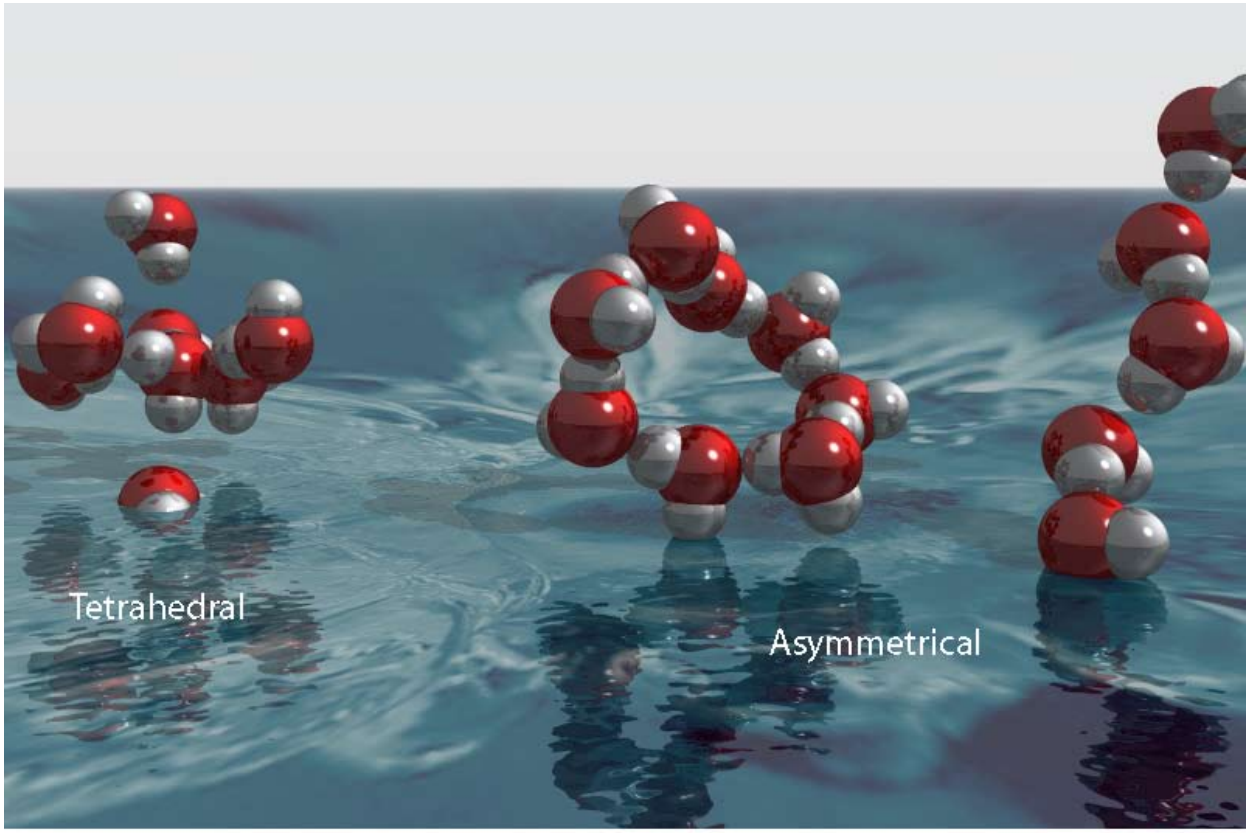
NSC News
National Supercomputer Centre at Linköpings universitet
2007:1

A Watery Surprise



The structure of the first coordination shell in liquid water. Illustration by Hirohito Ogasaware.

Recent experimental and theoretical applications of x-ray spectroscopies to liquid water shed new light on the hydrogen bonding network. The interpretation of the x-ray data questions the established understanding of liquid water.

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New Faces at NSC

Two new system experts have joined the NSC forces.

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The New NSC Computer Building

The construction of NSC:s new computer building is about to start.

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Infrastructure

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Maybe you have seen and read the Research Council's guide to infrastructure (www.vr.se). It is an ambitious document that summarizes the needs for infrastructure in the different branches of science. In the first line in the introduction is written "Common research infrastructure, from advanced particle accelerators to computational resources, digital networks and open databases, are often critical for high impact research". NSC is of course deeply involved in computational resources and to a large extent we are depending on digital networks. We have also started to look into a database system to handle the large datasets associated with meteorological data, the Meteorological Archive and Retrieval System, MARS. I have also had the opportunity to participate in the first stage of forming the Database Infrastructure Committee, DISC. An output from DISC will be the foundation of SND (Swedish National Dataservice). The role of SND (in relation to DISC) will be very similar to the relation between NSC (and other Swedish HPC centers) and DISC. We will follow the development of SND with great interest and hopefully we can establish some links to in order to share experience in working with large databases.

As concerns computational resources, it is of great interest to NSC to participate in the EU FP7 Capacities Work Programme on infrastructure. In the ESFRI Roadmap for research infrastructure one chapter is devoted to "European high-performance computing service". The HPC service is described as a pyramid where the local centers constitute the base, national and regional centers constitute the middle layer and a few high-end centers form the top. In the present call the investments will be directed to installations at the high-end and middle levels and amount to 100-200 M€ and 50-100 M€, respectively. In the context of these investments in infrastructure, NSC has been involved in a national initiative to team up with our Nordic neighbours, with the intention of forming a regional virtual center that becomes an important player at the European scale.

At the more close perspective NSC is now in the final phase of procurement of the new capability resource. The result of the procurement will be announced on the NSC homepage by the end of March. New resources require staff to handle both hardware and user support. We are very happy to welcome two new systems experts, Mattias Slabanja and Tom Langborg, to our team. Both Mattias and Tom are presented in this issue of NSC News. The NSC team, together with the new resources and the coming infrastructure investments, will make it possible for us to climb the European HPC pyramid, the future will tell how high up we can reach.

The New NSC Building

In order to host the new capability resource as well as other near future installations at NSC, Akademiska Hus is building a new computer building at the Linköping University Campus.

The new computer building will have a total area of 640 m^2 with a 270 m^2 main computer room and service areas for cooling equipment, UPS, and operations.

The cooling system will have an initial capacity of 0.5 MW, with an option to install water cooling, bringing the total cooling capacity to over 1 MW.

Starting from September 1, 2007 this new building will be in operation in parallel with our old computer building. In total, this will give us an excellent opportunity for expanding our resources and to further establish NSC as the leading provider of high performance computing resources in Sweden.

The building is commissioned by Linköping University and we are grateful for the generous support and interest the University is showing for the activities at NSC.

The Structure of Liquid Water

The accepted picture of liquid water is a dynamically distorted network of basically tetrahedrally coordinated molecules. This has been established mainly based on analysis of x-ray and neutron diffraction data and is strongly supported by all theoretical simulation models. Thus, it was not in order to discover anything new about water that Anders Nilsson and his experimental team for the first time used x-ray absorption spectroscopy (XAS) at high resolution to measure the spectrum of liquid water. The aim was to study ions and molecules dissolved in water, but to separate out the water background signal the water spectrum was needed. Similar to the photographer in Antonioni's movie *Blow up* it turned out that the background was even more interesting than the intended motive…

In the experiment x-ray photons are used to excite an oxygen 1s-electron in a molecule into unoccupied and mostly very extended states. The involvement of the strongly localized 1s core-electron makes XAS a very local probe, but still with a strong sensitivity to the structure of the environment due to the extended final state. The spectrum of crystalline, well-ordered ice was well-known and if the difference between ice and liquid water can be described mainly as distortions around a tetrahedral ice-like network, then a broadened ice-like spectrum without sharp features

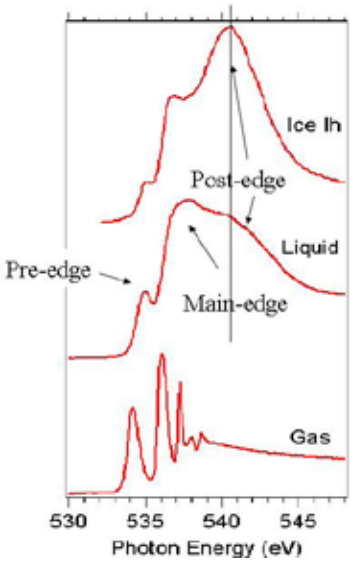

Figure 1 XAS spectra of (top to bottom) ice, liquid and gas phase water.

should be expected. Instead something very different was found (Fig 1): the liquid shows a sharp and well-defined pre-edge, a prominent main-edge while the post-edge, characteristic of ice, is strongly reduced.

To understand the origin of these features the theory team of Lars G.M. Pettersson did extensive simulations of XAS spectra based on structures from molecular dynamics (MD). The specific features of the liquid were found to arise uniquely when one hydrogen-donating bond was broken or strongly distorted. This theoretical prediction was confirmed in ultra-high vacuum measurements on the surface and bulk of crystalline ice giving experimental model spectra of fully coordinated, respectively asymmetrically bonded molecules. Using these to decompose the spectrum of the liquid the surprising result was that some 80% of the molecules could be viewed as asymmetrically bonded on the hydrogen side, i.e. with only one H-donating bond. Returning to theory we could use small cluster models to quantify how large distortions were required to generate the observed spectral features and then compare with structures from MD simulations. The result of the simulations is the opposite of the XAS experiment: 70–80% have both hydrogens participating in H-bonds. The large number of broken donating H-bonds deduced from the experiment naturally requires a similar number of broken acceptor bonds suggesting that the majority of molecules in the liquid only have two strong H-bonds, one accepting and one donating. This would be the case for, *e.g.*, chains or rings in the liquid. These results were published in two papers [1,2] that have received significant attention and caused a heated debate in the literature.

Going back to our Car-Parrinello MD (CPMD) simulations we calculate spectra using larger clusters (32 molecules) [3]. The simulation gives an ice-like spectrum (Fig. 2, CPMD), but this is the result also when we specifically select structures according to the

Tom Langborg

I came back again! From 1990 to 1995 I was a system administrator at the ITN department at Linköping University. Now I am back again as a storage specialist at NSC. It is work I am looking forward to. The last 7 years I have worked as a storage specialist at SMHI (Swedish Meteorologic and Hydrological Institute). Working as a storage system specialist at NSC gives me opportunities to work with the latest technology and with systems with bigger capacity.

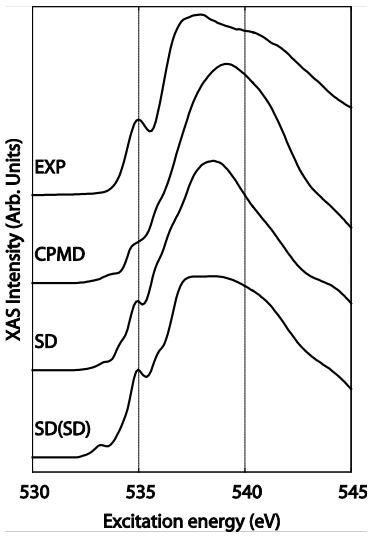

Figure 2 Experimental XAS spectrum of liquid water (top) compared with calculated spectra from CPMD simulation and by selecting structures according to a loose (SD) and tight (SD(SD)) asymmetry criterion.

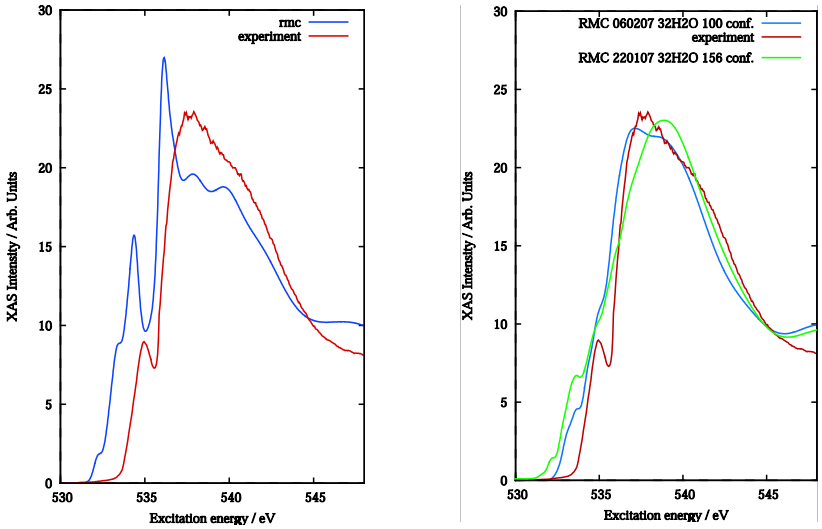

Figure 3 (3a, left) and (3b, right) compare computed and experimental XAS spectra.

criterion established in the *Science* paper (Fig. 2, SD). We are forced to modify our criterion to require the asymmetry to be even larger in order to obtain a spectrum that has some resemblance to the experiment (Fig. 2, SD(SD)). Such strongly asymmetric bonding situations are, however, extremely rare in the simulation and the important question arises whether the experimental x-ray and neutron diffraction data, normally viewed as giving symmetrical coordination, could also support a predominance of strongly asymmetric species – although the MD simulation does not.

To answer this we have now turned to Reverse Monte Carlo (RMC) simulations and use a new high-quality set of extended x-ray diffraction data [4] in combination with neutron data for four isotope mixtures. RMC makes random moves of the atoms in a periodic simulation box to reduce the difference between predicted and experimental diffraction data – or any data set that can also be predicted from only structural data. The great advantage with the RMC technique is the possibility to introduce constraints based on geometrical criteria as well as arbitrary distributions to also fit against, such as the ratio of asymmetric and tetrahedral species deduced from XAS.

Without any constraints at all we find a near-perfect fit to the diffraction data, but individual molecules are not kept intact; the average stoichiometry is H_2O, but there is a distribution around this. Constraining to molecules does not affect the quality of the fit, but the coordination in terms of H-bonds is surprisingly low with of the order 30–50% molecules with no donating H-bond at all; surprisingly, the connectivity is not forced by the diffraction data! Introducing the constraints derived in [3] and requiring 70% of the molecules to be very asymmetric and the remaining 30% in ice-like structures still gives the same near-perfect fit to the diffraction data and with some optimism we go to Monolith to compute spectra based on this structure (Fig. 3a). The pre-edge is very sharp and pronounced as is the main-edge, but both are at too low energy. The reason for this is that the internal geometry of some molecules has been distorted into very large internal bond angles, even linear molecules, in order to compensate the requirement of extreme asymmetry. In Fig. 3b we require also the distribution of bond-angles and internal OH distances as obtained from quantum simulations to be reproduced and now the data limit the amount of asymmetric species. Repeating the fit with the additional constraint the distribution becomes 50% very asymmetric and 20%

Mattias Slabanja

I came to Linköping from Göteborg and started working at NSC late last year. Previously I have, among other things, been working as a graduate student doing computational-intensive research – mostly various types of Monte Carlo simulations in the field of materials physics.

Here at NSC, my current duties mainly concern the administration of the storage system named Tank, and the evaluation of the future replacement of Monolith; and when the future becomes the present, the administration of the "monolith-replacer" will become my primary occupation.

tetrahedral; the remaining species show one strong donating and two accepting (20%) or two donating and one accepting (10%) constituting overall agreement with [2]. The fit to the diffraction data is not affected.

Having found a solution in agreement with the requirements imposed by XAS as well as a reasonable internal geometry we return to Monolith for the calculation of the 100–200 spectra required to generate a summed model spectrum of the liquid. The parallelization is ideal with one spectrum per processor. The result is shown in Fig. 3b (green line). It represents a definite improvement over the previous spectrum, but has intensity at too low energy, has no well-defined pre-edge and has the main-edge at the wrong energy.

Much of the intensity at too low energy is due to the formation of pockets in the model where non-H-bonded OH groups stabilize the excited electron. To avoid this artifact we add a positive charge to all hydrogens and require also the Coulomb repulsion to be minimized in the fit. Again we have the same near-perfect fit to the diffraction data and an improvement in the spectrum (Fig. 3b, blue line). It is clear that the information content in the diffraction data alone is very limited allowing many different structural solutions and further experimental data are needed to narrow the possibilities. We now include also vibrational Raman data in the fit and have available Compton scattering difference profiles to put further constraints on the solutions. Every experimental data set represents integration over different aspects of the structure and complementary data must be used for a reliable structural model, but XAS does provide a very sensitive probe of the structure.

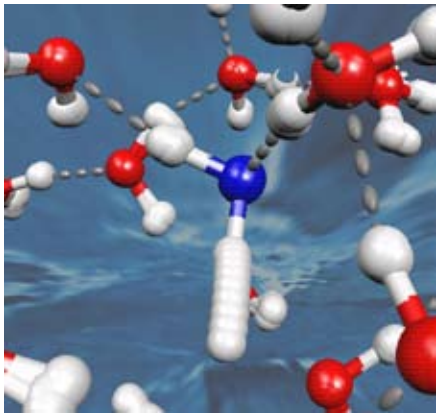

Figure 4 Ultra-fast dissociation induced by resonant core-excitation of asymmetric species.

The core-excited state in XAS has a life-time of the order of 4 *fs* with one decay channel through emission of an x-ray photon. This is the basis for x-ray emission spectroscopy (XES) which measures the occupied valence orbitals providing an additional experimental technique. However, there is a complication in H-bonded water in that, even during this short life-time, dissociation can occur. Using a combination of isotope substitution experiments and molecular dynamics simulations we have shown that this ultra-fast (0–10 femtosecond) proton transfer can be probed with XES [5]. In the simulation we introduce the core-hole and extract spectra along the trajectory to simulate the experiment.

The molecular dynamics is strongly dependent on the nature of the electronic core-excited state, and by scanning the excitation energy different reaction dynamics can be probed. In Fig. 4, resonant excitation of an asymmetric species leads to dissociation of the non-H-bonded OH. Different nuclear masses give rise to differences in the dynamics and the observed isotope effect in XES is direct evidence of the importance of such processes. This is of great importance to the understanding of radiolysis of aqueous systems and, furthermore, knowledge of the core-excited dynamics is a prerequisite for extracting structural information from higher resolution XES.

The work presented is the result of a strongly coupled experimental and theory effort with contributions from a large number of people. On the computational side we specially acknowledge Michael Odelius and present PhD students Mikael Leetmaa, Thor Wikfeldt and Mathias Ljungberg. Earlier valuable contributions have been given by Yi Luo, Lars Ojamäe and Matteo Cavalleri. We are grateful for funding from VR and SSF, the grant of CPU time at NSC and PDC and thank Jan Swenson for introducing us to RMC.

References

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Lars G.M. Pettersson is professor in Quantum Chemistry and heads the theory effort within the Surface Chemical Physics group at FYSIKUM, Stockholm University.

Anders Nilsson is professor in Synchrotron Radiation Physics at Stanford Synchrotron Radiation Laboratory and guest professor at FYSIKUM, Stockholm University, heading the experimental effort within the Surface Chemical Physics group.

UPCOMING EVENTS

HPC 2007; High Performance Computing Symposium

March 25–29, 2007, Norfolk Virginia, USA.
http://hosting.cs.vt.edu/hpc2007/

IPDPS 2007; 21st IEEE International Parallel & Distributed Processing Symposium

March 26–30, 2007, Long Beach, California, USA.
http://www.ipdps.org//

CAC 2007; The Workshop on Communication Architecture for Clusters (held in conjunction with IPDPS 2007)

March 26–30, 2007, Long Beach, California, USA.
http://www.c3.lanl.gov/cac2007/

HCW 2007: The Sixteenth International Heterogeneity in Computing Workshop

March 26, 2007. Long Beach, California, USA.
http://navet.ics.hawaii.edu/hcw2007/

HiCOMB 2007; 6th International Workshop on High Performance Computational Biology

March 26, 2007, Long Beach, California, USA.
http://www.hicomb.org/

Lustre User Group 2007

April 23–25, 2007, Miami Beach, Florida, USA
http://www.clusterfs.com/lustre2007.html

GPC 2007; Second International Conference on Grid and Pervasive Computing

May 2–4, 2007, Paris, France.
http://www-lipn.univ-paris13.fr/GPC2007/

ACM International Conference on Computing Frontiers

May 7–9, 2007, Ischia, Italy.
http://www.computingfrontiers.org/

NOTUR 2007

May 9–11, 2007, Oslo, Norway.
http://www.notur.no/conferences/

CCGrid07; 7th IEEE International Symposium on Cluster Computing and the Grid

May 14–17, 2007, Rio de Janeiro, Brasil.
http://ccgrid07.lncc.br/

DEISA Symposium; Towards Petascale Computing in Europe

May 21–22, 2007, Munich, Germany.
http://www.deisa.org/symposium

SGIUG 2007; SGI User Group Conference 2007

May 21–25, 2007, Minneapolis, USA
http://www.sgiug.org/index.php

Worldcomp 07; The 2007 World Congress in Computer Science, Computer Engineering, and Applied Computing

June 25–28, 2007, Las Vegas, Nevada, USA.
http://www.worldacademyofscience.org/worldcomp07/ws

ISC 2007; International Supercomputer Conference

June 26–29, 2007, Dresden, Germany.
http://www.supercomp.de/isc2007/

HPDC 2007; IEEE International Symposium on High Performance Distributed Computing

June 27–29, 2007, Monterey Bay, California, USA.
http://www.isi.edu/hpdc2007/

PASCO 2007; Parallel Symbolic Computation

July 27–28, 2007, London, Canada.
http://www.orcca.on.ca/conferences/pasco2007

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