

Experimental report

17/02/2020

Proposal: 6-05-1010

Council: 4/2019

Title: Low temperature proton dynamics of Phosphoric Acid (PA) and PA-water mixtures

Research area: Physics

This proposal is a new proposal

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Experimental team:

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Samples: H₃PO₄
P₂O₅ R x H₂O

Instrument	Requested days	Allocated days	From	To
IN16B	18	3	10/01/2020	13/01/2020

Abstract:

Phosphoric acid (H₃PO₄ or PA) and (P₂O₅-R H₂O; R mol-% water) and related phosphates play an important role in biological systems, as proton conductor in PA fuel cells and PA-doped high-temperature polymer electrolyte fuel cells. A good understanding of the dynamics of phosphoric acids is of great scientific as well as of practical importance. Surprisingly, details of basic properties, as the proton transport mechanism or vitrification have only recently gained high scientific interest and are related to the unique properties of PA's hydrogen bond network. Frustration of the network and fast reorientations of the bonds are related to the imbalance in proton donor and acceptor numbers, which is affected strongly by the addition of water.

We propose to exploit fully IN16B in order to understand the ns-ps dynamics of phosphoric acid and PA/water with focus on the local motions between T_g and T_m. Si111 scans, simultaneous with dielectric scans, will provide an overview over the dynamics in a wide frequency range for three different water concentrations. BATS experiments will provide the detailed spectral shape, Si311 spectra the access to high Q with μ eV energy resolution.

Samples

$P_2O_5 - H_2O$,(or $H_3PO_4-R \cdot H_2O$) mixtures

Sample	R	x	IN16B
S1	1.5	-0.75	fws-c, fws-h
S2	2	-0.5	-
S3	2.5	-0.25	-
S4	3	1	fws-c
S5	4	0.5	fws-c, fws-h, 1 QENS
S6	5	1	fws-c, fws-h, 7 QENS

Six samples with different ratio $R := H_2O:P_2O_5$. or x , defined as the fraction crystalline $H_3PO_4 \cdot x H_2O$, were prepared as sealed batches at the MPI Stuttgart (see table). IN16-type flat Aluminium sample holders were coated with gold on the inside and sealed with Indium wire. The nominal sample thickness was 0.3 mm. All samples were filled and sealed in a glove bag under Argon atmosphere after the relative humidity had decreased to below 2% RH @ $\sim 21^\circ C$ and by continuing Ar-flushing during filling.

Only 4 samples, S6, S5, S4 and S1, could be measured within the time given by fixed window scans and only for S6 a sufficient number of QENS spectra could be recorded (7 temperatures plus the base temperature); in addition 1 QENS spectrum + base temperature were measured for S5 and no further QENS for the other samples.

Due to the crystallisation tendency measuring scans both in cooling and in heating was required, which was possible for S6, S5 and S1, but not for S4. For S1 there was not sufficient time to heat up to temperatures where the maximum in the IFWS can be seen. The measurements carried out during the beam time are summarised in the last column of the above table.

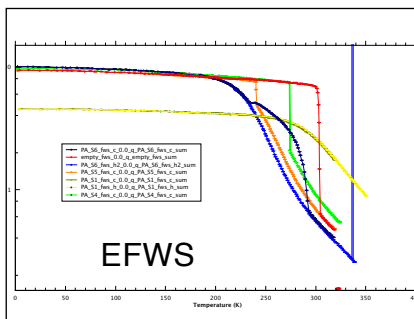


Fig.1a

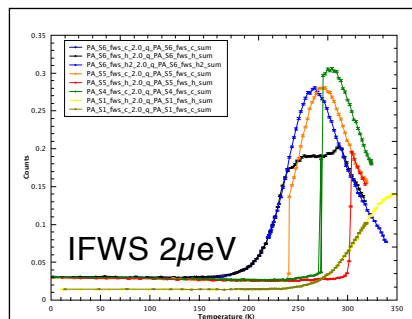


Fig.1b

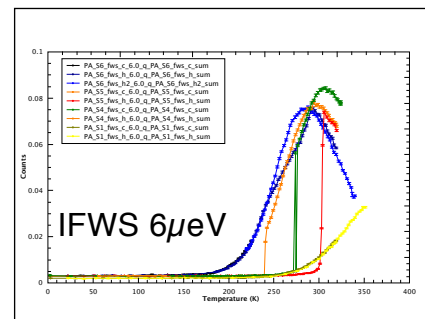


Fig.1c

The following figures give an overview of the Q-averaged ($0.19 \text{ \AA}^{-1} < Q < 1.75 \text{ \AA}^{-1}$) elastic and inelastic fixed window scans (EFWS & IFWS; ramps with 0.5 K/min and 2.5K/min at low temperature) at an energy transfer of $0 \mu eV$ (30 s), $2 \mu eV$ (1 min) and $6 \mu eV$ (2

min). Most samples, S4, S5 and S6, crystallised in heating and S4 and S5 as well in cooling. S1 did not crystallise in the measured temperature range. The IFWS figures indicate clearly that in the investigated temperature-range the time scale of dynamics of S6, S5 and S4 matches well the time range accessible on IN16B. The best match is for PA-S6, therefore QENS spectra were measured in detail on this sample.

Sample 6 - R = 5

S6 did not crystallise in cooling, but it did in the 1st heating scan at ~235 K, followed by melting near T~290K. QENS spectra were then measured in cooling followed by another FWS in a second heating run up to 340 K, where S6 did not crystallise anymore.

Fixed window scans [1]:

Investigating the IFWS temperature scans at individual Q's we find that in the low Q-range there are two peaks visible (at both energy offsets studied 2 μeV and 6 μeV). A low temperature maximum of the IFWS intensity located at T_{max}^l , the location of which seems to be independent of Q. A second peak is observed at slightly higher temperature T_{max}^d which decreases clearly with increasing Q before merging at high Q with the low temperature peak. This is illustrated in Fig.2. Thus for this sample we find both a local and a diffusive process. A detailed evaluation of the Q-dependence and data interpretation is in progress.

QENS - Doppler spectra:

QENS was measured with $\pm 30 \mu\text{eV}$ @ $\pm 75 \text{ mm}$ amplitude and HSNR [2] between 220 K and 340 K for S6 only. Q-summed spectra are shown in Fig3. For S5 we could measure at 280K and a short run at 320K. For all other samples there was not enough time to do QENS runs.

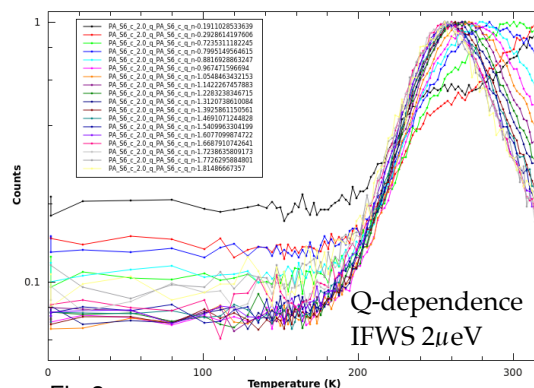


Fig.2

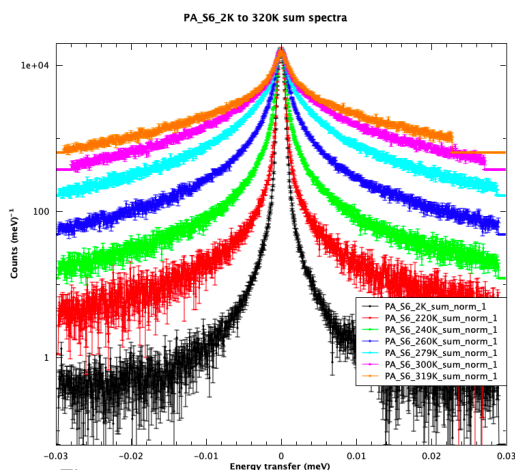


Fig.3

Data evaluation is in progress. A continuation experiment is needed for measuring fws-scans on S2 and S3 (important change in dynamics with respect to S4) as well as for measuring S1 - S4 by QENS at selected temperatures. The change of the dynamics with Q will be evaluated as a function of water content.

[1] B. Frick, J. Combet, and L. van Eijck, Nucl Instrum Meth A 669, 7 (2012).

[2] M. Appel and B. Frick, Rev Sci Instruments 88, 036105 (2017).