Supporting Information: Proton Conductivity in Hydrogen Phosphate/Sulfates from a Coupled Molecular Dynamics/Lattice Monte Carlo (cMD/LMC) Approach

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Supporting Information

Convergence Behavior

The full numerical values of the diffusion coefficient with respect to the simulated AIMD length are shown in table 1. The diffusion coefficients obtained from the cMD/LMC approach only differ by a factor of two for variations of the underlying AIMD trajectory length. An excellent agreement up to a factor of two between diffusion coefficients obtained from AIMD and cMD/LMC approach can be reported for trajectory lengths larger than 30 ps. As expected, for simulated times in the range of 30 ps the AIMD diffusion coefficients strongly deviate from their corresponding values for longer simulations.

So we can state that the cMD/LMC approach enables us to estimate the diffusion coefficient from a very short AIMD simulation. A 30 ps AIMD trajectory is sufficient to decide if a compound shows a high proton conductivity or not.

Table 1: Diffusion Coefficients [Å^2/ps] from different compounds with respect to different AIMD trajectory lengths.

	CsH_2PO_4 cubic (HTP) 510K	CsH_2PO_4 monoclinic (LTP) 490K	CsH_2PO_4 cubic (HTP) 610K	$CsHSO_4$ tetragonal (HTP) 420 K
	30 ps underlying AIMD tajectory			
D_k cMD/LMC	$(4.9 \pm 1.0) \cdot 10^{-3}$	~ 0.0 [a]	$(1.1 \pm 0.2) \cdot 10^{-2}$	$(2.0 \pm 0.5) \cdot 10^{-3}$
D_k AIMD	$(2.0 \pm 0.6) \cdot 10^{-2}$	~ 0.0 [a]	$(1.0 \pm 0.2) \cdot 10^{-2}$	$(5.7 \pm 4.1) \cdot 10^{-3}$
	60 ps underlying AIMD tajectory			
D_k cMD/LMC	$(5.9 \pm 1.0) \cdot 10^{-3}$	~ 0.0 [a]	$(2.1 \pm 0.2) \cdot 10^{-2}$	$(2.0 \pm 0.5) \cdot 10^{-3}$
D_k AIMD	$(8.3 \pm 1.5) \cdot 10^{-3}$	~ 0.0 [a]	$(2.0 \pm 0.3) \cdot 10^{-2}$	$(1.8 \pm 1.5) \cdot 10^{-3}$
	120 ps underlying AIMD tajectory			
D_k cMD/LMC	$(5.4 \pm 1.0) \cdot 10^{-3}$	~ 0.0 [a]	$(2.6 \pm 0.2) \cdot 10^{-2}$	$(2.6 \pm 0.5) \cdot 10^{-3}$
D_k AIMD	$(2.7 \pm 0.4) \cdot 10^{-3}$	~ 0.0 [a]	$(1.8 \pm 0.1) \cdot 10^{-2}$	$(0.7 \pm 1.0) \cdot 10^{-3}$
experimental D_k	0.5 - $6.5 \cdot 10^{-3}$ [b] 2.9 - $25 \cdot 10^{-3}$ [d]	~ 0.0 [b]	$\sim 5.5 \cdot 10^{-2}$ [c] (560 K)	$\sim 1 \cdot 10^{-3}$ [c]

[a] D_k very small ($\leq 3 \cdot 10^{-5}$) and error larger than the value itself

[b] Baranov, Khiznichenko, Shuvalov, *Ferroelectrics*, 100, **1989**,135-141.

[c] Belushkin, Carlile, Shuvalov, *J. Phys.: Condens. Matter*, 4, 2, **1992**, 389-398.

[d] Ishikawa, Maekawa, Yamamura, Kawakita, Shibata,Kawai, *Solid State Ionics*, **2008**, 179, 2345-2349.

Jump Rate of CsH_2PO_4 and $CsHSO_4$

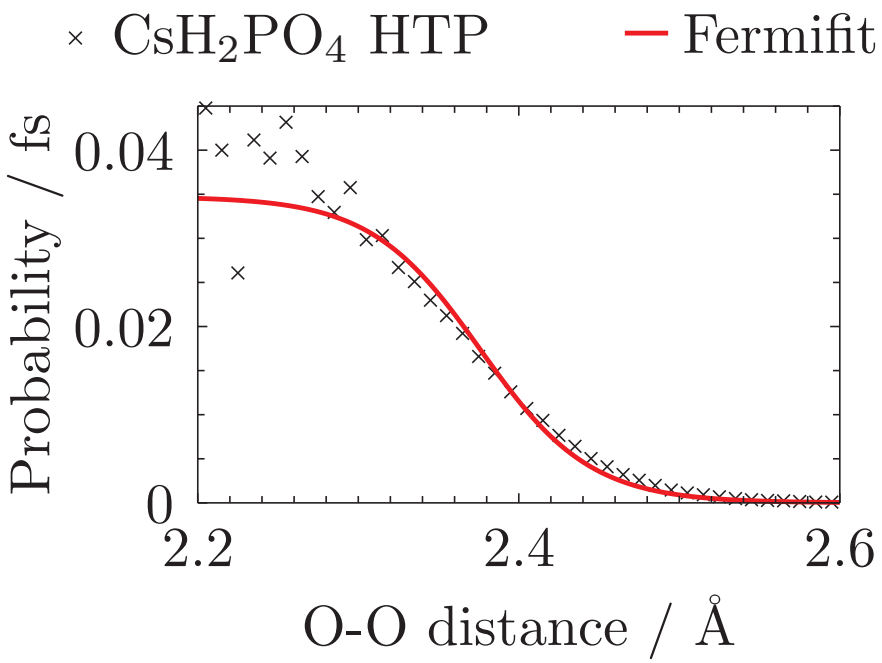
The distance dependent jump rates obtained from the AIMD and the resulting Fermi fit function are depicted in figure 1.

From this figure it becomes clear that the magnitude of the jump rate of $CsHSO_4$ is two orders decreased compared to CsH_2PO_4. The Fermi fit was done according to:

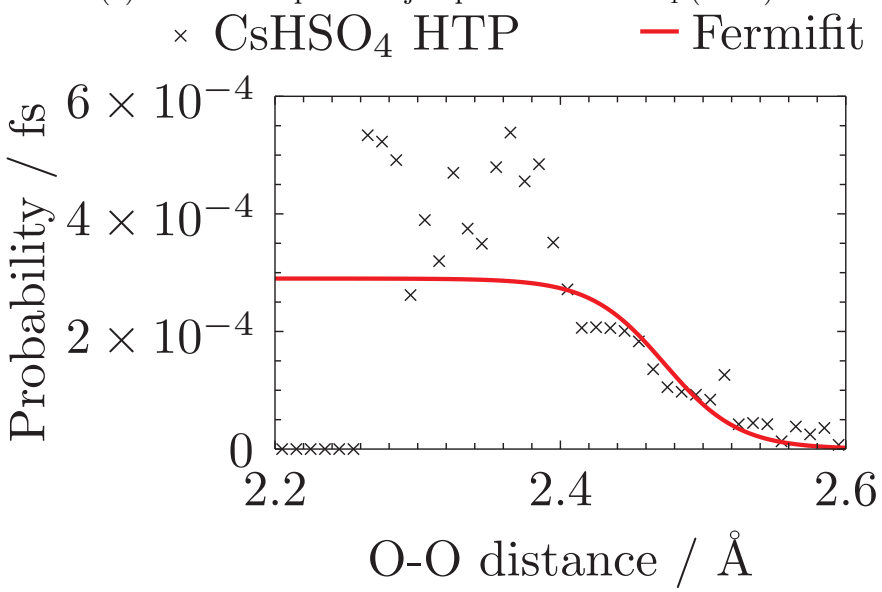
$$\omega(d) = \frac{a}{1 + \exp(\frac{d-b}{c})} \tag{1}$$

Thermostat Coupling and Jump Rate

The jump rates of CsH_2PO_4 (HTP) obtained from AIMDs with two different time constants of the thermostat (100 fs and 1000 fs) are depicted in figure 2. A ten fold increased time constants of the thermostat, corresponding to a drastically reduced coupling of the thermostat, does not significantly alter the jump rate. So we conclude a minor influence of the coupling strength of the thermostat on the proton transfer rates.



(a) Distance dependent jump rate of $CsHSO_4$ (HTP).



(b) Distance dependent jump rate of CsH_2PO_4 (HTP).

Figure 1: Comparison of distance dependent jump rates. The jump rates differs by a factor of 100.

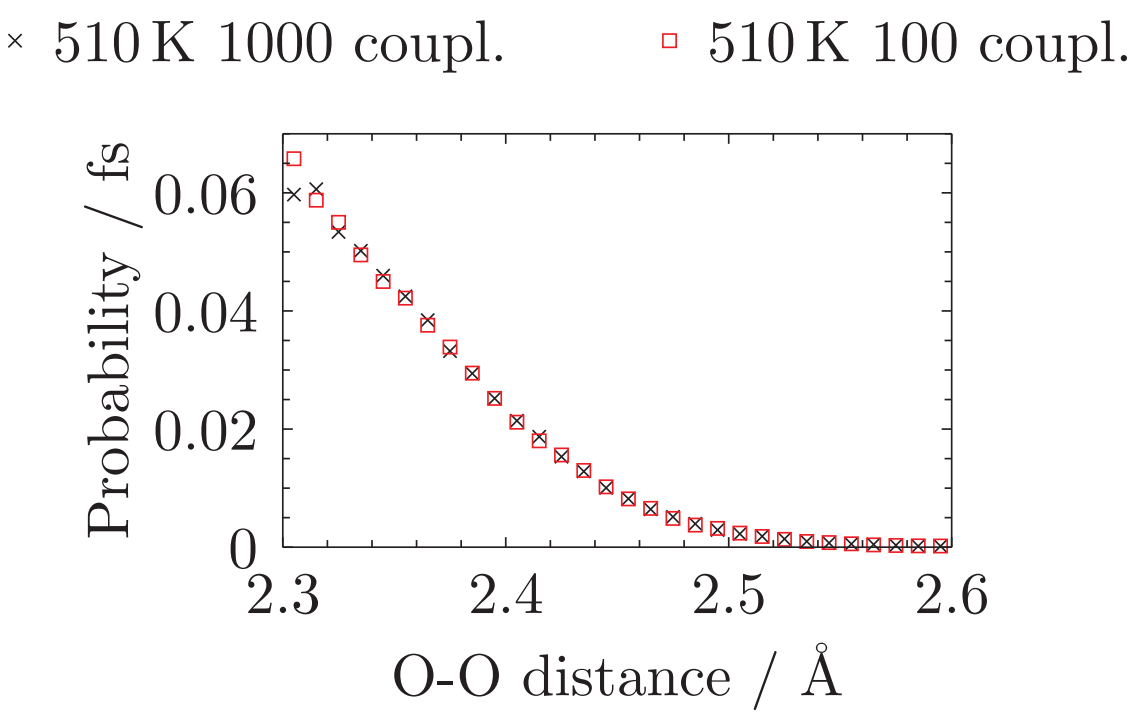


Figure 2: Comparison of the jump rates of CsH_2PO_4 (HTP) obtained from AIMDs with two different time constants of the thermostat (100 fs and 1000 fs).