Mechanism of Proton Conduction in Solid-State Protonic Conductors: Method and Results from Investigations by QENS Techniques

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The proton conduction mechanism in $M_3H(XO_4)_2$ crystals has been employed as an example for demonstrating, how such a mechanism can be broken up into a number of different types of proton motion starting with internal and lattice vibrations at short times of the order of 10^{-13} s and ultimately leading to H^+-diffusion on the 10^{-9} s to 10^{-8} s time-scale as required for proton conductivity. The central process is the alternation between formation and rupture of H-bonds within the H-bonding network of the protonic conductor [1] (see Table 1).

Table 1: Proton motions in the proton conducting phase of $Rb_3H(SeO_4)_2$ at 500 K

type of motion	energy range (HWHM) (μeV)	correlation time (s)
lattice and internal vibrations	3000 (to 10^5)	10^{-13} (to 10^{-15})
fast trigonal "reorientation", *i.e.* localized diffusion (LD)	1200	10^{-12}
OH-librations, overdamped	~300	4×10^{-12}
H-bond formation and breaking, *i.e.* intracrystalline chemical reaction (ICCR)	~30	4×10^{-11}
H-bond transfer, asymmetric, *i.e.* proton transfer to neighbouring oxygen center (PTOC)	~5	3×10^{-10}
H^+-Diffusion, symmetr. H-bond (TD)	~0.3	4×10^{-09}

The method allowing us to isolate specific types of motion from the rather complex motional mechanism is based on the variation of experimental observation time in a series of measurements, where

suitable energy resolution widths are chosen [2]. This technique permits us to perform scans along the Fourier time axis, where specific motions are discovered and measured separately in suitable time windows. From the results the total scattering functions including all motions are then reconstituted on the energy axis and on the time axis. As an example, localized diffusive proton motions in the solid-state protonic conductor $Rb_3H(SeO_4)_2$ were studied at 500 K with quasielastic incoherent neutron scattering on the 10^{-11} s to 10^{-10} s time scale. The experimentally determined model-independent "apparent" EISF was used as a guidance to deduce an approximate proton density distribution for this time interval, as the starting point for developing the trigonal-asymmetric hydrogen bond (TAHB) model [3].

The incoherent scattering function of this model was derived and the resulting theoretical EISF compared to the experiment. The obtained values of the model parameters, the order parameter η and the jump distance R_{21}, indicate that – in spite of its very fast relaxational motions in the neighbourhood of the oxygen – the proton essentially remains bonded to a selenate top oxygen for a period of the order of at least 10^{-10} s. Nevertheless, but with rather low probability, it is also making brief steps into the hydrogen bridge in the 10^{-11} s to 10^{-10} s time interval. We interpret these observations as the consequence of a dynamic disorder in the form of an intracrystalline chemical equilibrium reaction (Fig. 1): alternation between the association of the monomers $[HSeO_4]^{1-}$ and $[SeO_4]^{2-}$, resulting in the dimer $[H(SeO_4)_2]^{3-}$ (H-bond formation) and the dissociation of the latter into the two monomers (H-bond breaking).
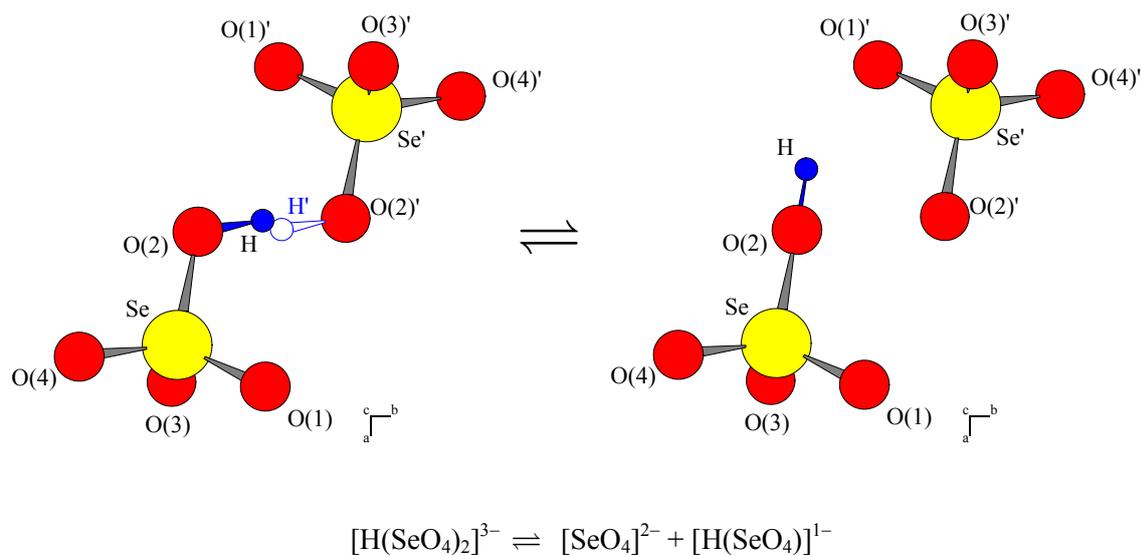

$$[H(SeO_4)_2]^{3-} \rightleftharpoons [SeO_4]^{2-} + [H(SeO_4)]^{1-}$$

Fig. 1 Intracrystalline chemical reaction equilibrium [5,6] in trigonal $Rb_3H(SeO_4)_2$.

At 500 K, this reaction has a rather asymmetric character: The average life-time of the dimer is about 20 times shorter than that of the monomers.

References

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