Experimental report

23/11/2021

Proposal: **9-12-648** **Council:** 4/2021

Title: Diffusion dynamics of water and citrate molecules on the surface of iron oxide nanoparticles

Research area: Chemistry

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Samples: iron oxide nanoparticle powder

Instrument	Requested days	Allocated days	From	To
IN16B	5	5	22/09/2021	27/09/2021

Abstract:

Iron oxide nanoparticles (IONPs) are employed in many areas ranging from biomedicine to heterogeneous catalysis and feature a solid-liquid interface in many applications. Despite much progress in the structural characterization of NPs, experimental insight into the structure and dynamics of solid-liquid interfaces is rare. Quasielastic neutron scattering (QENS) was used to access the dynamics of water molecules at the surface of TiO_2, SnO_2 and $BaSO_4$ NPs. Yet, the dynamics of ligand molecules are largely unknown up to now, although they are commonly employed for size-selective NP synthesis and long-term colloidal stability.

Our recent EASY proposal at IN16B has shown that fixed window scans both elastic and inelastic provide information about the dynamics of the citrate molecules in dry powders and of water in wet powders. Now, we wish to investigate rotational and translational diffusion modes for citrate-capped IONPs at 4 relative humidities, corresponding to nominally dry powders (11%), mono- (43 %) and bilayers (68 %), and multiple layers (96 %). From these data, as well as a for D_2O-equilibrated sample, we expect a detailed insight into the complex interfacial ligand dynamics.

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1. Scientific background

Iron oxide nanoparticles (IONPs) are of significant interest in many fields like biomedicine or industrial heterogeneous catalysis, in all of which they feature solid-liquid interfaces. Even though much effort has been put into the characterization of the solid structure of NPs, only little is known about this interface and the diffusion dynamics of the liquid molecules in the interfacial regime. Mamontov et al.[1] and Stack et al.[2] have shown by quasielastic neutron scattering (QENS) on wet powders of TiO_2-, SnO_2- and $BaSO_4$-NPs, that rotational and translational diffusion dynamics of water molecules within the first three water layers are affected by the interface. Organic ligands like citrate are commonly employed to establish long-term colloidal stability and achieve shape-selective synthesis. The dynamics of such organic ligand molecules in both dispersion and nominally dry powders is largely unknown and lacks experimental evidence. Yet, MD simulations have predicted that citrate diffusion on ZnO NPs occurs on the time scale of some tens of picoseconds.[3] With QENS, the interfacial dynamics of water and ligand molecules near the surface of citrate-capped IONPs with different water contents can be investigated.

2. Experiment

Several samples of 7 nm citrate-capped iron oxide nanoparticles (IONPs) were examined, each equilibrated at different humidities (8, 57, 85 and 98 % RH). The samples were prepared to different sample thicknesses depending on the hydrogen content in the samples and sealed in Al cells with indium wire to keep the humidity. In order to disentangle the ligand (citrate) and water dynamics, the 85 % RH sample was equilibrated in both D_2O and H_2O to highlight the ligand diffusion in the D_2O-equilibrated sample. Elastic and inelastic fixed window scans (EFWS and IFWS) were measured at an offset of 3 μeV in a temperature range from 2 K to 380 K. In addition, QENS spectra were measured at different temperatures (temperature range also 2 K to 380 K). Furthermore, a measurement of the vanadium standard for background correction and an empty can measurement were performed.

3. Preliminary results

The data obtained corresponds to the assumptions made previously, thus showing the reproducibility of the results. Figure 1 shows the EFWS between 2 and 380 K of a dry and a wet sample of citrate-capped IONPs.

References

[1] E. Mamontov, L. Vlcek, D. J. Wesolowski, et al., J. Phys. Chem. C 2007, 111, 4328-41

[2] A. G. Stack, J. M. Borreguero, T. R. Prisk, et al., Phys Chem Chem Phys 2016, 18, 28819-28

[3] T. Milek, D. Zahn, Z. Anorg. Allg. Chem. 2016, 642 (16), 902–905

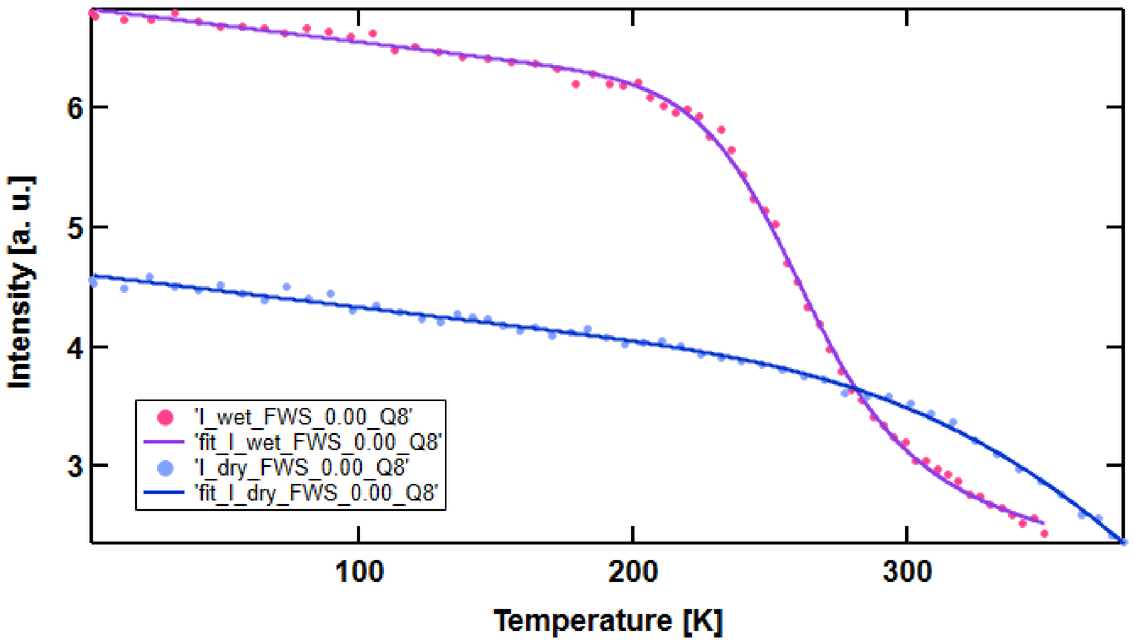

Figure 1: EFWS of two samples dry and wet

As expected, the EFWS on the dry sample shows a loss of intensity with increasing temperature. The EFWS on the wet sample on the other hand shows a much sharper drop from about 220 K onwards to 300 K. This feature is clearly related to the diffusion of water molecules. The activation energy could be determined.

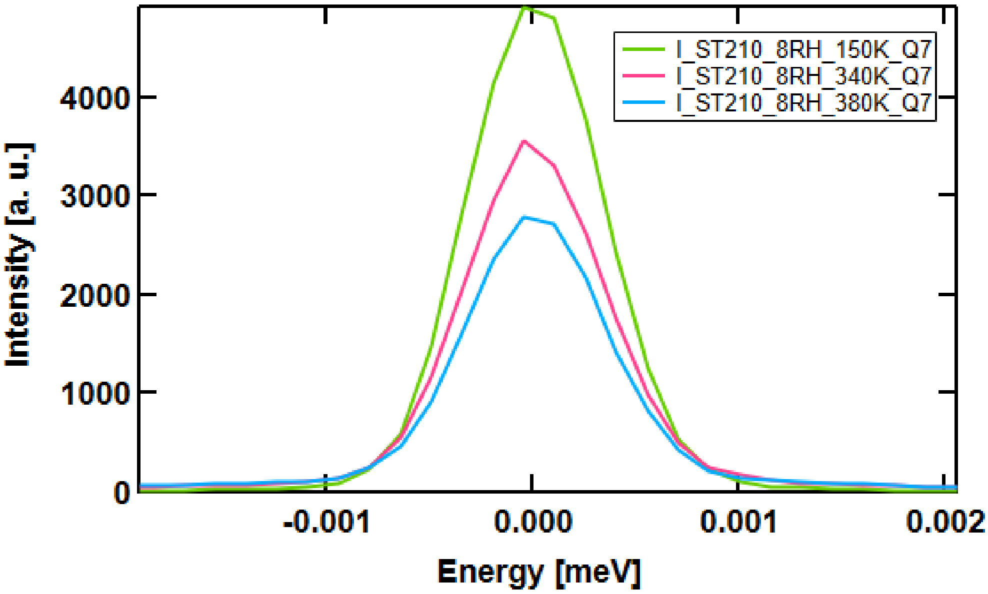

Figure 2: QENS Spectra of a dry sample at three different temperatures 150 K, 340 K and 380 K

Figure 2 shows the QENS spectra of a dry sample at temperatures 150 K, 340 K and 380 K. It can be seen, that the elastic signal decreases and the QENS signal broadens with increasing temperature. The description of the data requires two Lorentzian lines and a gaussian line. The Q-dependence of the QENS signal is being investigated. All results will be compared to the received data of the samples at other humidities. A PhD student for the thesis associated to DFG grant ZO 369/3-1 was recently recruited. The evaluation of the data received is ongoing and will take several months.