Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Effect of anion reorientation on proton mobility in the solid acids family CsH_yXO_4 (X = S, P, Se, y = 1, 2) from ab initio molecular dynamics simulations

Christian Dreßler[1] and Daniel Sebastiani*[1]

[1] *Institute of Chemistry, Martin-Luther-University Halle-Wittenberg, Von-Danckelmann-Platz 4, 06120 Halle (Saale)*

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*daniel.sebastiani@chemie.uni-halle.de

1 Derivation of the equation for extrapolation of experimental diffusion coefficients at 500 K for $CsHSO_4$ and $CsHSeO_4$

A linear correlation between the logarithm of the diffusion coefficient and the inverse temperature is immediately apparent from Figure 3 of [Blinc, Dolinsek, Lahajnar, Zupancic, Shuvalov, Baranov, *phys. stat. sol. (b)*, **1984**, 123: K83-K87]. Thus, we obtained the following equations for the calculation of the diffusion coefficient D with respect to different temperatures T by careful linear parametrization of the curves shown in Figure 3 reported by Blinc et al.:

$$\log(D) = m \cdot \frac{1000}{T} + n \tag{1}$$

For $CsHSO_4$, we obtain m = -4.36 and n = 10.37. For $CsHSeO_4$, we obtain m = -4.00 and n = 10.25.

2 Intermolecular hydrogen-oxygen RDFs

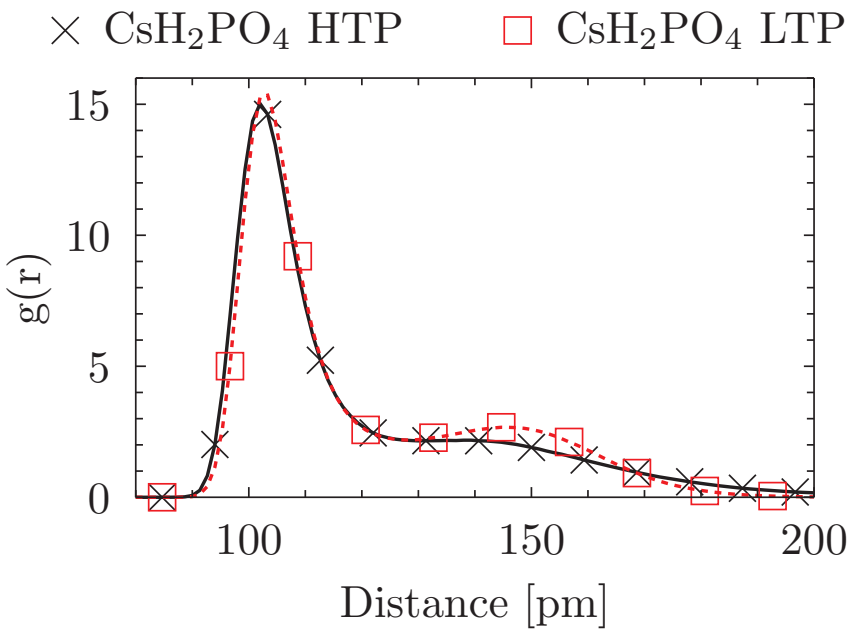


Figure 1: RDF of the intermolecular oxygen-hydrogen distances for the solid acid CsH_2PO_4.

The intermolecular hydrogen-oxygen RDFs for the solid acids are depicted in Figures 1 - 3. The RDFs show no significant difference for the comparison of the HTP and LTP of a given compound.

$CsHSO_4$ and $CsHSeO_4$ show almost the same distribution of the H-O distances, whereas the RDF of CsH_2PO_4 is significantly changed. For CsH_2PO_4 smaller O-O distances can be observed, indicating again shorter and stronger hydrogen bonds.

In summary, there are no (significant) differences between the oxygen-oxygen and oxygen-hydrogen RDFs of the HTPs and LTPs. HTPs and LTPs form hydrogen bonds in a similar amount and strength.

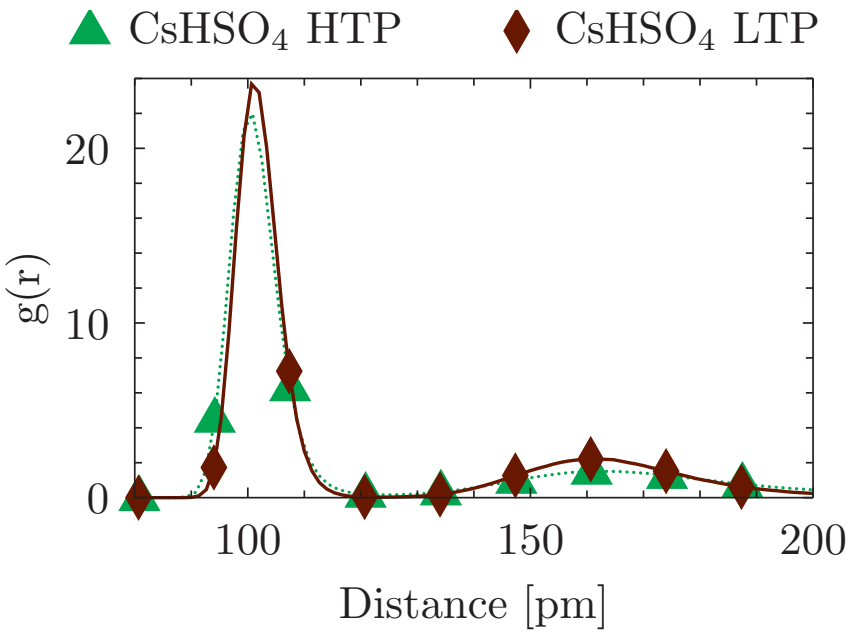


Figure 2: RDF of the intermolecular oxygen-hydrogen distances for the solid acid $CsHSO_4$.

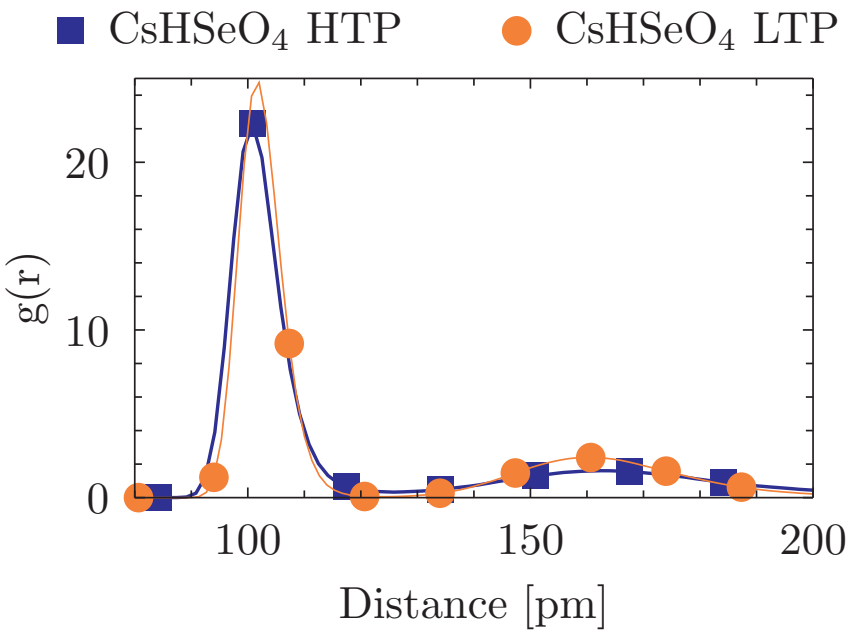
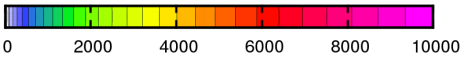
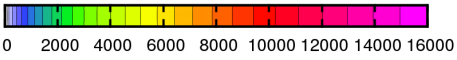


Figure 3: RDF of the intermolecular oxygen-hydrogen distances for the solid acid $CsHSeO_4$.

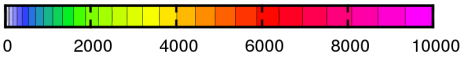
3 Distinction between proton conductors and insulators: Combined Distribution Functions (CDF)



(a) Color bar of the CDF of the HTP of CsH_2PO_4.



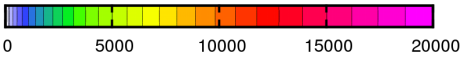
(b) Color bar of the CDF of the LTP of CsH_2PO_4.



(c) Color bar of the CDF of the HTP of $CsHSO_4$

(d) Color bar of the CDF of the LTP of $CsHSO_4$

(e) Color bar of the CDF of the HTP of $CsHSeO_4$



(f) Color bar of the CDF of the LTP of $CsHSeO_4$.

Figure 4: Color bars associated with the Combined Distribution Function (CDF) of the HTPs and LTPs of CsH_2PO_4, $CsHSeO_4$ and $CsHSO_4$ from the main article.