Experimental report

24/11/2021

Proposal:	**EASY-636**	**Council:**	10/2019
Title:	Water dynamics on iron oxide nanoparticles		
Research area:	Chemistry		

This proposal is a new proposal

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Experimental team:	
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Samples: iron oxide nanoparticles

Instrument	Requested days	Allocated days	From	To
IN16B	16	16	17/08/2020	18/08/2020

Abstract:

Nanoparticles (NPs) still come along with many open questions, concerning even basic properties like their defect inventory or the structure of the interfaces in solution. Recently, we made a significant contribution by proving a restructuring of water around NPs reaching out to some three layers through careful PDF analysis. However, the infiltration of the solvent into the ligand shell remains unknown. With this proposal, we want to take a different approach by deriving structural evidence from dynamical information. We expect that motions of water and ligand molecules at NP surfaces occur in different time regimes, largely unknown at present. Nevertheless, they should become apparent in fixed window scans in backscattering spectroscopy, both in the elastic and inelastic mode (offset by ~3 times the instrumental energy resolution). TGA and water vapour sorption measurements support this. With this application, we propose to undertake an exploratory endeavor by fixed window scans on IN16B. We will use 7 nm , citrate-capped IONPs. For two suggested runs on IN16B, we will prepare a nominally dry sample and one with a nominal coverage of the IONPs by 2 layers of water molecules.

Water dynamics on iron oxide nanoparticles

Experiment easy-636

1. Scientific background

Nanoparticles (NPs), although already in common use today, still come along with many open questions. This concerns even basic properties like their defect inventory and a structural surface relaxation of direct relevance for their growth, as well as the structure of the interfaces when in solution. In general, the situation is more complex as NPs are stabilized by ligands, which attach to the surface to limit particle growth and avoid NP agglomeration. In a recent attempt, we tried to make the ligand shell visible in SANS experiments. However, the results were inconclusive, as we did not succeed in a satisfactory description of the data by involving core-shell models. We argue that is due to a more complex ligand solvent structure, which involves e.g. an unknown surface density and a complex geometry of the ligand due to steric arrangements on the flat surfaces, edges and corners of the NPs, as well as an infiltration of the ligand by the solvent. A direct measurement of the ligand-solvent structure is challenging, although we have recently made a significant contribution by proving a restructuring of the water reaching out to some three layers through a careful PDF analysis.[1] However, the infiltration of the solvent into the ligand shell remains unknown. With QENS as a different approach the derivation of structural evidence from dynamical information, in particular for the ligand-water interface is possible. It is to expect that motions of water present in the ligand or local motions of ligand units should become apparent in fixed window scans in backscattering spectroscopy, both in the elastic and inelastic mode. Those motions could become observable as intensity steps of characteristic shape at specific temperature values, depending on the water content or the type of ligand with different amounts of hydrogen.

2. Experiment

The samples studied were a powder of citrate capped iron oxide NPs which was equilibrated at three different relative humidities (8, 75 and 85 % RH) in an aluminium sample holder sealed with Indium wire. Fixed window scans (FWS) were performed in the elastic and inelastic mode (offset by 3 µeV) in a temperature range from 2 K to 330 K. Also, QENS scans were carried out at different temperatures ranging from 2 K to 380 K, yet with rather short counting time and hence far from ideal signal-to-noise ratio. Furthermore, a vanadium standard for background correction and an empty can measurement were performed.

[1] Sabrina L. J. Thomä, Sebastian W. Krauss, Mirco Eckardt, Phil Chater, and Mirijam Zobel, Nat. Commun. 10 (2019)

3. Preliminary results

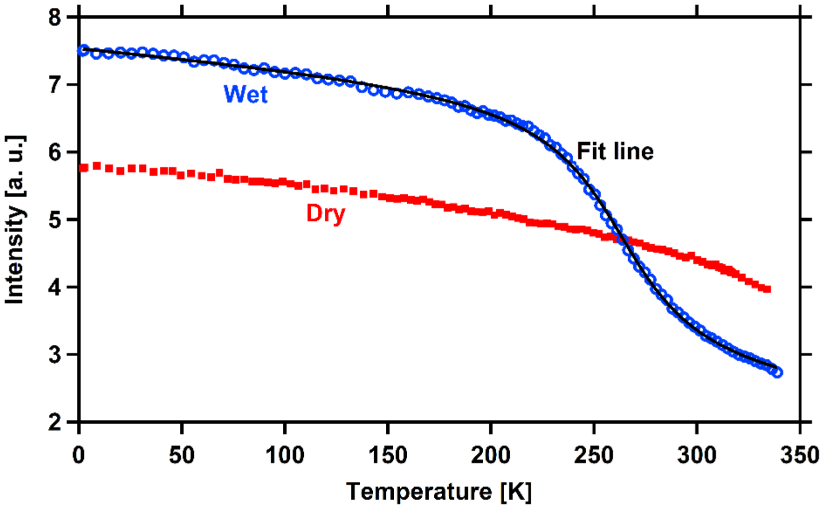

Figure 1: EFWS on dry (red line) and wet (blue line) sample. The black line is an Arrhenius-type fit curve.

The elastic fixed window scan (EFWS) on the dry sample (Figure 1) shows a small continuous decrease of intensity with increasing temperature as it is about expected for Debye Waller behaviour. Above freezing temperature, the decrease appears to get a bit stronger than expected. For the wet sample, there is a significant drop in intensity at ca. 230 K, with a midpoint of the steplike drop at around 265 K. This curve can be modelled with an Arrhenius-behaviour (black line) [2], and an activation energy of 0.35 eV is found.

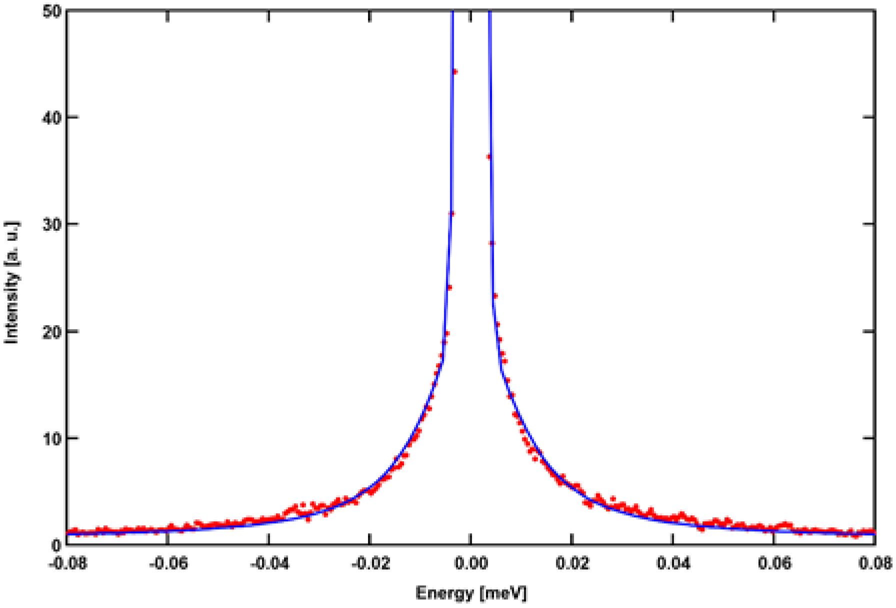

Figure 2: QENS spectrum of the wet sample at 330 K

QENS spectra were measured at different temperatures and Figure 2 shows one spectrum of the wet sample (75 % RH) at 330 K fitted with two Lorentzian lines and an elastic component. The broadening of the elastic signal is clearly visible. To determine the type of diffusion, the Q-dependence of the data will be evaluated, too, and data analysis is ongoing. A PhD student was recently recruited for this DFG-funded project on QENS experiments for the observation of diffusion dynamics of water molecules on the surface of iron oxide nanoparticles.

[2] H.-H. Grapengeter, B. Alefeld, and R. Kosfeld, Colloid & Polymer Sol 1987, 265, 226-233