Experimental report

12/02/2021

Proposal:	**7-05-500**	**Council:**	10/2018
Title:	Measuring the Force Constant of Semiconductor Nanocrystal Ligands		
Research area:	Materials		

This proposal is a new proposal

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Samples:
Ag2Se
PbS
1,2-Ethanedithiol
1,4-Benzenedithiol
Dodecanethiol

Instrument	Requested days	Allocated days	From	To
IN16B	3	3	14/02/2020	17/02/2020

Abstract:

Understanding of long range thermal transport systems in semiconductor nanocrystals (NC) for energy applications, requires understanding of the inter-nanoparticle vibrations. We have shown that it is possible detect these inter-particle modes using inelastic neutron scattering at the FOCUS beamline (PSI, Switzerland) by tuning the nanoparticle size. In continuation experiments at FOCUS we plan to investigate the role of the NC surface ligands on these inter-particle vibrations. We propose to use neutron backscattering spectroscopy at ILL to determine a force constant for the NC ligands, to quantify their stiffness. Combining the FOCUS and ILL measurements will allow to draw conclusions about the dependence of the interparticle vibrational modes on the stiffness of the ligands used. Furthermore, we will compare these experimental results to our computational model and test strategies for optimizing these modes.

Measuring the Force Constant of Semiconductor Nanocrystal Ligands

Proposal 7-05-500 on In16B

Experimenters: M.Jansen, F.Juranyi, T.Seydel, V.Wood

The purpose of this experiment was to study the elastic properties of organic ligands used to stabilize and functionalize semiconductor nanocrystals. For this purpose we performed Quasi Elastic Neutron Scattering (QENS), Elastic and Inelastic Fixed Window scans (E/IFWS) at IN16B on 3.2 nm diameter PbS NCs. The ligand systems we investigated were 1,2-Ethandithiol, 1,6,-Hexanedithiol, 1,4-Benzenedithiol, as well as the single functionalized 1-Hexanethiol and 1-Dodecanethiol. For each ligand type we measured the ligands when bound to the NC-surface (powder) and the pure ligand itself. For the purpose of clarity all datasets presented in this report are from the 1-Dodecanethiol samples.

EFW scans were performed over a temperature range of 10-300K, both on pure ligands, as well as on NCs coated with the same ligands. In the low temperature regime (<100K) the atomic motion is harmonic, for higher temperatures anharmonic contributions from local motions need to be considered, which can either be done by a generic term or by considering the explicit local motion contributing to the mean square displacement. The according data and fits are shown in Fig.1a. and the resulting mean square displacement is shown in Fig.1b. as a function of temperature. From the low temperature regime we extract the effective spring constant $< k >$. [1] As seen in Fig. 1c the measured spring constants scale proportionally with spring constant calculated via DFT.[2] In Fig 1d. we compare the spring constants of the bound ligands to those of the free ligands and can see that for most ligands the spring constant of the bound ligand state is lower than that of the free ligands.

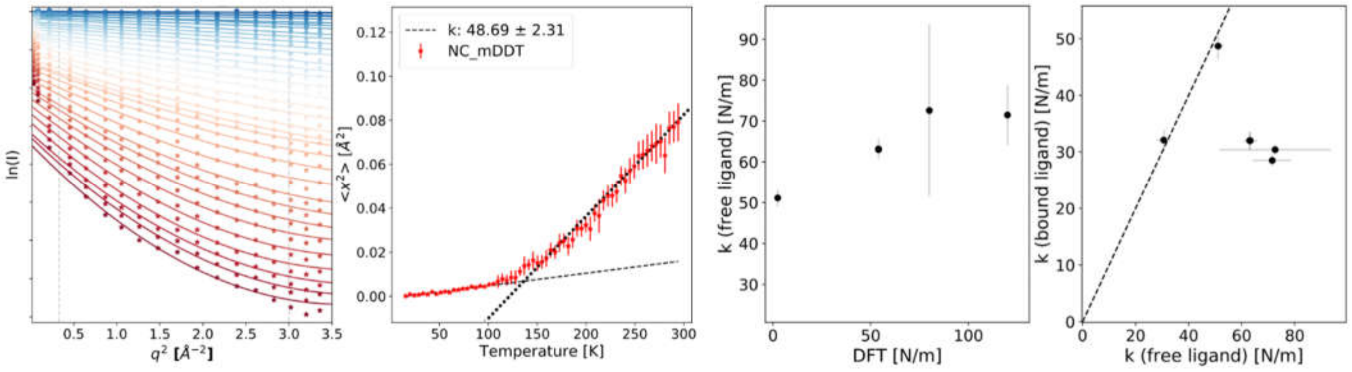

Fig.1 a) Temperature and Q-dependence of the FWS data with fits b) Mean square displacement from the fits in a), with the linear fits used to extract the spring constant. c) simulated spring constants in relation to the measured spring constant of the free ligand. d) free-ligand spring constants vs bound ligand spring constant: the dashed line indicates equal values of free and bound ligand spring constants.

The IFWS scans provide further information about the temperature dependence and the activation energy of the ligand motion. From the lack of q-dependence in the IFWS (as well as from the QENS data presented later) we attribute all motion in the system to localized processes. From the IFWS we further deduce that the ligands can undergo two different types of localized motion. The corresponding data and fits are shown in Fig.2.

For the NC+ligand system we measured full QENS spectra both at 300K for investigating the thiols surface dynamics and at 10 K for obtaining resolution functions to allow for conclusive fitting and modelling of the data. For all measured ligand systems the QENS spectra is phenomenologically well described by two Lorenzians. These are associated with a slower process, fit by a narrow Lorentzian and a faster process at the edge of the instrument range. A representative spectra is shown in Fig.3a. The faster process is also observed in our QENS measurement at the time-of-flight spectra FOCUS at PSI. Utilizing the results from FOCUS, shown in Fig.3b, enables a robust fit even of the process close to the edge of the instrument resolution. We fit across the entire Q-range (Fig.3c) and observe no Q dependent broadening of the quasi-elastic contributions, which is a further indication of the localized nature of the motions.

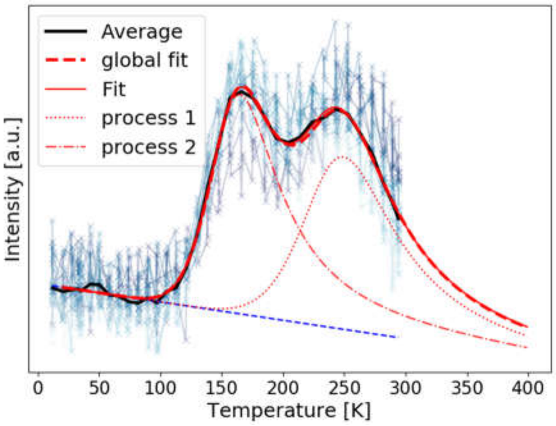

Fig. 2. IFWS temperature dependence for individual q-values (blue), the average over the entire Q-range (black) and the fits (red).

The observation of these two localized processes is consistent across all NC-ligand systems. However, their intensities and linewidths vary with ligand chemistry. The underlying model is based on two possible localized motions, which differ based on the chemical environment of the ligands. One motion allows for a tethered rotation around an axis, whereas the second motion is associated with sterically more hindered ligands. These models are fit to the EISF, as shown in Fig. 4b.

This model goes beyond the few previous literature reports on similar systems, which were limited to coarser energy resolutions.[3], [4] As our measurements are sensitive to a wider range of characteristic time scales we can assess a more complete picture of the ligand behavior on the nanocrystal. A publication with the full model and all insights is currently being prepared.

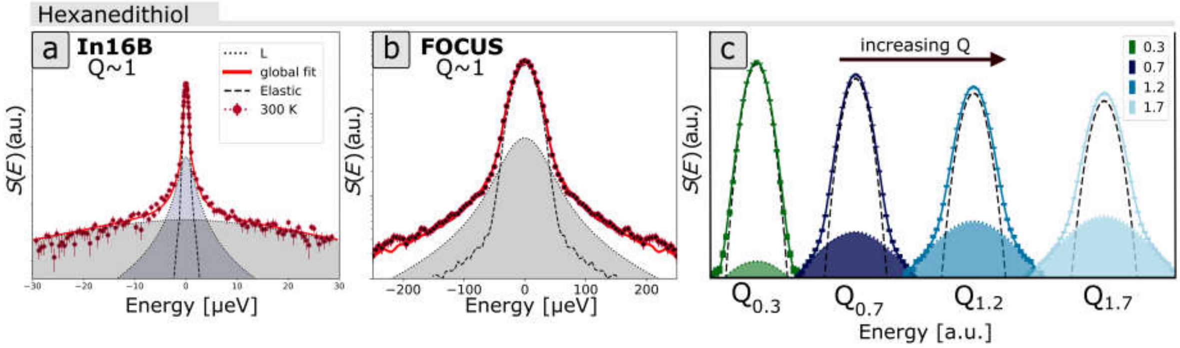

Fig. 3.a QENS spectra from IN16B for Q~1, 300K data is dotted in red, quasi-elastic contributions are shaded in and elastic dashed in black. The best fit is plotted in red. All fits are convoluted with the 10K measurement. b) Same as in a) for data from FOCUS c) Q-dependent fitting with a quasi-elastic contribution of fixed width.

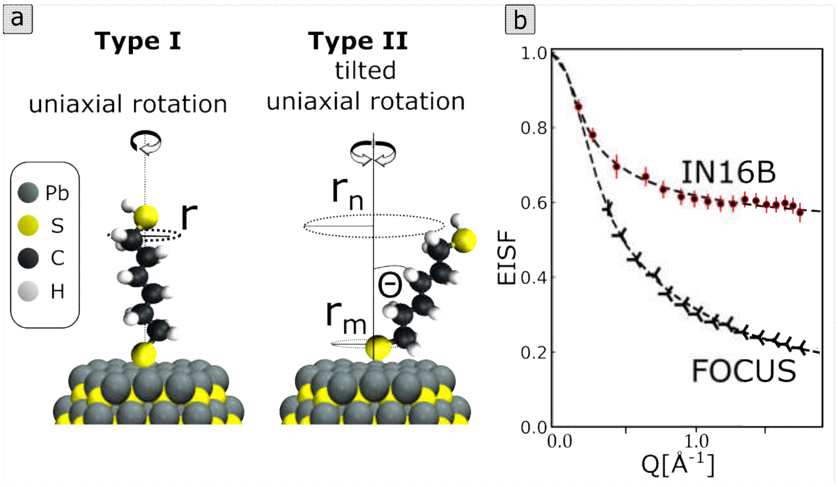

Fig. 4.a Visualization of the possible rotations of the surface bound ligands. Type I rotates around the axis of the ligand backbone, Type II motion includes the rotation of the entire ligand chain around a central axis. b) EISFs of IN16B and FOCUS, fit with the models presented in a)

[1] G. Zaccai, “How soft is a protein? A protein dynamics force constant measured by neutron scattering,” *Science (80-.).*, vol. 288, no. 5471, pp. 1604–1607, 2000.

[2] N. Yazdani *et al.*, “Nanocrystal superlattices as phonon-engineered solids and acoustic metamaterials,” *Nat. Commun.*, vol. 10, no. 1, p. 4236, Dec. 2019.

[3] T. Pradeep, S. Mitra, A. S. Nair, and R. Mukhopadhyay, “Dynamics of Alkyl Chains in Monolayer-Protected Au and Ag Clusters and Silver Thiolates: A Comprehensive Quasielastic Neutron Scattering Investigation,” *J. Phys. Chem. B*, vol. 108, no. 22, pp. 7012–7020, Jun. 2004.

[4] R. Mukhopadhyay, S. Mitra, M. Johnson, V. R. Rajeev Kumar, and T. Pradeep, “Evolution of the alkyl-chain dynamics in monolayer-protected gold clusters,” *Phys. Rev. B*, vol. 75, no. 7, p. 075414, Feb. 2007.