science and Technology, Univ. Coimbra, Portugal
 ³ISIS Facility, STFC Rutherford Appleton Laboratory, Didcot, OX 11 0QX, UK
 ⁴Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Chilton, UK

Water plays a vital role in biochemical processes in a living organism. Within a cell, intracellular water structure and dynamics are known to be changed by metabolites or extrinsic entities (*e.g.* drugs), while water properties are prone to affect the function of biomolecules and therefore cell viability. Hence, intracellular water may be a potential secondary drug target. This is an innovative way of tackling a drug's pharmacodynamics, searching for alternative receptors in order to improve chemotherapeutic efficiency. The first neutron scattering study of intact human cells is reported, addressing the subject of solvent-slaving to a drug by directly probing intracellular water to ascertain structural and dynamical variations upon drug exposure. Inelastic (INS) and quasi-elastic (QENS) neutron scattering spectroscopy experiments with isotope labelling were performed, for monitoring interfacial water response in low prognosis metastatic human breast cancer cells, upon exposure to the widely used drug cisplatin or to a Pd-based anticancer agent [1-4].



Intracellular water was found to behave differently in drug-free drug-exposed and cells: concentration-dependent structural changes coupled to a progressive mobility reduction were revealed, concurrent with variations in the native organisation of water molecules within the intracellular medium [5] (see Figure). These are the first reported experimental results

on a drug's impact on the cytomatrix by neutron techniques, and allow a better understanding of the *in vivo* mode of action of antitumour agents, at a molecular level, hopefully contributing to a rational design of improved drugs.

References

[1] S.M. Fiuza et al., Chem.Biol.Drug Design 77 (2011) 477.

[2] S.M. Fiuza et al., New J.Chem. 39 (2015) 6274.

- [3] A.L.M. Batista de Carvalho et al., PLoS ONE 11 (2016)
- [4] A.L.M. Batista de Carvalho et al., Faraday Disc. 187 (2016) 273.

[5] M.P.M. Marques et al., PCCP 19 (2017) 2702.

Neutron Diffraction and Resonance Capture Analysis from Sumerian pottery from the citystate of Abu Tbeirah

<u>M. Nardini^{1,2}</u>, C. Andreani^{1,2,3}, F. D'Agostino⁵, L. Romano⁵, A. Scherillo⁴, R. Senesi^{1,2,3}, G. Festa^{2,1}

¹Centro NAST- Università degli Studi di Roma "Tor Vergata", Italy;

²Centro Fermi - Museo Storico della Fisica e Centro Studi e Ricerche "Enrico Fermi", Italy;

³Dipartimento di Fisica - Università degli Studi di Roma "Tor Vergata", Italy;

⁴ISIS, STFC, Rutherford Appleton Laboratory, Didcot OX11 0QX, United Kingdom;

⁵Dipartimento Istituto Italiano di Studi Orientali – Sapienza – Università di Roma, Italy

The recent reprise of archaeological activities in southern Iraq is offering the opportunity of analyze the Sumerian material culture coming from contexts excavated with modern techniques and documented with up-todate methodology. Excavations are performed by an Iraqi –Italian mission led by Italian archaeologists from "Sapienza – Università di Roma". This poster shows results of non-invasive analyses on 36 pottery samples from the Sumerian site of Abu Tbeirah, a 3rd millenium BC site located in Southern Iraq, in the S-E periphery of Nasiriyah city.

A combination of two techniques, Neutron Diffraction [1] that uses thermal neutrons and simultaneous Neutron Resonance Capture Analysis [2] that exploit epithermal range of the incident neutron flux, are used to determine crystalline phase and elemental composition of samples. Experiments are performed at INES diffractometer at the ISIS pulsed neutron source. Neutron Diffraction data have shown crystalline phases and their weight percentage while Neutron Resonance Capture Analysis permitted to determine the elements/isotopes in the ceramics.

Keywords: Neutron diffraction; neutron resonance capture analysis

References

[1] W. Kockelmann and A. Kirfel. Non-destructive Phase Analysis of Archaeological Ceramics using TOF Neutron

Diffraction. Journal of Archaeological Science (2001) 28, 213-222

[2] A. Pietropaolo,G. Gorini, G. Festa, E. Reali, F. Grazzi, and E. M. Schooneveld. A Neutron Resonance Capture Analysis Experimental Station at the ISIS Spallation Source. Applied Spectroscopy V. 64, N. 9, 2010, 1068-1071

Optimization of gamma detection methods for neutron energy analysis on eV neutron spectrometers

<u>D. Onorati¹</u>, C. Andreani¹, L. Arcidiacono¹, G. Festa¹, M. Krzystyniak², T. Minniti², G. Romanelli², A. Scherillo², P. Ulpiani¹, R. Senesi¹

¹University of Rome Tor Vergata, Department of Physics and NAST Center, Rome, Italy ²ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK

This work provides the analysis of the gamma spectrum emitted by the gold analyser foil used on VESUVIO spectrometer (ISIS pulsed neutron source) after irradiation by epithermal neutrons. For this purpose, a bi-parametric data acquisition [1] has allowed the simultaneous measurement of both neutron time-of-flight and gamma pulse height (energy) spectra. Such acquisition permitted to separate the signal and background components.

VESUVIO employs the resonance detector (RD) technique to detect eV energy neutrons, and allow Deep Inelastic Neutron Scattering experiments. YAP (Yttrium-Aluminium-Perovskite) scintillators, currently in use on the instrument, are set with a low-level discrimination (LLD) threshold at 600 keV [2]. Analysis of the spectra associated with resonant and non-resonant neutron absorption have shown that the observed signal is composed of three main components: (i) X-ray emission, (ii) radiative capture emission and (iii) Compton continuum in the low-energy region of the spectrum. The component (i) is the most intense one, in particular in the energy range between 60 keV - 80 keV. The component (ii) is a clear identification of the resonant neutron absorption and represents a significant fraction of the overall observed signal. The component (iii) is induced by radiative prompt gamma not fully absorbed in the detector. The measured energies and the relative intensity of the 197Au lines in the energy spectrum associated to the resonance neutron absorption are in good agreement with the available database. The data analysis shows that the gold dominant contribution is in the energy region between 0 keV - 400 keV, discarded by VESUVIO YAP detectors in the present set-up. The results suggest the best operating energy range for the spectrometer, and it points out that selecting energy windows in the gamma-ray cascade spectrum from the resonance analyser, is a key strategy to increase signal-to-background ratio. Such a development would allow selecting only those peaks emitted by the analyser foil, and it would remove other contributions due to the background. An improved data quality from Deep Inelastic Neutron Scattering experiments would result in a wider science programme on VESUVIO.

Keywords: Resonance detector; Time of flight spectroscopy; Radiative capture

References

[1] G. Festa, L. Arcidiacono, A. Pappalardo, T. Minniti, C. Cazzaniga, A. Scherillo, C. Andreani, and R. Senesi. Isotope identification capabilities using time resolved prompt gamma emission from epithermal neutrons. Journal of Instrumentation, volume 11, 29 March 2016.

[2] M. Tardocchi, G. Gorini, A. Pietropaolo, C. Andreani and R.Senesi. YAP scintillators for resonant detection of epithermal neutrons at pulsed neutron sources. Rev. Sci. Instru. Vol. 75, No.11 2004.

Observation of the stretch mode in H₂ and D₂ by INS spectroscopy

S. F. Parker,¹ R. A. Ewings,¹ F. Fernandez-Alonso¹ and D.Colognesi²

¹ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK ² Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi, via Madonna del Piano 10, I-50019 Sesto Fiorentino, (FI), Italy

The study of molecular hydrogen (H₂, dihydrogen) in or on materials is relevant to areas such as catalysis [1], hydrogen storage [2] and fuel cells [3]. Inelastic neutron scattering (INS) is well-suited to studies of such systems because the large 1H cross section and the transparency of most materials to neutrons means that most of the information obtained directly relates to the adsorbed dihydrogen. These studies are almost invariably carried out with the $J \ 0\ \mbox{\ensuremath{\mathbb{R}}}1$ rotational line at 120 cm-1 of parahydrogen as the probe of choice. The reasons for this are that the transition energy is sensitive to the local environment and the instruments generally have their best resolution in this energy region.

In this poster we show spectra recorded on MAPS [4] at ISIS of H_2 and D_2 across the energy range 0 -2 eV. For H_2 the low energy region shows the expected $J \rightarrow 1$ rotational line, at higher energies the H–H stretch mode is observed, see Figure 1. This is seen recoiling from the gas phase value of 516 meV. This is the first observation of this mode by INS spectroscopy, the only previous work [5] was

the mode is still visible in



inconclusive. Surprisingly, Figure 1: $S(Q, \omega)$ of solid H₂ at 7 K recorded on MAPS with an incident energy of 2000 meV.

liquid H_2 at 16 K. We were also able to detect the D–D stretch in D_2 despite the much smaller cross section

Keywords: Inelastic neutron scattering; hydrogen; deuterium

References

[1] K. Christmann, Surf. Sci Rep. 9 (1988) 1-163.

[2] A.J. Ramirez-Cuesta, M.O. Jones and W.I.F. David, Materials Today 12 (2009) 54.

[3] P.C.H. Mitchell, S.F. Parker, J. Tomkinson and D. Thompsett, J. Chem. Soc. Faraday Trans. 94 (1998)

[4] https://www.isis.stfc.ac.uk/Pages/maps.aspx

[5] W. Langel, D.L. Price, R.O. Simmons and P.E. Sokol, Phys. Rev. B 38 (1988) 11275-11283

^{1489-1493.}

Hydrogen mean force and anharmonicity in polycrystalline and amorphous ice

A. Parmentier¹, C. Andreani^{1,2}, G. Romanelli^{3,1}, J. J. Shephard^{4,5}, C.G. Salzmann⁴, R. Senesi^{1,2}

¹Università degli Studi di Roma Tor Vergata, Dip. di Fisica e Centro NAST, Roma, Italy

²CNR-IPCF Sezione di Messina, Messina, Italy

³ISIS Facility, Rutherford Appleton Laboratory, Chilton, UK

⁴University College London, Dept. of Chemistry, London, UK

⁵Durham University, Dept. of Chemistry, Durham, UK

The hydrogen mean force from experimental neutron Compton profiles is derived using deep inelastic neutron scattering on amorphous and polycrystalline ice. The formalism of mean force is extended to probe its sensitivity to anharmonicity in the hydrogen-nucleus effective potential. It is found that the shape of the mean force for amorphous and polycrystalline ice is primarily determined by the anisotropy of the underlying quasi-harmonic effective potential, and that data from amorphous ice shows an additional curvature reflecting the more pronounced anharmonicity of the effective potential, with respect to that of ice Ih.

Keywords:

Potential of mean force, neutron Compton profile; nuclear quantum effects; path integral representation; anharmonicity

References

[1] M. Ceriotti, W. Fang, P. G. Kusalik, R. H McKenzie, A. Michaelides, M. A. Morales, T. E. Markland, Nuclear Quantum Effects in Water and Aqueous Systems: Experiment, Theory, and Current Challenges, Chem. Rev. 116(5), 7259-7550 (2016).

[2] J. M. F. Gunn, C. Andreani, J. Mayers, A new approach to impulsive neutron scattering. Journal of Physics C Solid State Physics 19, L835–L840 (1986).

[3] C. Andreani, D. Colognesi, J. Mayers, G. F. Reiter, R. Senesi, Measurement of Momentum Distribution of Light Atoms and Molecules in Condensed Matter Systems using Inelastic Neutron Scattering, Adv. Phys. 54(5), 377-469 (2005).

Towards a better understanding of the self-cross-linking behaviour of smectite clays

J. T Rawlings¹, E. Budennaia¹, C. V Brown¹, M.Krzystyniak^{1,2}, G. Romanelli^{2,3} and F. Gao¹

¹School of Science & Technology, Nottingham Trent University, Clifton Lane, Nottingham, NG11 8NS, UK ²ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK ³Università degli Studi di Roma Tor Vergata, Dipartimento di Fisica and NAST Centre, Via della Ricerca Scientifica 1, 00133, Roma, Italy

A growing area of interest in nanocomposite science and technology is the use of layered structure smectite clay minerals as a filler material. They have been shown to widely enhance engineering properties such as mechanical strength, fire retardancy and dielectric performances. Work at Nottingham Trent University has furthered the use of smectite clays into nanocomposite materials for use as dielectric insulators, bacteria cellulose hydrated gels and bubble-foam systems. Much of this work has focused on two types of smectite clays with very similar structures, commercially known as Cloisite Na+ and Lucentite SWN. Despite the similarities of these materials the exhibited properties are shown to vary significantly depending upon the choice of clay. Although both clays exhibit physical self-cross linking behaviour, the rate of this is shown to be much more significant in SWN, with a high level of self-cross linking behaviour at very low concentrations (>2wt%) while the Cloisite Na+ does not exhibit the same properties. The purpose of this study is to determine what mechanisms dominate this physical self-cross linking behaviour, and the significant differences between the two very similar clays. The production of a clay-water sol system is highly complex, with a possibility of three different states being generated; micro scale clay particle aggregates, separated micro scale individual clay particles or nano scale individual silicate layers. In these investigations we have applied a high level of mechanical shear in order to produce a high-extent of layer delamination. The levels of this exfoliation have been evaluated using laser light scattering. The results obtained thus far show that the SWN clay has a higher particle aggregation rate in comparison to that of the Cloisite Na+ as shown by dynamic laser light scattering. The formation of a gel is also evidenced in the SWN by a intersection of the storage and loss moduli in oscillatory rheology, where as the Cloisite Na+ does not exhibit such an intersection. Through the use of neutron Compton scattering, the hydrogen momentum distributions of the two clays were obtained showing the anisotropy of the hydrogen binding, where the Cloisite Na+ is shown to have a higher than that of the SWN. This suggests that the SWN particles have a higher interaction with themselves as apposed to water molecules leading to a more rapid self-cross linking behaviour. Such a scenario is likely to be associated with the lower aspect ratio of the SWN, meaning more exfoliated sheets may be present than in the case of the Cloisite Na+ at the same mass concentration, leading to a reduced diffusion distance for particle collision and hence a higher likely-hood of cross linking.

Recent Upgrades on the VESUVIO Spectrometer

G. Romanelli,¹ and M. Krzystyniak¹

¹ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK

The VESUVIO spectrometer [1] at the ISIS pulsed neutron and muon source has recently witnessed a series of upgrades, related to both software and instrumentation. As such, VESUVIO is becoming an epithermal and thermal neutron station [2], where a number of techniques can be used at the same time, including neutron diffraction, neutron transmission, neutron Compton scattering, and neutron resonance capture analysis. Topics discussed in this poster include the recent upgrade of the water moderator serving the VESUVIO spectrometer, resulting on an increase in the neutron flux in the thermal region of a factor ca. 2.5 [3] (see Figure 1, left). Also, an extension of the neutron energy range towards cold neutrons has been achieved, owing to the collection of data during the time neutrons are generated in the second target station. Such an upgrade has doubled the d-spacing range for neutron diffraction up to 8 A (see Figure 1, right), and has lowered the lower energy limit for neutron transmission to a fraction of meV [3, 4]. Finally, the upgrade of the data acquisition electronics, allowing a higher count rate before saturation, and the new software for instrument control, IBEX, are presented.



Figure 1. Left: Incident neutron beam flux at the VESUVIO spectrometer before (blue) and after (black) the upgrade of the water moderator. **Right:** Extension of the energy range (red) in diffraction spectra owing to the upgrade of the VESUVIO data acquisition electronics.

 ${\bf Keywords:} \ {\bf Neutron} \ {\bf Diffraction}; \ {\bf Neutron} \ {\bf Transmission}; \ {\bf Neutron} \ {\bf Compton} \ {\bf Scattering}$

References

[1] https://www.isis.stfc.ac.uk/Pages/vesuvio.aspx

[2] C Andreani, M Krzystyniak, G, R Senesi, F Fernandez-Alonso, Electron-volt neutron spectroscopy: beyond fundamental systems, Advances in Physics (2017) 1-73.

[3] G. Romanelli, M. Krzystyniak, R. Senesi, D. Raspino, J. Boxall, D. Pooley, S. Moorby, E. Schooneveld, N. J. Rhodes, C. Andreani, F. Fernandez-Alonso, Characterisation of the incident beam and current diffraction capabilities on the VESUVIO spectrometer, Measurement Science and Technology 28 (2017) 095501.
[4] LA Rodríguez Palomino, J Dawidowski, JI Márquez Damián, GJ Cuello, G Romanelli, M Krzystyniak, Neutron total cross-section of hydrogenous and deuterated 1-and 2-propanol and n-butanol measured using the VESUVIO spectrometer, Nucl. Instruments and Methods in Physics Research Section A, 870 (2017) 84-89.

Benchmarking acidic and basic dopants with respect to facilitating the ice V to XIII and ice VI to XV hydrogen-ordering phase transitions

A. Rosu-Finsen, Z. Sharif and C. G. Salzmann

Department of Chemistry, University College London, Christopher Ingold Building, 20 Gordon Street, London, WC1H 0AJ, United Kingdom

Hexagonal ice I is a common occurrence in nature, however, from the elucidation of the various and complex crystal structures of the high-pressure phases of ice, a new avenue of research has opened up. Percy Bridgman pioneered the field of high-pressure ices in early 1900, discovering the unusual properties of compressed ice, *e.g.*, ice VI melting above 100 C° [1]. Since then, and with the use of neutron diffraction as a vital tool, the crystal structures of new phases of water ice have been determined. Seventeen polymorphs of ice have been discovered so far meaning that this simple, ubiquitous, and intriguing molecule may still harbour some secrets. Due to the extensive polymorphism of ice and the potentially essential role of ice in the chemical origins of life, there are still outstanding questions which continue to drive the field of research into ice [2].

Recent work into adding dopants to water have shown remarkable differences in the crystal structures, indeed this was how ices XI, XIII, XIV and XV were discovered [3]. Addition of dopants forces the otherwise expected hydrogen-bonded network to alter and depending on the concentration of the dopant, and indeed depending on the type of dopant, greater or lesser changes in molecular dynamics of ice have been observed [4]. Addition of dopants shows the extent of sensitivity of water structures with, for example, HCl being a critical component in facilitating molecular reorientations in ice which are needed for hydrogen-ordering phase transitions to take place at low temperatures. Doping ice is therefore not a new idea, however, to date, research into the use and effects of dopants has not been done in a systematic fashion and with a direct comparison.

The present work follows the effect of doping on the ice V to XIII and ice VI to XV hydrogenordering phase transitions using 0.01 M solutions of LiOH, NaOH, KOH, HF, HCl, HClO4, and HBr as the initial sample solutions. Each ice sample is made by compression and heating of the ordinary ice Ih at 0.5 GPa or 1.0 GPa, for ices V/XII and VI/XV respectively, in pre-cooled stainless steel pressure dies before quenching to 77 K. The product ices were verified to be pure with X-ray diffraction. Enthalpies and entropies of the ices were gathered with differential scanning calorimetry while vibrational characterisation was performed through Raman spectroscopy. Acid and base doping is shown to exhibit regions of order and disorder of the ice structure upon heating. From these experiments, HCl doping of ice XIII and XV is shown to exhibit the most promising characteristics and the highest energies of hydrogen ordering along with Pauling entropy. This is attributed to a combination of the high acid strength and the comparatively small size of the chloride anion.

Keywords: H2O; Ice XIII; Ice XV; Dopants; Energy; Raman Spectroscopy; Differential Scanning Calorimetry

References

- [1] P. McMillan, Nat. Mater., 2005, 4, 715
- [2] C. G. Salzmann, P. G. Radaelli, B. Slater and J. L. Finney, Phys. Chem. Chem. Phys., 2011, 13, 18468
- [3] C. G. Salzmann, P. G. Radaelli, A. Hallbrucker, E. Mayer and J. L. Finney, Science, 2006, 311, 1758
- [4] J. J. Shephard and C. G. Salzmann, Chem. Phys. Lett., 2015, 637, 63

Supreme toughness in Aluminium enriched cements

M. Salha,¹ Fu Song,¹ Kun V. Tian,² and Gregory A. Chass,^{1,*}

¹ School of Biological and Chemical Sciences, Queen Mary University of London, London, UK

² Department of Chemical Science and Technologies, University of Rome Tor Vergata, Rome, Italy

* Correspondence: g.chass@qmul.ac.uk

Modern cements are high in strength but lack toughness over time. Aluminium substitution of silicon in a cementitious environment has been linked to increases in intrinsic fracture toughness. Ancient roman cements, with relatively high Al-contents, are known to be significantly tougher than modern cements.₁₋₂ We therefore initiated computational characterisations of interfacial models towards resolving the atomic-scale structural and dynamic bases of the observed toughening. A novel molecular cluster approach was used, with models ranging from 1-3 nm³. Results showed increased flexibility of Al-O-X bond angles (X = Si, H, Al), with Al thus serving as a hinge-point in the networks especially at interfaces. Structurally, Al-geometries were populated by tetrahedral, trigonal bipyramidal, square pyramidal and octahedral coordinations, with facilitated distortion and interconversion, equating to increased flexibility and effective dispersion of applied forces. These Alrich structures were amorphous with irregular pores with an overall increased free volumne (Vf), relative to Al-poor ones. Future endeavours include carrying out neutron-compton scattering experiments on cements with differing Al-contents to resolve their constituent atomic cohesions, preand post-setting.

Keywords: Al-tobermorite; cement; fracture toughness; atomic cohesion

References

M. D. Jackson, E. N. Landis, P. F. Brune, M. Vitti, H. Chen, Q. Li, M. Kunz, H.-R. Wenk, P. J. M. Monteiro and A. R. Ingraffea, *Proc. Natl. Acad. Sci.*, 2014, 111, 18484–18489.
 H. Youssef, D. Ibrahim, S. Komarneni and K. J. D. Mackenzie, *Ceram. Int.*, 2010, 36, 203–209

Analysis of Neutron Activation Decay on the VESUVIO beam line at ISIS

<u>V. Scacco</u>¹, A. Zaganelli¹, G. Campa¹, L. Arcidiacono ^{2,3}, C. Cazzaniga⁴, G. Festa², M. Krzystynyak⁴, D. Onorati¹, G. Romanelli⁴, G. Skoro⁴, R. Senesi^{1,2,5}

¹Università degli studi di Roma "Tor Vergata", Dipartimento di Fisica e Centro NAST, Rome, Italy ²Centro Fermi-Museo Storico della Fisica e Centro Studi e Ricerche "Enrico Fermi", Rome, Italy ³UCL Institute of Sustainable Heritage, University College London, London, UK ⁴STFC-Rutherford Appleton Laboratory, ISIS Facility, Chilton, OX11 0QX, UK ⁵CNR-IPCF Sezione di Messina, Messina, Italy

Vesuvio is a neutron spectrometer, which uses epi-thermal neutrons to study atomic momentum distributions in materials, with atomic mass-separation capability. Neutron detection on the spectrometer makes use of gamma-sensitive scintillators. The spectrometer's blockhouse gamma radiation background is composed of prompt (beam-on) and activation (beam-off) components. Here the activation background was studied to identify, both blockhouse's radiation decay time and the main elements contributing to the spectrometer activation.

Exploring new areas of the ice phase diagram for metastable ice V with varying degrees of hydrogen-order

Z. Sharif,¹ A. Rosu-Finsen¹ and C. G. Salzmann¹

¹Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, United Kingdom

Hydrogen-disordered ice V is well-known to exist in a thermodynamic range of stability of 0.35 and 0.63 GPa and 210 and 270 K.[1, 2] However some ice phases, such as ice XII, have been observed to exist outside their expected thermodynamic ranges of stability in metastable forms.[3] Here we demonstrate that ice V can exist within other regions of the ice phase diagram in a metastable form as well, where ices II, VI and XIII would usually be observed.[4] From the metastability domain of ice V, we also investigate the phase transition of ice V to its hydrogen-ordered counterpart ice XIII in this metastable region. On producing 0.01 M doped HCl ice V at 0.5 GPa, samples have subsequently been quenched, subjected to a series of higher pressures, then heated and before being slow-cooled to 77 K. These samples have been analysed using differential scanning calorimetry to assess the impact this has on the hydrogen-ordering of each sample. To further resolve the effect of this pressure variation on the hydrogen-ordering, combinatorial neutron diffraction of similarly treated 0.01 M DCl samples would be crucial in assisting the determination of the deuterium (hydrogen) occupancies. This direct indicator of hydrogen-ordering from neutron diffraction will provide the conclusive evidence required to define our samples with respect to their deuterium occupancies. [5]

Keywords: ice; hydrogen-ordering; differential scanning calorimetry; crystal structure; phase diagram; pressure effects

References

[1] C. G. Salzmann, P. G. Radaelli, J. L. Finney and E. Mayer, Physical Chemistry Chemical Physics, 2008, **10**, 6313–6324.

[2] B. Kamb, A. Prakash and C. Knobler, Acta Crystallographica, 1967, 22, 706–715.

[3] C. Lobban, J. L. Finney and W. F. Kuhs, Nature, 1998, **391**, 268–270.

[4] C. G. Salzmann, P. G. Radaelli, B. Slater and J. L. Finney, Physical Chemistry Chemical Physics, 2011, 13, 18468–18480.

[5] C. G. Salzmann, P. G. Radaelli, A. Hallbrucker, E. Mayer and J. L. Finney, Science, 2006, 311, 1758–1761.

Neutron scattering on atomic structure, stabilities and dynamics of cement

Fu Song¹, K. V. Tian², and G. A. Chass¹*

¹School of Biological and Chemical Science, Queen Mary University of London, Mile End Road, London E1 4NS, UK,

²Department of Chemical Science and Technologies and centro NAST, Università degli Studi di Roma TorVergata, Via Orazio Raimondo, 18, 00173 Roma RM, Italy *g.chass@qmul.ac.uk

The work involves characterising the microscopic and mesoscopic structure, dynamics and mechanical properties during and after setting of ordinary (Portland) cement OPC, as true understanding of the atomic-level structure and function remains scarce, particularly with respect to observed mechanical properties. Molecular cluster models based on DFT methods have generated encouraging synergies between experiment and computation. These non-periodic cluster models have no geometric restrictions, therefore are truly amorphous and dynamic. The approach has successfully predicted interfacial structure and dynamics of bioactive dental cements. Hence a battery of neutron and coherent-THz techniques are being employed, guided by the theoretical results, to track the changes in structure, dynamics and functional properties over setting time, OPC and other cementitious systems. D2O has been popularly used in detecting dynamic properties during cement hydration process in neutron scattering. The two peaks (2.564 and 2.633 Å) generated in C-S-D are not shown in C-S-H (Fig.1).



Fig.1 (a) Energy transfer in d-space by neutron diffraction. Two peaks (2.564 & 2.633 Å) increase during setting in C-S-D.

Keywords: Cement; C2S; C3S; D2O; dynamic models; RDF; hydration; neutron scattering

References

- [1] Tian, Kun V., et al. Nature communications 6 (2015)
- [2] Jennings, Hamlin M. Cement and Concrete Research 38.3 (2008): 275-289
- [3] FitzGerald, S. A., et al. Journal of Materials research 14.03 (1999): 1160-1165

Water gelation as a structural scaffold in cementitious materials

M. B. Umarji,¹ F. Song,¹ K. V. Tian² and G. Chass^{3,*}

¹School of Biological and Chemical Science, Queen Mary University of London, London, UK

²Department of Chemical Science and Technologies and centro NAST, Università degli Studi di Roma TorVergata, Roma, Italy

³Department of Chemistry, The University of Hong Kong, HK SAR, China <u>*g.chass@qmul.ac.uk</u>

In addition to being the industry with the highest energy consumption and release of CO2, Cement is the largest mass produced material in the world. Most commonly used in concrete or mortar, little is understood about the atomistic structure or its contributions to the observed bulk mechanical properties. The contributions to functionality from water are the least well understood and are essential to characterise due to cement's 40-50% H2O content. We therefore initiated synergistic experimental-computational investigations into the role of H2O and D2O during and post-setting in selected cementitious materials; focus being on the interfacial and inter-particle H2O gelation and subsequent network formation.

Preliminary results demonstrate cage-type H2O structures forming around Ca-Silicate particles, facilitating further gelation and particle-agglomeration. The free molecular cluster models employed have effectively informed the design of coherent-THz and neutron scattering/diffraction measurements of the structure and dynamics of all H2O, D2O and Ca-silicate particles in the cementitious ensembles, contributing towards resolving the formation of the cages.

Enhancing the YAP detector's discrimination threshold installed in the VESUVIO spectrometer at the ISIS spallation neutron source

<u>P. Ulpiani</u>¹, C. Andreani¹, L. Arcidiacono¹, C. Cazzaniga², G. Festa¹, M. Krzystyniak², D. Onorati¹, G. Romanelli², E. M. Schooneveled², R. Senesi¹.

¹University of Rome Tor Vergata, via della Ricerca Scientifica 1, Rome, Italy ²ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, United Kingdom

The eV neutron spectroscopy represents a fundamental type of material characterization thanks to its unique properties. For this reason in recent years many scientists are trying to improve neutron spectrometers, both from instrumental and acquisition point of view.

This work provides a description of the detection improvement obtained in the forward photon sensitive Yttrium- Aluminum-Perovskite (YAP) detectors, installed in the VESUVIO spectrometer at the ISIS spallation neutron source (ref. [1]). YAP detectors work with a Low Level Discrimination (LLD) threshold measuring only photons with energy greater than a certain energy value (ref. [2]), at this moment the LLD threshold is fixed at 600 keV.

There are two types of photons detected: background photons, coming from the blockhouse of the spectrometer, and signal photons, coming from the resonant Gold foil in front of the detector which converts scattered neutrons to gamma ray trough radiative neutron capture. The most intense signal prompt gamma emission peaks from radiative neutron capture emitted by the resonant Gold foil are concentrated at energies lower than the actual threshold (ref. [3]).

Our intention is to find a new threshold for the Gold Resonance Detection configuration.

This work shows an improvement on the statistical poissonian error bars and counting fluctuation in the Time Of Flight (TOF) spectra after the LLD threshold change. It leads to a more precise and sensible measurements of the atom momentum distribution (which is one of the most important information obtained using the VESUVIO spectrometer) paving the way to a new kind of experiments.

Keywords: eV spectroscopy; detection improvement

References

[1] Seel A. G., Krzystyniak M., and Fernandez-Alonso F; The VESUVIO Spectrometer Now and When?

[2] Tardocchi M. et al. YAP scintillators for resonant detection of epithermal neutrons at pulsed neutron sources.

[3] G. Molnar. Handbook of Prompt Gamma Activation Analysis.