Supplemental Information

On the nanosecond proton dynamics in phosphoric acid - benzimidazole and phosphoric acid - water mixtures

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QENS:

Background Correction:

A brief description of the background correction procedure was given in the main paper. Here we add a few additional comments:

From the original IN16B data we have discarded the last two detectors because the experiment was conducted in the early stage of IN16B where the less tall old IN16 analysers were used and therefore the one analyser at the highest Q was completely shadowed by the PST-chopper. Thus the usable Q-range of IN16B in the early time was 0.19 Å⁻¹ < Q < 1.79 Å⁻¹.

For all spectra shown in the figures of this paper the energy channel width was binned in LAMP to a width of 0.3 µeV, however for fitting the data the original channel width was maintained.

An empty Aluminium sample can with and without Teflon was measured for background correction. The 25µm thick Teflon liner, used to protect the aluminium cells, caused by its coherent scattering some uncertainty in data correction. The effect was relatively small but clearly visible at high temperatures when the quasielastic scattering becomes broad and weak. Eventually a sharp elastic intensity was visible, either slightly negative (over-corrected) or too positive (under-corrected) in some detectors of the same run after background subtraction. This appeared in spite of having taken both the Aluminium and Teflon scattering length and absorption in the LAMP correction macro ‘calc_absor_flat’ into account. We
suspect that a slightly unequal Teflon content and/or foil stretching in the different sample holders might be the reason. Therefore we have tried to minimise this effect for each sample by judging from the highest temperature runs with the widest QENS and by trying out different subtraction weights by adding to the empty cans with Teflon liner some empty can runs without Teflon liner. This method has the advantage that strength of the Teflon Bragg contamination could be slightly varied without affecting the flat background arising from other sources. The same weight of subtraction was then used for all temperatures of each sample. We conclude that in nearly all cases this subtraction problem can be considered as minor and does not affect the results from data fitting.

**Data Fitting:**

Data were fitted using the LAMP module ‘str_fit’. Macros written in IGOR Pro 7 were then used to extract and visualize the fit results. In a first step we tried to keep the fit model in LAMP as simple as possible, in order to avoid correlation of fit parameters.

**Model ‘LorBg’:**

This is the most simple fit model used which gave quite reasonable results as described in the paper. A single Lorentzian convoluted with the experimental resolution function in addition to a flat background is used. The flat background is the signature of fast picosecond proton motions seen in the wider energy window of neutron TOF instruments and known from simulation to happen on the sub-ps time-scale.

**Phosphoric Acid (PA), H3PO4:**

At temperatures measured below the melting temperature (185K, 248K, 278K, 290K) the fitted Lorentzian FWHM was much smaller than the resolution (at T=290K a fitted Lorentzian FWHM~ 0.1 – 0.2 µeV). The first measured temperature for which PA did show a significant broadening (0.8 µeV < FWHM < 30 µeV) was T = 339 K (PA339). The most important parameters of the fit are summarized in Fig. SI-QENS_2. It can be seen that the peak intensity of the Lorentzian drops down very fast with Q along with a broadening of the line. There are small oscillations seen in the Q-dependence of the FWHM at high Q, which show up systematically in most fits of PA. The fact that the flat background shows ‘anti-oscillation’ for the same Q-values, indicates that the wider lines and the flat background become correlated.
Individual fits for PA339 in Fig. SI-QENS_3 evidence that the quality of the fit at 339 K is quite good at all Qs, neglecting the subtraction problems near E=0 in some detectors. The fit quality for PA359K is similarly good. At the two highest measured temperatures T = 386 K and T = 423 K the fits become clearly unreliable at high Q-values where the fitted FWHM reaches or even surpasses the instrumental energy transfer range of IN16B. Fig. SI-QENS_4 show similar plots for PA386.

Fig. SI-QENS_1: Fit of PA at T = 339 K showing the corrected data points (red crosses) and the total fit curve (blue line) on the l.h.s. for all measured Q-values between $Q_{\text{min}}=0.1979$ Å$^{-1}$ and $Q_{\text{max}}=1.79$ Å$^{-1}$. The smaller graphs on the r.h.s. from top to bottom are the peak intensity of the single Lorentzian plotted against $Q^2$, the log-log plot of the fitted FWHM versus $Q^2$, the fitted flat background and the Chi² parameter indicating the goodness of the fits.
Fig. SI-QENS 2: Fit curves for the LorBg model for PA at T = 339 K (red: total fit; dashed green: flat background; orange: resolution convoluted Lorentzian).

Fig. SI-QENS 3: Fit curves and parameters for PA at T = 386 K (symbols and lines as before).
Other Simple Fit Models:

Other simple fit models were tried in order to see how stable and reliable the resulting fit parameters are: ‘ElLorBg’, with an additional elastic resolution signal, ‘LorLor’, which only two Lorentzians convoluted with the resolution function and ‘LorLorBg’, where an additional flat background was added. Fig. SI-QENS_6 shows a comparison of the different fit methods for some detectors of PA at T = 336 K. This comparison shows that the simplest model, ‘LorBg’, describes for PA the measured data pretty well, with only a small improvement of the Chi$^2$ factor for most detectors and temperatures. A similar or better fit quality is reached at higher temperatures.
Fig. SI-QENS_5: Comparison of different fit methods for PA at T = 339 K presented in 4 quadrants for four selected $Q$-values ($Q=0.19$ upper left quadrant, 0.58 upper right, 1.07 lower left and 1.73 Å$^{-1}$ lower right quadrant). Each of these $Q$-quadrants contains a quadrant of four different fit types. The fit type is labeled by concatenating its abbreviation to the sample label in the upper left corner of each subfigure (e.g. PA339LorLor indicates the sample, temperature and fit type ‘LorLor’). In the upper right corner of each figure the FWHM of the Lorentzians and the $\text{Chi}^2$ factors are noted (symbols are data points, red lines correspond to the total fit curve and dashed lines to the fit components).

Master plots of fitted FWHM:

As model independent check for $Q$-regions where the width follows a $\text{FWHM} \sim Q^2$ behaviour we plot $\log_{10}(\text{FWHM})$ versus $\log_{10}(Q^2)$. This is shown in Fig. SI-QENS_8 for PA. The dotted horizontal lines indicate the start of the region where the fitted FWHM is either smaller 20% of the instrumental resolution or larger than the instrumental energy window, thus regions where the fitted data have to be taken with extreme care. For example at the lowest temperature the instrumental resolution is clearly not sufficient to detect broadening. At the two highest temperatures (423K and 386K) the fitted FWHM is as wide as the energy window.
of the instrument and there might be additional systematic contributions to the fitted error bars which are not taken into account when only the error bars resulting from the fit program are shown. Furthermore, for such large linewidth there is a strong correlation with the fitted flat background. This can be evidenced for a part of the oscillating FWHM at high Q, where a minimum in the FWHM corresponds to a maximum in the flat background.

The FWHM of PA show at all temperatures above T_m a region where FWHM~Q^2 (dashed line marked slope=1) and turn away from this Q-dependence before leveling off at high Q in a roughly Q-independent linewidth, as would be expected for jump models like (Singwi-Sjölander, Hall-Ross, Chudley-Elliott) for which the high Q region can be interpreted by the FWHM being proportional to the inverse residence time in between fast proton jumps. Clearly, this leveling off is observed even for temperatures for which the fitted FWHM at high Q is in a range considered as reliable. From such type of plots we have determined shift factors for each temperature, which superimpose the data in an optimum way to a master-curve as is shown for PA in Fig. 7 in the manuscript. The nice superposition in all Q-range
suggests that we see the same dynamic process in the investigated spectral and Q-range of IN16B. It furthermore underlines that jump diffusion dynamics is observed because the shape of FWHM(Q) seems to be invariant under scaling.

6PA1BI:

For 6PA1BI spectra at low temperatures 250K, 298K, 318K as well as the following high temperatures were measured: T=336, 356, 374, 393, 412 and 439K. In contrast to PA for 6PA1BI ‘LorBg’ fits for T= 298K and 318K measured astonishingly render already linewidths which clearly surpass the energy resolution at higher Qs. Figures SI-QENS 8 and SI-QENS 9 show the resulting fit parameters for 298K and the single detector fit curves for 318K, respectively. Only at 250K the FWHM is much smaller than the spectrometer resolution (FWHM≈ 0.1 – 0.2 μeV), whereas the fitted FWHM at 318K ranges between 1 and 4.4 μeV for Q > 0.5Å⁻¹. In addition the fitcurves do not describe the experimental lineshapes properly and in consequence chi² is relatively high (Figures SI-QENS 9). We ascribe this to the presence of an additional elastic contribution, though we cannot exclude from these fits that the fast
component, described as a flat background, may have a curvature in the energy window of the spectrometer.

![Graphs showing energy transfer vs. intensity for 6PA1BI at different temperatures](image)

**Fig. SI-QENS 9:** Fit curves for single detectors of 6PA1Bi at T = 318 K (legend, symbols and lines as before).

The parameters and individual detector fits for 6PA1BI at higher temperatures are shown in **Fig. SI-QENS 10** to **Fig. SI-QENS 13**. Even at T=336 K figures **SI-QENS 10** and **SI-QENS 11** evidence that the quality of the fit at 339 K is still modest at all Qs. Mounting further in temperature the fit quality improves. At T=393 K there are only weak systematic deviations left (**SI-QENS 12** and **SI-QENS 13**), but the FWHM also starts to reach the window size at high Q. In spite of the mentioned insufficiencies of the ‘LorBg’ fits we attempt for 6PA1BI like for PA to construct master plots. **Fig. SI-QENS 14** and **SI-QENS 15** show the result for ‘LorBg’ fits. It can also be seen from **Fig. SI-QENS 14** and **SI-QENS 15** that less Q-values follow a Q² behaviour in contrast to PA. If the logarithmic shift factors versus 1000/T (inset) are fit by a straight line at high temperatures only (T >= 374K), then the activation energy for 6PA1BI turns out to be E_{act}~0.21 eV and thus very similar to PA (see main paper).
Fig. SI-QENS 10: Fit curves and parameters for 61PA1BI at $T = 336$ K (symbols and lines as before).

Fig. SI-QENS 11: Fit curves with fit type 'LorBg' for single detectors of 6PA1BI at $T = 336$ K (legend, symbols and lines as before).
Fig. SI-QENS_12: Fit curves and parameters for 61PA1BI at T = 393 K (symbols and lines as before).

Fig. SI-QENS_13: Fit curves with fit type 'LorBg' for single detectors of 6PA1BI at T = 393 K (legend, symbols and lines as before).
Fig. SI-QENS 14: Log-log plot of FWHM versus log($Q^2$) for 6PA1BI resulting from fits with one Lorentzian and a flat background (‘LorBg’) at several temperatures.

Fig. SI-QENS 15: Log-log master plot of FWHM versus log($Q^2$) for 6PA1BI by applying a T-dependent shift factor for superimposing the curves. The FWHM result from fits of type ‘LorBg’. The inset shows the T-shift factors.
3PA1BI:

For 3PA1BI spectra were measured at the same low and high temperatures as for 6PA1BI and were fitted with ‘LorBg’ type fits. In contrast to 6PA1BI the sample with lower PA content, 3PA1BI, does not show as much QENS which exceeds the energy resolution at T= 298K and 318K. Figure SI-QENS_16 shows the resulting fit parameters for 3PA1BI at T=336K and figure SI-QENS_17 the single detector fit curves for 318K. Single detector fit curves for 356K and 393K follow in figures SI-QENS_18 and SI-QENS_19. For T=318K the fitted FWHM stays below FWHM~ 0.6 µeV at all Q-values and even at 336K the maximum FWHM fitted reached only 1.6µeV. At higher temperatures where the fitted FWHM exceeds clearly the resolution, as for T = 356 and 374K and even for 393K we observe again that the fit-curves do not describe the experimental line-shapes properly and that \( \chi^2 \) is relatively high (Figures SI-QENS_18). We ascribe this to the presence of even stronger additional elastic contributions or a change in line shape, though again we cannot exclude from these fits that the fast component, described as a flat background, has a curvature in the energy window of the spectrometer.

Fig. SI-QENS_16: Fit curves and parameters for 61PA1BI at T = 393 K (symbols and lines as before).
Fig. SI-QENS_17: Fit curves with fit type 'LorBg' for single detectors of 3PA1BI at $T = 318$ K.

Fig. SI-QENS_18: Fit curves with fit type 'LorBg' for single detectors of 3PA1BI at $T = 356$ K.
Fig. SI-QENS_19: Fit curves with fit type 'LorBg' for single detectors of 3PA1BI at T = 393 K.

Fig. SI-QENS_20: Log-log plot of FWHM versus log(Q^2) for 3PA1BI resulting from fits with one Lorentzian and a flat background ('LorBg') at several temperatures.
Fig. SI-QENS 21: Log-log ‘master plot’ of FWHM versus log($Q^2$) for 3PA1Bl by applying a T-dependent shift factor for superimposing the curves calculated from the two first detectors. At high Q data do not superimpose. The FWHM result from fits of type ‘LorBg’. The inset shows the T-shift factors fitted for the 4 highest temperatures.

Fig. SI-QENS 22: Log-log master plot of FWHM versus log($Q^2$) for 6PA1Bl by applying a T-dependent shift factor for superimposing the curves calculated from average over all detectors. The FWHM result from fits of type ‘LorBg’. The inset shows the T-shift factors and the $E_{act}$-fit from the last figure was not modified and the 3 highest temperatures are consistent with the same activation energy.
**6PA1bisBI:**

For 6PA1bisBI spectra we could measure the temperatures $T = 248, 284, 327, 362, 379, 394$ and 430K, which were fitted again first with ‘LorBg’ type fits. Spectra at $T=284$K do not show much QENS with the Lorentzian FWHM not exceeding 0.5µeV. At higher temperatures the fitted FWHM exceeds clearly the resolution, at $T=327$K (Figure **SI-QENS_23**) a maximum fitted FWHM is 3.4 µeV and for $T = 362, 379K$ and for 394K we observe again that the ‘LorBg’ fits do not describe the experimental lineshapes properly and that chi$^2$ is relatively high (**Figures SI-QENS_23 - SI-QENS_26**). We ascribe this to the presence of even stronger additional elastic contributions or a change in line shape, though again we can not exclude from these fits that the fast component, described as a flat background, has a curvature in the energy window of the spectrometer.

![Fig. SI-QENS_23: Fit curves with fit type ‘LorBg’ for single detectors of 6PA1bisBI at $T = 327$ K.](image-url)
Fig. SI-QENS24: Fit curves with fit type 'LorBg' for single detectors of 6PA1bisBl at $T = 362$ K.

Fig. SI-QENS25: Fit curves with fit type 'LorBg' for single detectors of 6PA1bisBl at $T = 379$ K.
Fig. SI-QENS26: Fit curves with fit type 'LorBg' for single detectors of 6PA1bisBI at $T = 394$ K.

Fig. SI-QENS27: Fit curves with fit type 'LorBg' for single detectors of 6PA1bisBI at $T = 362$ K.
Fig. SI-QENS_28: Log-log plot of FWHM versus log($Q^2$) for 6PA1bisBI resulting from fits with one Lorentzian and a flat background ('LorBg') at several temperatures.

Besides at low $T$ all $Q$-data superimpose. The FWHM result from fits of type 'LorBg'. The inset shows the $T$-shift factors fitted for the 4 highest temperatures.

Fig. SI-QENS_29: Log-log 'master plot' of FWHM versus log($Q^2$) for 6PA1bisBI by applying a $T$-dependent shift factor calculated from the two first detectors. The FWHM result from fits of type 'LorBg'.
Activation energies:

In the following we try to get a realistic estimate for the errors of the activation energies extracted from ‘LorBg’-fits. In the chapters before the activation energies were determined either from fitting the shift factors in the low Q-range and the standard deviation resulted from this fit or from ~DQ2 fits in the low Q range. The corresponding fit error bars seem somewhat low and depend on the Q- and temperature range chosen for scaling the FWHM data and they do not take into account systematic errors. Here we try to find a better error estimate from temperature scaling of single Q FWHM-values, i.e. for FWHM(T,Qi). For each Qi we calculate the optimum T-shift factors s(Tj,Qi) which scale to a single point FWHM*(Tref,Qi). For the temperature dependence of s(Tj,Qi) we assume an Arrhenius behavior and fit a Q-dependent activation energy Eact(Qi).

Fig. SI-QENS_30: Activation energies extracted from scaling the T-dependence of the FWHM at each Q-value. Data points are fits to an Arrhenius temperature dependence of the shift factors at each Q and in the temperature range given in the legend. Error bars correspond to their fit-errors. The final activation energy and its legend correspond to the average over all Q-values.
These Q-dependent activation energies are shown in Fig.SI-QENS30 a) – c) for all investigated samples. A perfect master-curve, i.e. perfect Q-independent superposition would show up as a horizontal straight line. For estimating the error bar we limit us then to a Q- and T-range for which the QENS signals are out of the resolution and still well within the energy window of IN16B and the chosen reference temperature $T_{\text{ref}}$ fulfills the same criteria. These values are shown in the legend of each figure.

From the procedure described in context with Fig.SI-QENS30 we deduce the following activation energies and error bars: $\text{PA}: E_{\text{act}} = 0.21 \pm 0.03 \text{ eV}$, $\text{6PA1BI}: E_{\text{act}} = 0.21 \pm 0.05 \text{ eV}$, $\text{3PA1BI}: E_{\text{act}} = 0.29 \pm 0.03 \text{ eV}$ and $\text{6PA1bisBI}: E_{\text{act}} = 0.23 \pm 0.01 \text{ eV}$. We conclude that the activation energies determined for PA and 6PA1BI, the mixture with high PA content, are about the same, whereas the other two samples show a higher activation energy. The bisBI sample with high PA content is closest in activation energy to PA, but the sample with high BI content, 3PA1BI is clearly off. We may add as a critical comment that the fit quality of the LorBg fits is not taken into account in this estimation.

**Fits to HWHM versus Q data**

In the main text a selection of fit models for the Q dependence of HWHM for the different samples is discussed. In the following the all DQ^2 fits are shown through which diffusion coefficients in fig. 11 in the main text have been obtained. Additionally we show the HR and SS model fits for all samples and temperatures.

The diffusion length on the nanosecond scale calculated with the Smolukowski-Einstein relation from the diffusion coefficient $D$ and time $\tau$ of the HR fit is shown in figure SI-QENS 35. We speculate that this length scale does not correspond to an individual jump length, but rather to a diffusion length on the nanosecond scale, as individual transfer events occur already on the picosecond scale. We plan to investigate this question again when evaluating additional neutron data taken on a ps-time scale. With free fit parameters, i.e., not fixing D to values obtained through PFG-NMR as in previous works (see main text), no clear trends in temperature dependence can be observed. Scattering is rather large due to the uncertainty in fitting $\tau$. We feel that by itself there is at this moment insufficient additional information in this length scale.
Fig. SI-QENS_30 HWHM (LorBg) versus Q for PA at different temperatures $D \sim Q^2$ fit and included points are shown in orange, HR fit in red, and SS fit in black.
**Fig. SI-QENS. 32** HWHM (LorBg) versus Q for 6PA1Bl at different temperatures $D \sim Q^2$ fit and included points are shown in orange, HR fit in red, and SS fit in black.
Fig. SI-QENS_33. HWHM (LorBg) versus Q for 3PA1Bl at different temperatures $D \propto Q^2$ fit and included points are shown in orange, HR fit in red, and SS fit in black.
Fig. SI-QENS_34. HWHM (LorBg) versus Q for 6PA1bisBl at different temperatures $D^\sim Q^2$ fit and included points are shown in orange, HR fit in red, and SS fit in black.
NMR measurements and evaluation

$^1$H relaxation times have been recorded at a magnetic field strength corresponding to 400 MHz proton resonance frequency using an inversion recovery sequence. Measurements have been performed in the temperature range $T = -30$ to 160 °C (Bruker VTU) with sufficient waiting time for temperature equilibration (~30 min) and were reproducible in heating and cooling run. No deviations from a single exponential recovery of the nuclear magnetization could be seen (See Fig S1 for an example fit). The evaluation was conducted assuming dominating $^1$H - $^1$H dipol-dipol relaxation (see Supplemental Information of Aihara et al. for an excellent and comprehensive discussion of relaxation routes in $\text{H}_3\text{PO}_4$).
Fig 1. F1=|f1|+exp(-T1)
Region 1 from 0.317 to -1.147 ppm
T1=826.99999999999999 ms

**1H NMR inversion recovery measurement for neat H3PO4 at T = 335 K**

$^{17}$O relaxation times for H3PO4 and H2O in H3PO4/H2O mixtures have been recorded at two different magnetic field strength corresponding to 400 MHz proton resonance and 300 MHz proton resonance using an inversion recovery sequence T > 120°C. Activation energies have been obtained from the generally low relaxation rates (see fig2 S for example).
Fig. NMR-S2. Arrhenius plot of $^{17}$O $T_1$ relaxation rates at $\lambda = 4.58$ recorded at 9.6 T.