Supplementary Information:

Proton dynamics in molecular solvent clusters as an indicator for hydrogen bond network strength in confined geometries

Clara-Magdalena Saak[1], Clemens Richter[2], Isaak Unger[1], Melanie Mucke[1], Christophe Nicolas[3], Uwe Hergenhahn[*2,4], Carl Caleman[1,5], Marko Huttula[6], Minna Patanen[6], and Olle Björneholm[1]

[1]Department for Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden
[2]Leibniz Institute of Surface Engineering (IOM), Permoserstr. 15, 04318 Leipzig, Germany
[3]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192, Gif-sur-Yvette, Cedex, France
[4]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany
[5]Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron, Notkestr. 85, 22607 Hamburg, Germany
[6]Nano and Molecular Systems Research Unit, Faculty of Science, P.O.Box 3000, 90014 University of Oulu, Finland

1 Error Determination of Relative Isotope Effect

To capture the uncertainty of the difference traces that describe the PTM-CS effect, as determinded by the absolute value of the area under the difference trace, the following analysis is performed: First, the fit function is subtracted from the data set to yield the residual. The residual of the fit is then projected onto the y-axis to give the spread of the residual around baseline. This projection of the residual has the shape of a probability distribution around zero, and we refer to it as the "noise-function" below. The noise-functions of the experimental measurements presented in the main text are shown in 1. The noise-function is then fitted using a Gaussian distribution to obtain a standard deviation σ. The standard deviation σ of the noise-function is then used to define an upper and lower bound around the central fit that was used to determine the area of the difference trace. The upper and lower bound of the area, as well as the centre fit, can be seen in Figure 2.
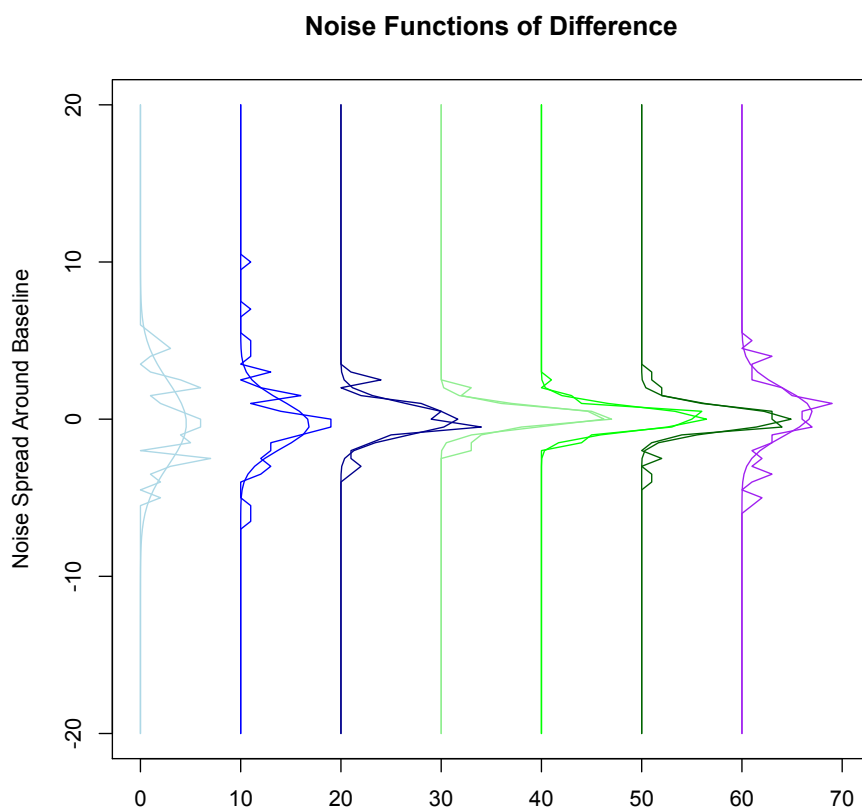
To guide the upper and lower bounds reasonably smoothly to 0 the offset that is added/subtracted to the data points of values less than sigma was scaled by the distance of the value from zero. The upper and lower bounds are then used to calculate the upper and lower limits of the area, within $1\,\sigma$ of the difference trace's noise-function.

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[*]Also at: Max Planck Institute for Plasma Physics, 17491 Greifswald, Germany

Supplementary Table 1: Summary of experimental conditions used in this work.

	Backing Pressure [bar]	Reservoir Temperature [°C]	Nozzle Temperature [°C]	Backing/Carrier Gas -
H₂O small	3	50	61	N₂
H₂O large	3	50	23	N₂
D₂O small	3	50	60	N₂
D₂O large	3	50	23	N₂
MeOH small	2.2	50	60	N₂
MeOH large	2.5	23	48.5	N₂
d4-MeOD small	3.25	70	50	N₂
d4-MeOD large	2.55	40	50	N₂
DME	-	-	15	He
d6-DME	-	-	15	He

Supplementary Figure 1: Error funktions of the difference traces. From left to right: small water clusters, large water clusters, bulk liquid water, small methanol clusters, large methanol clusters, bulk liquid methanol, dimethyl ether clusters
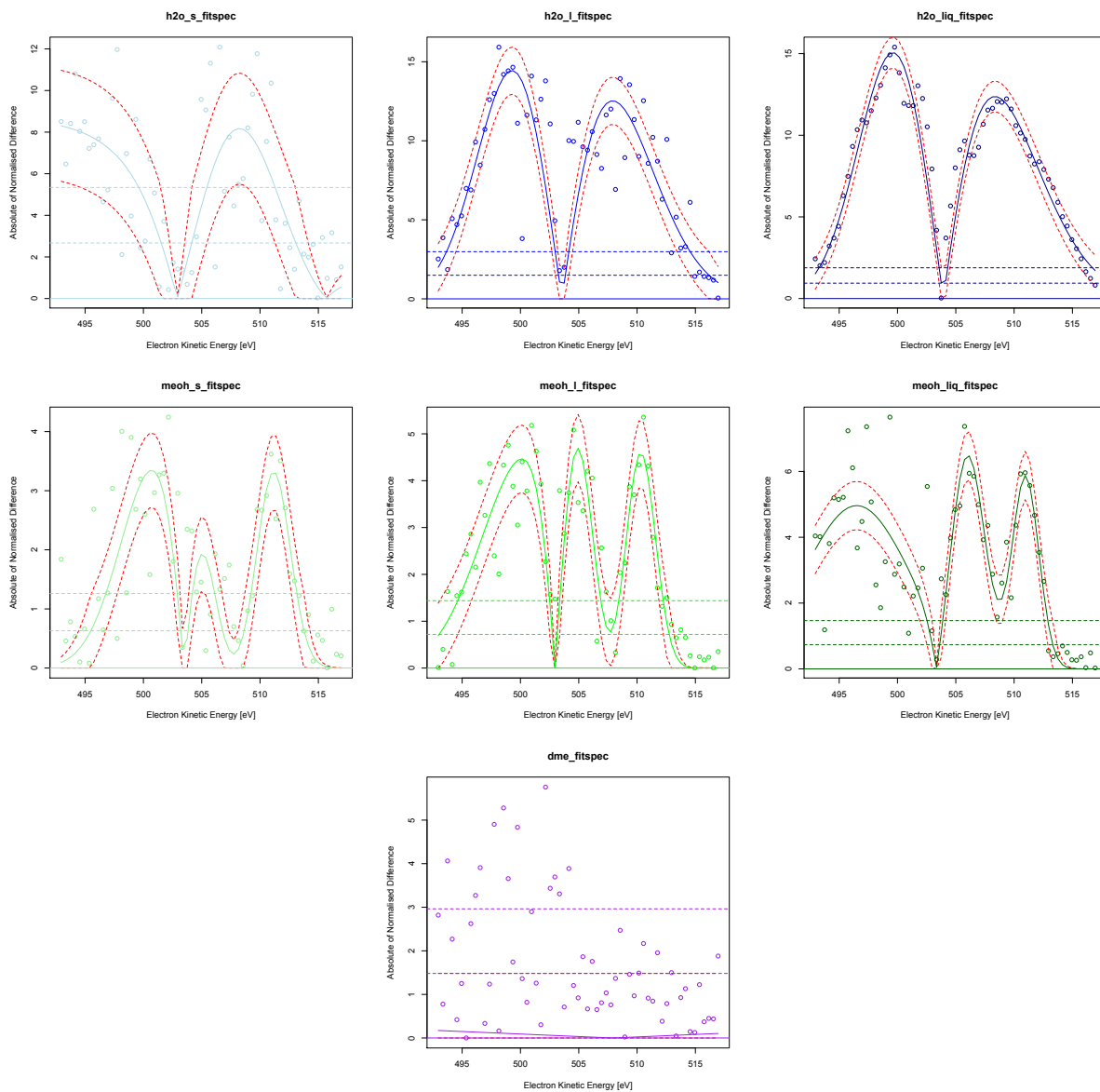
Supplementary Figure 2: Error analysis on the difference traces. The individual panels show the absolute of the difference traces of the individual data-sets. The solid center line corresponds to an "area-fit" of the difference trace. The dashed horizontal lines indicate one and two σ of the noise function. These noise functions are shown in Figure 1 and correspond to the spread of the noise that remains once the area-fit is subtracted from the data-set. The red dashed traces determine the upper and lower bounds of the "area-fit" within one σ.