

## Supplement „Hydrogen bond dynamics of superheated water and methanol by ultrafast IR-pump and EUV-photoelectron probe spectroscopy”

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### Statistics of aggregate formation in the molecular dynamics simulations.

The results of the molecular dynamics simulations may depend on the number of trajectories analysed to reproduce the ensemble average observed in the experiment. The most sensible result in this respect should be the formation of hot water aggregates since this is a spontaneous process and the size distribution may be brought. Therefore, we analysed the hot water aggregate distribution for a different number of trajectories. The following three figures show the aggregate distribution of water at 775 K taken from 8 (4 trajectories with two sides each), 14 and 26 phase evolutions (the same as in Figure 7D of the manuscript). As can be seen the distribution of small aggregates differ only slightly between 14 and 26 phase evolutions although the number of independent simulations has been doubled.

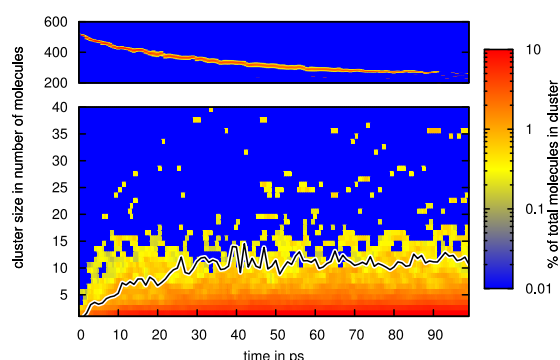


Figure 1: Aggregate size distribution from 8 phase evolutions.

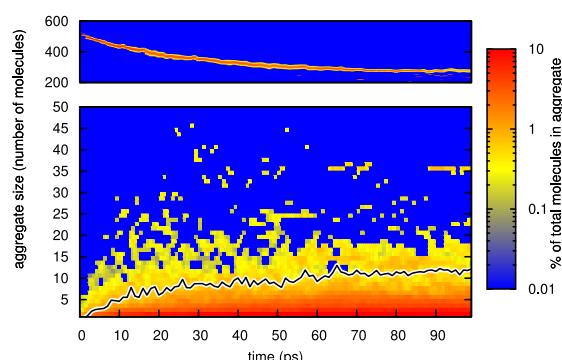


Figure 2: Aggregate size distribution from 14 phase evolutions.

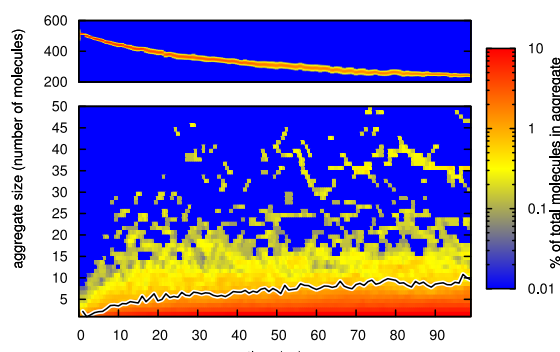


Figure 3: Aggregate size distribution from 26 phase evolutions.

## Molecular Dynamics simulations of methanol at 500K.

The experimental uncertainty of the methanol temperature let us also analyse the phase evolution of methanol at 500K, significantly below the 650 K reported in the manuscript. The results for the hydrogen bond dynamics and the formation of aggregates are shown below. As can be seen the cluster formation is also present at this temperature although not so pronounced and the hydrogen bonds are preserved as discussed in the Results section of the manuscript.

