



Max-Planck-Institut für Festkörperforschung, Stuttgart

*Max-Planck-Institute for Solid State Research*

# Solid Proton Conducting Electrolytes: Conduction Mechanism, Phenomenology and New Materials for Fuel Cell Applications

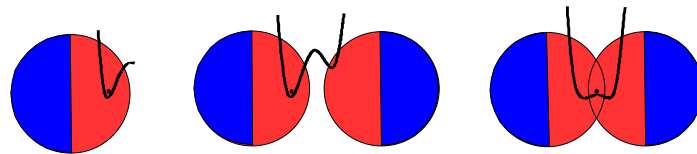
K.D. Kreuer

Max-Planck-Institut für Festkörperforschung, Stuttgart

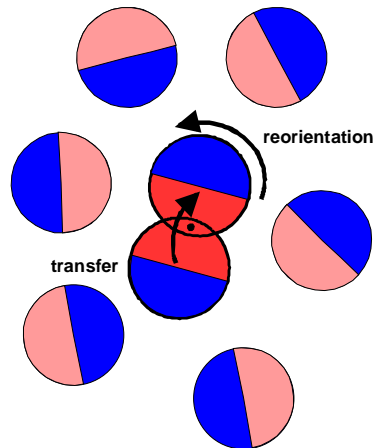
kreuer@fkf.mpg.de



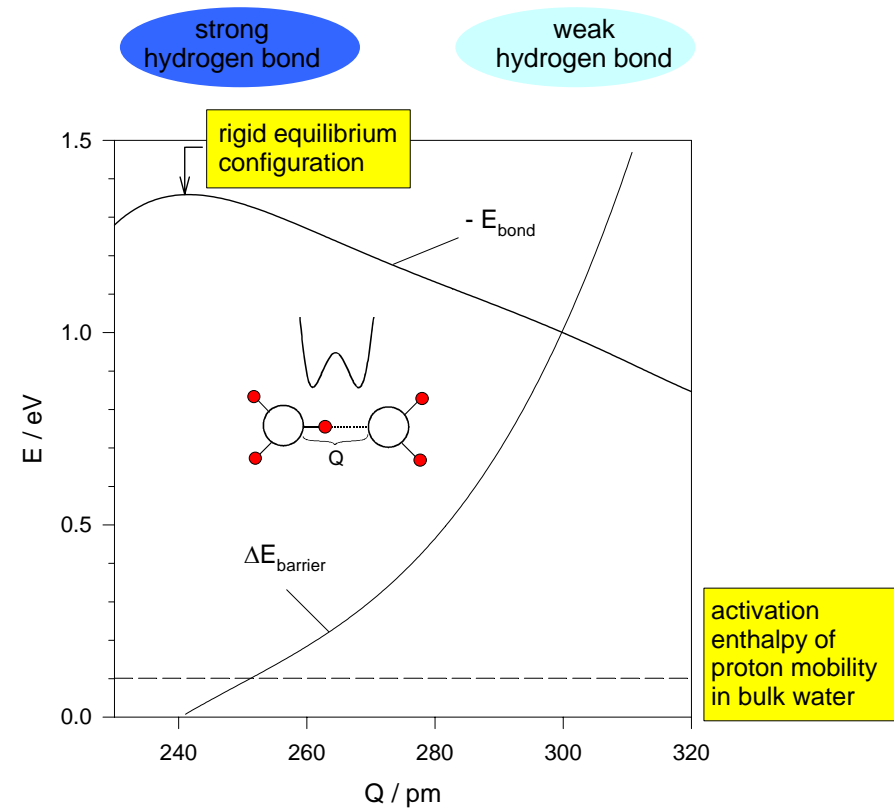
## • A Fundamental Problem hydrogen bonding and long range proton transport



two-step reaction mechanism



energies in the isolated dimer  $\text{H}_5\text{O}_2^+$

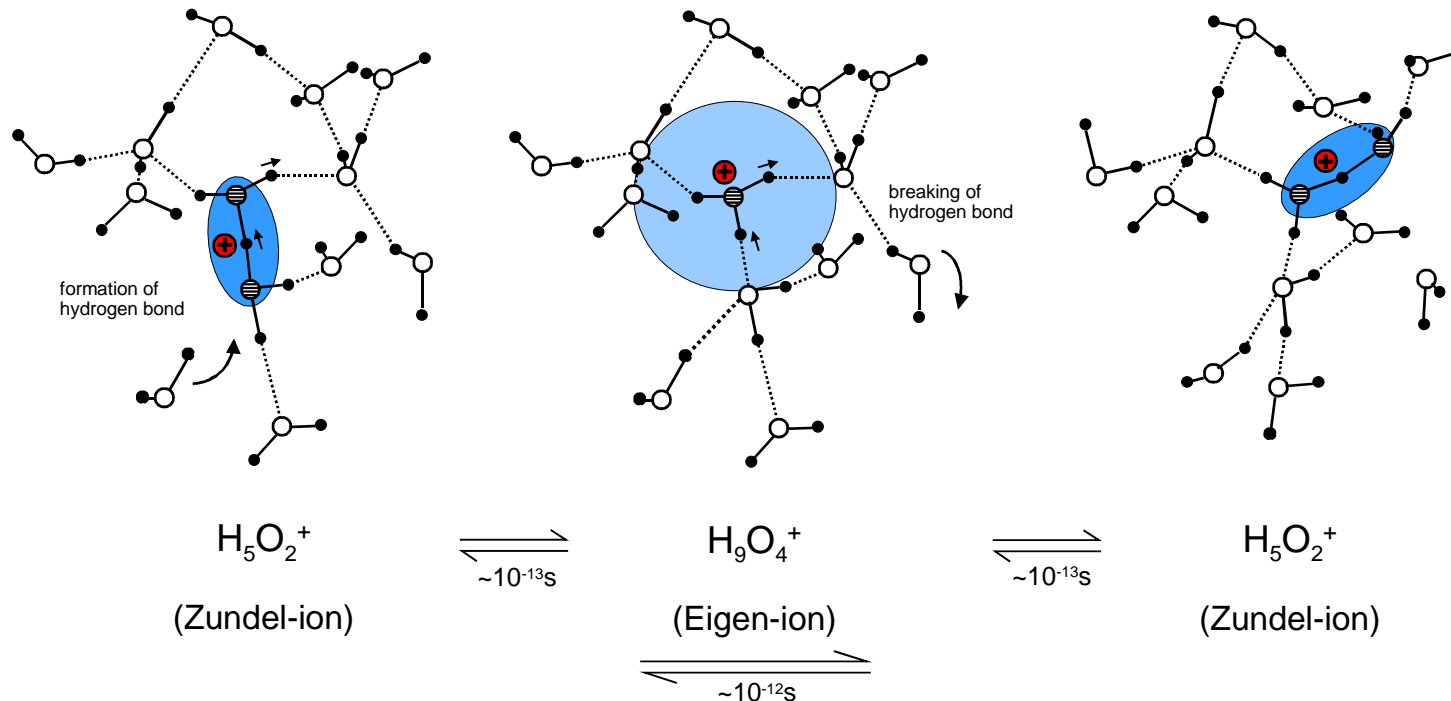


→ long range proton transport is typically related to extended ensembles in the liquid state



## proton transport mechanism in water *a liquid with solid-like properties*

Ab - initio - MD - Simulation (M.E. Tuckerman et al., J.C.P. **103**, 150 (1995))  
revisited (K.D. Kreuer, Solid State Ionics **136-137**, 149 (2000))



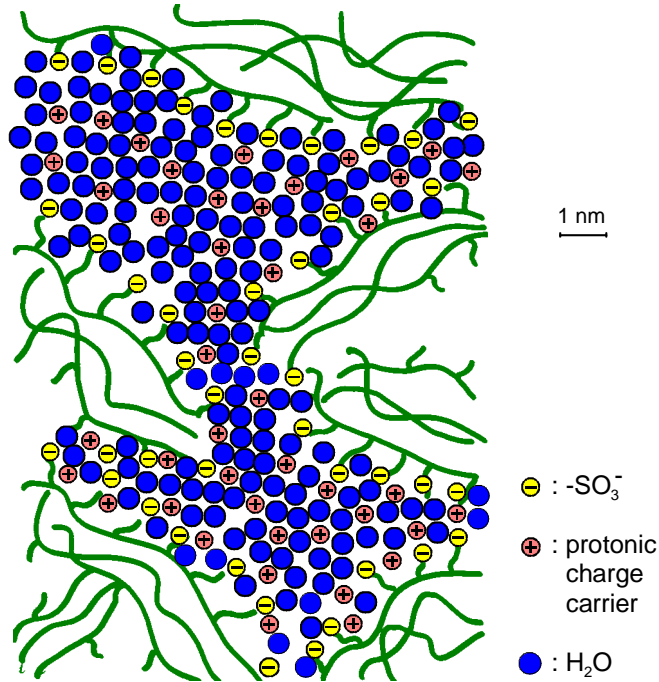
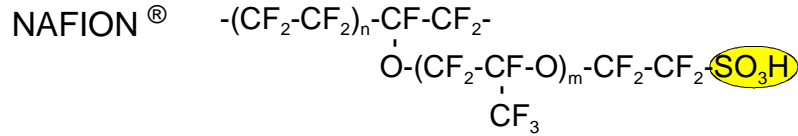
- protonic charge follows the centre of symmetry of hydrogen bond - pattern
- bond breaking and forming (reorientation) in weakly bond outer part of complex
- proton transfer in contracted central part of complex
- strong coupling of both processes

very high proton conductivity in the solid state? solids with liquid-like properties?



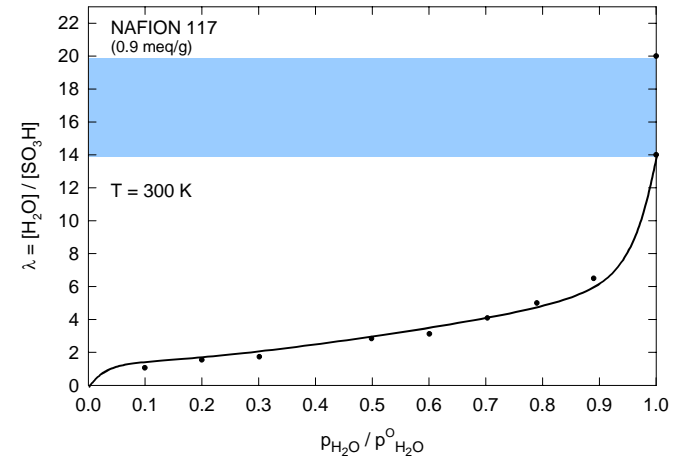
• A few Technological Problems

Membranes for PEM - Fuel Cells

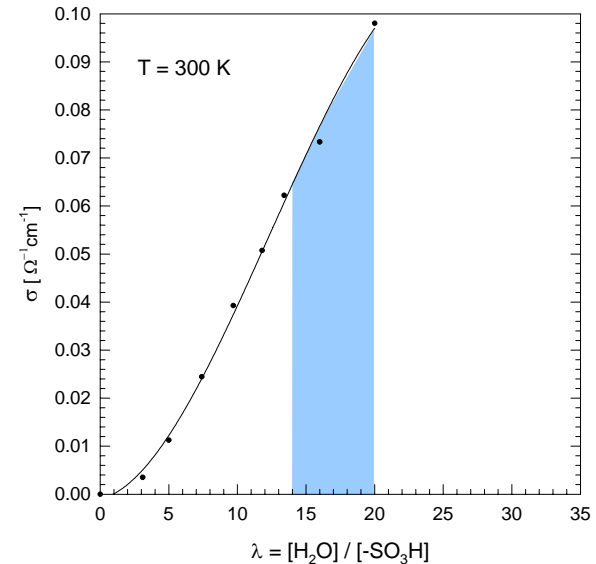


required high conductivity related to presence of **liquid water** as a second phase (two phase effect)

hydration isotherme

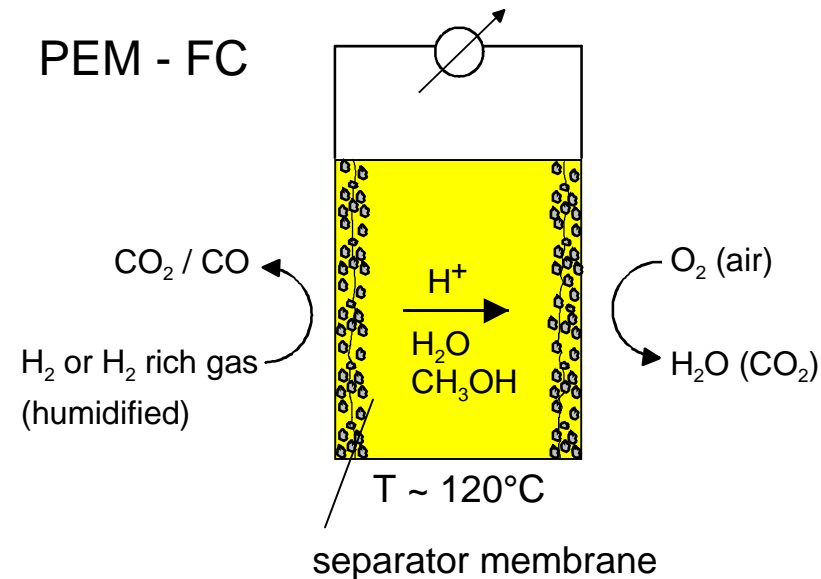


conductivity





## Consequences for PEM - Fuel Cell Technology



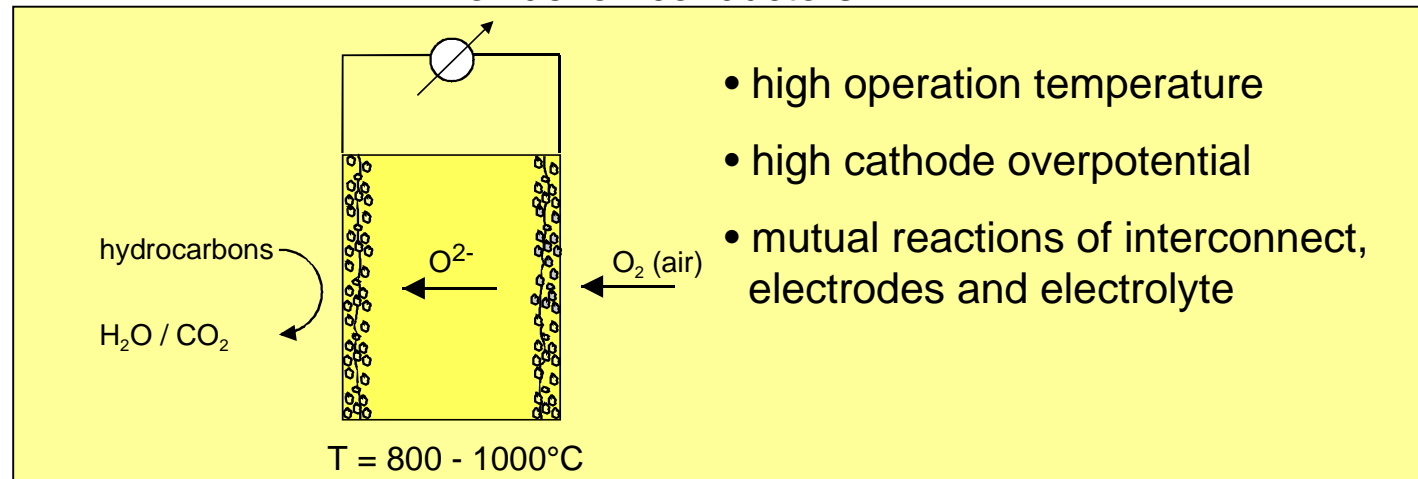
only conducting in the hydrated state

- limited operation temperature ( $< 100^\circ\text{C}$ )  
*low activity of electrocatalyst (Pt)*  
*CO-poisoning of Pt*  
*expensive heat management*
- high water/methanol "cross-over"  
(electroosmotic drag, permeation, chemical diffusion)  
*expensive water/methanol management*

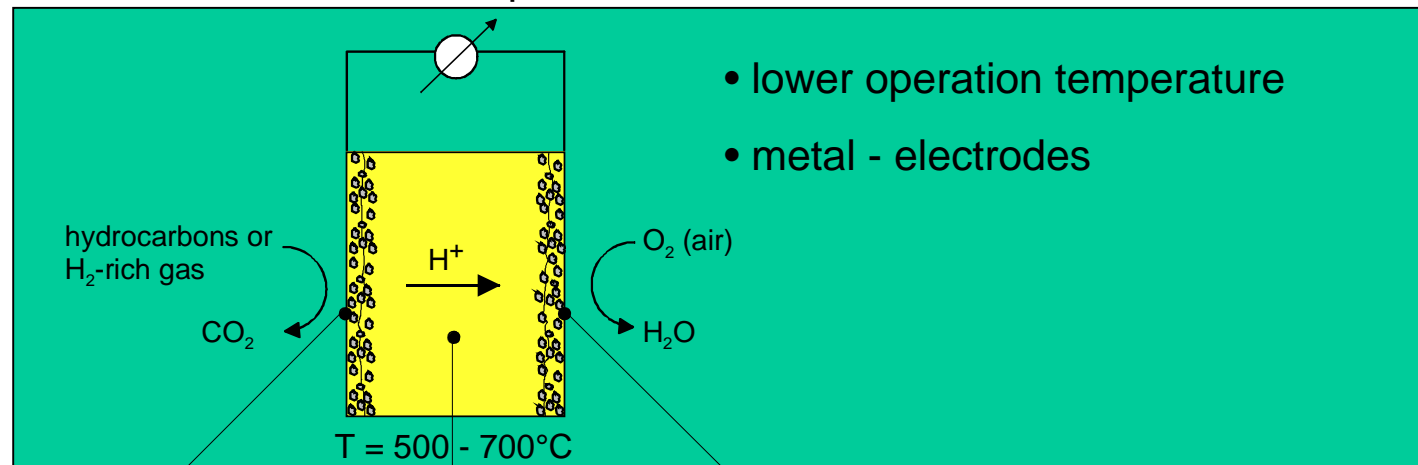


## Separator Materials for SOFC

### oxide ion conductors



### proton conductors



stable with high CO<sub>2</sub> activities

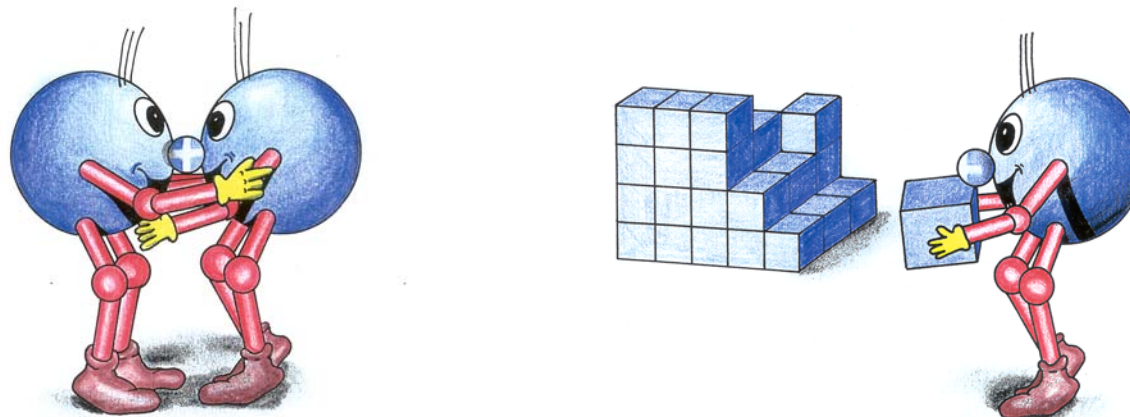
high protonic conductivity

stable with high water activities



- hydrated acidic polymers
  - fully polymeric proton conductors based on heterocycles and phosphonic acid as proton solvent
  - proton conducting oxides
- } —————> PEM-FC
- > SO-FC

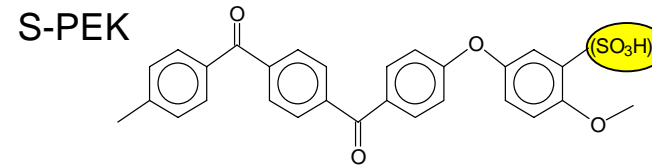
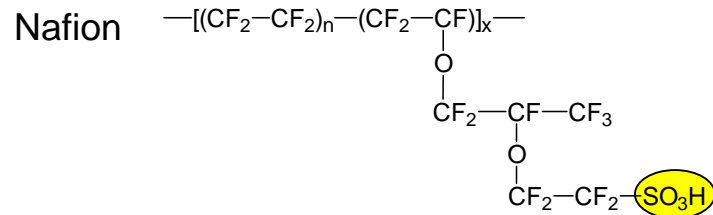
from elementary reactions to new materials





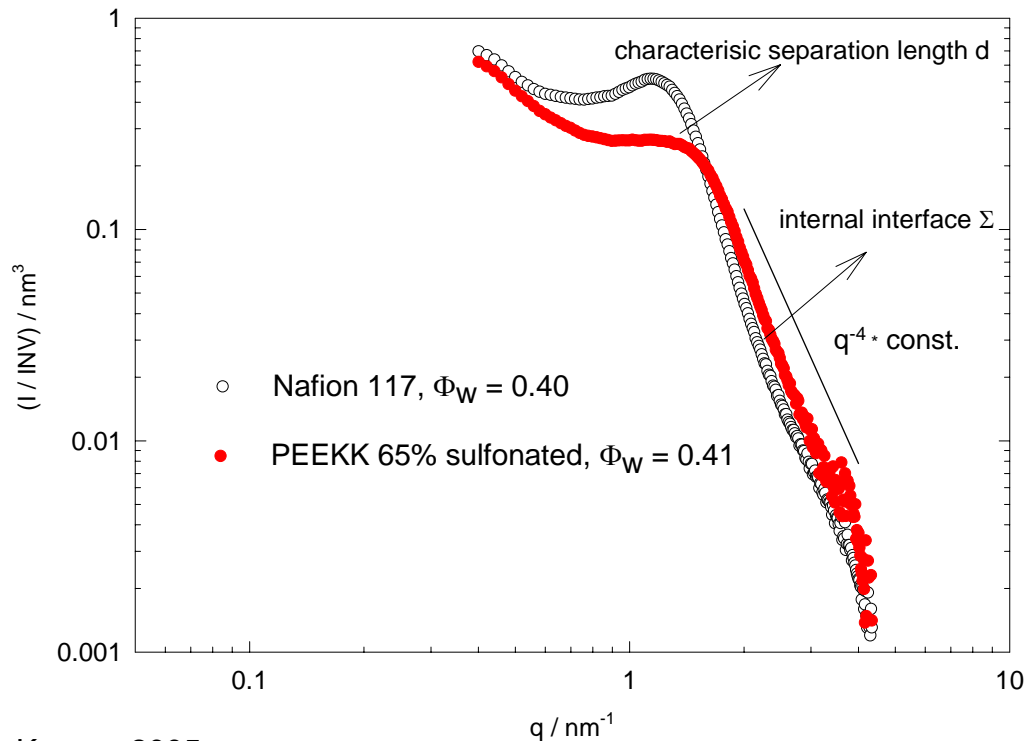
# • Hydrated acidic polymers

*relation between microstructure and transport properties of hydrated acidic polymers*



→ hydrophobic/hydrophilic nano-separation (especially in the presence of water)

microstructure from SAXS



$$d = \frac{2\pi}{q}$$

$$\Sigma = \lim_{q \rightarrow \infty} \frac{q^4 I(q)}{INV} \cdot \pi \cdot \Phi_w \cdot (1 - \Phi_w)$$

$$INV = \int_0^\infty I(q) \cdot q^2 dq \quad : \text{scattering invariant}$$

$\Phi_w$  : volume fraction of absorbed water

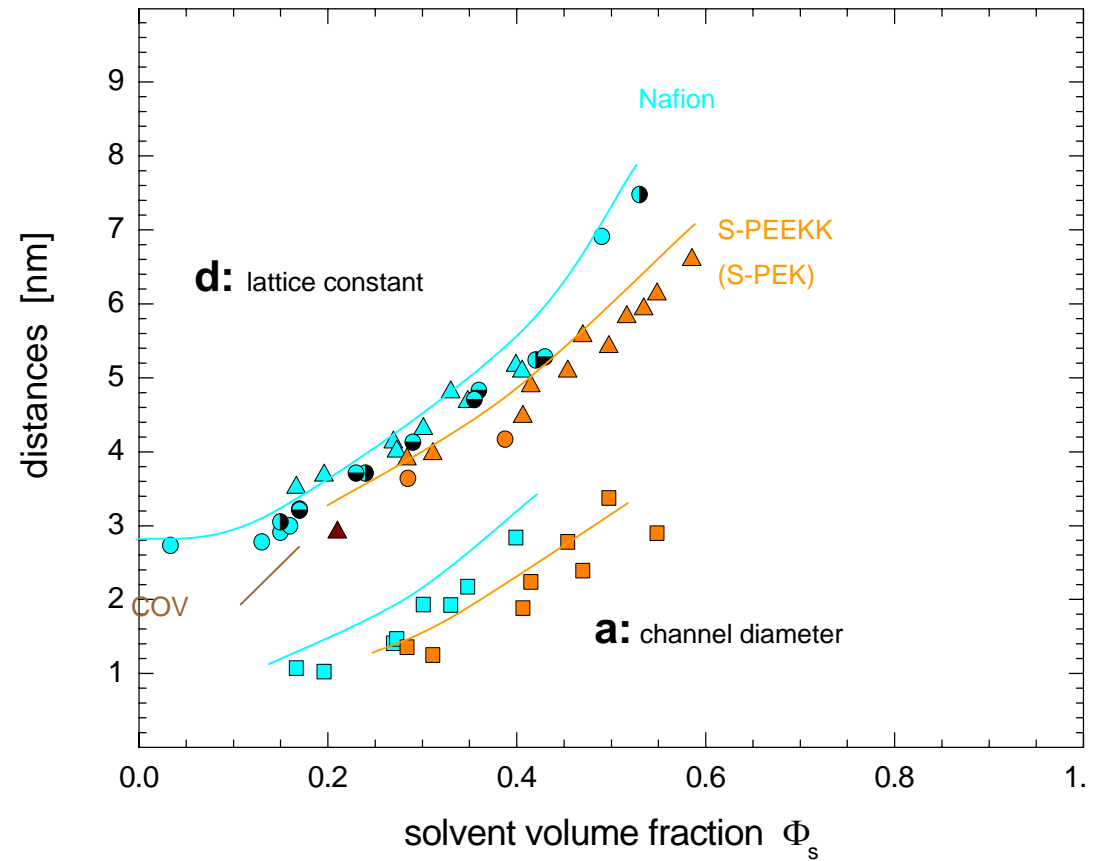
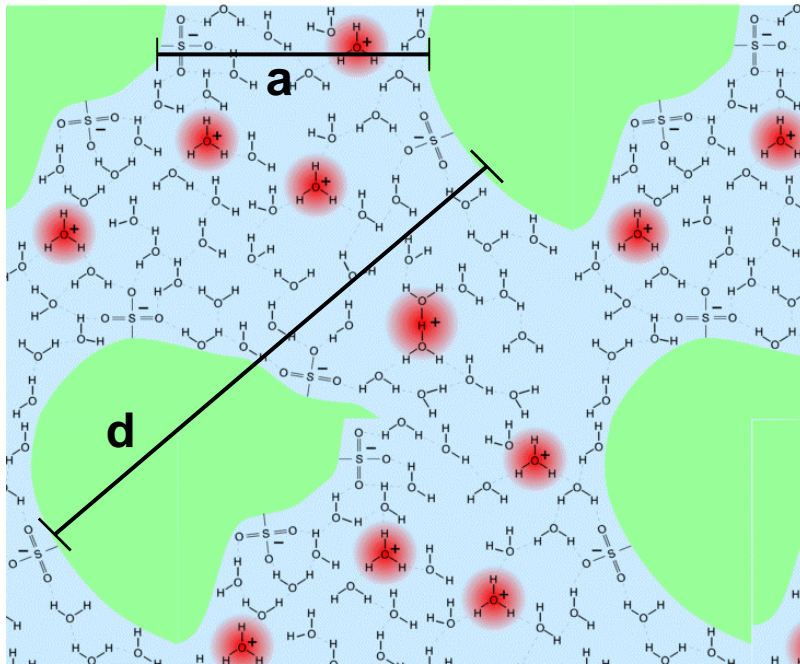
M. Ise; Dissertation, Uni-Stuttgart (2000)

K.D. Kreuer, J.Membrane Science 185, 29 (2001)



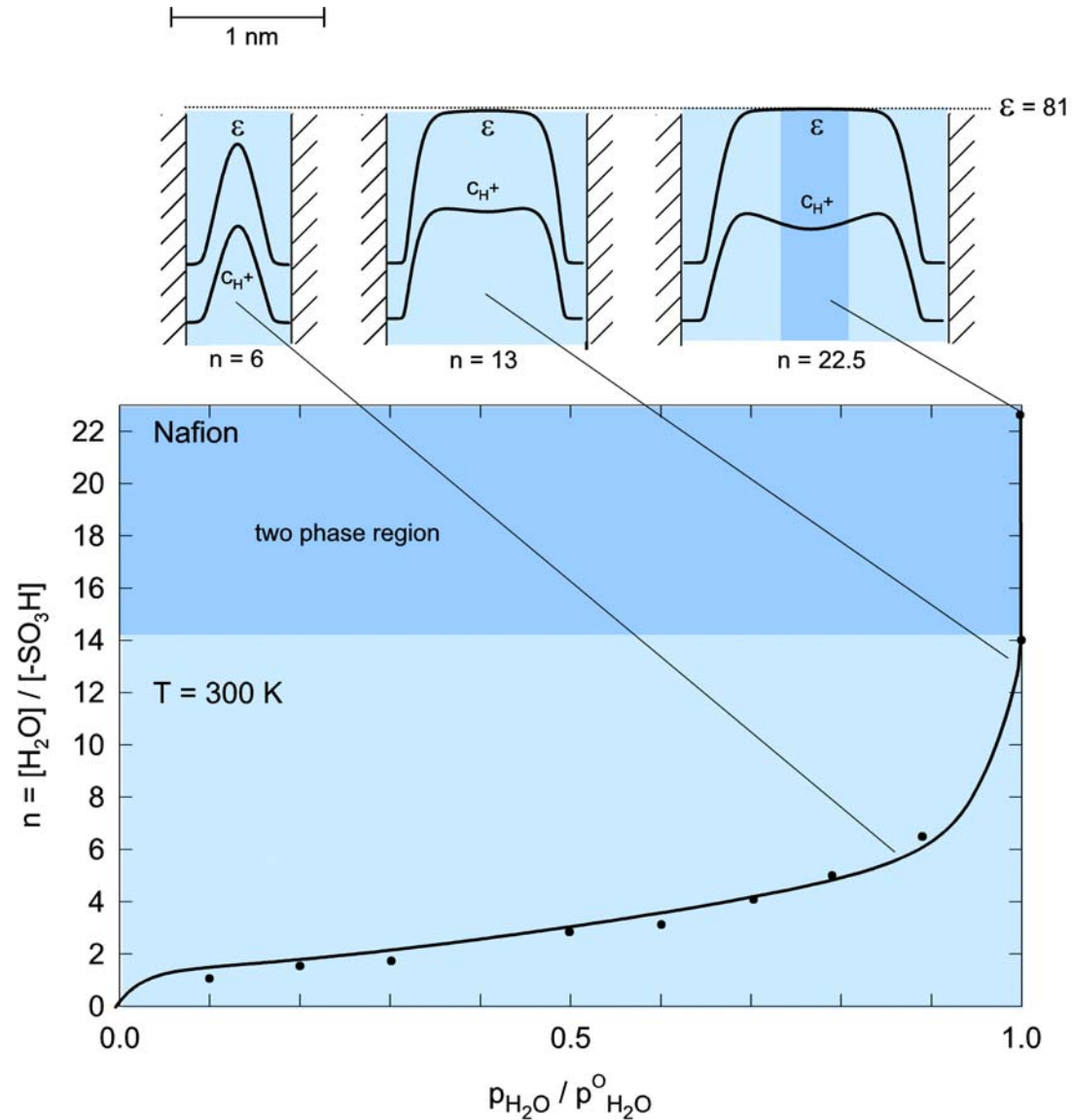


## separation length and channel diameter





## formation of protonic defects





transport matrix  
 phenomenology

$$\begin{pmatrix} \bar{j}_{\text{H}^+} \\ \bar{j}_{\text{H}_2\text{O}} \\ \bar{j}_{\text{MeOH}} \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{21} & L_{22} & L_{23} & L_{24} \\ L_{31} & L_{32} & L_{33} & L_{34} \end{pmatrix} \begin{pmatrix} \bar{\nabla} \tilde{\mu}_{\text{H}^+} \\ \bar{\nabla} \tilde{\mu}_{\text{H}_2\text{O}} \\ \bar{\nabla} \tilde{\mu}_{\text{MeOH}} \\ \bar{\nabla} P_{\text{total}} \end{pmatrix}$$

$\tilde{\mu}_i = \mu_i + F\Phi$   
 with  $L_{ij} = L_{ji}$

	driving force	method
<p><b>proton conductivity</b></p> $\sigma = F^2 L_{11}$	$F \nabla \Phi$	<b>ac impedance</b>
<p><b>self-diffusion</b></p> $D_{\text{H}_2\text{O}} = \frac{RT}{c_{\text{H}_2\text{O}}^2} \frac{dc_{\text{H}_2\text{O}}}{d \ln a_{\text{H}_2\text{O}}} L_{22}$ $D_{\text{CH}_3\text{OH}} = \frac{RT}{c_{\text{CH}_3\text{OH}}^2} \frac{dc_{\text{CH}_3\text{OH}}}{d \ln a_{\text{CH}_3\text{OH}}} L_{33}$	RT	<b>PFG-NMR</b> <i>pulsed magnetic field gradient NMR</i>
<p><b>electroosmotic drag</b></p> $K_{\text{H}_2\text{O}} = \frac{F^2}{\sigma} L_{12} = \frac{L_{12}}{L_{11}}$ $K_{\text{CH}_3\text{OH}} = \frac{F^2}{\sigma} L_{13} = \frac{L_{13}}{L_{11}}$	$F \nabla \Phi$	<b>E-NMR</b> <i>electrophoretic NMR</i>
<p><b>permeation</b></p> $L_{24}, L_{34}$	$\bar{\nabla} P_{\text{total}}$	<b>permeation cell</b>



## measuring electroosmotic drag by E-NMR

superconducting magnet  
 $B_0(\text{max}) = 8 \text{ T}$   
(inhomogeneity ca. 1 ppm)

tuning and matching  
capacitors

rf saddle coil on quartz tube

anti-Helmholtz gradient coil  
 $G_{\text{max}} = 0.5 \text{ T/cm}$   
(water-cooled)

connections to rf amplifier/receiver,  
temperature controller, power supply for  
constant current (E-NMR)

bifilar wound ohmic heater  
(temperatures from RT to 500 °C)

glass dewar

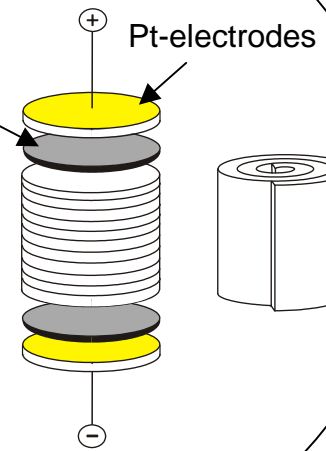
sample (thermally and mechanically isolated  
from gradient coil)

current (PFG)  
T-Control  
air  
water  
(for cooling)

### E-NMR probe

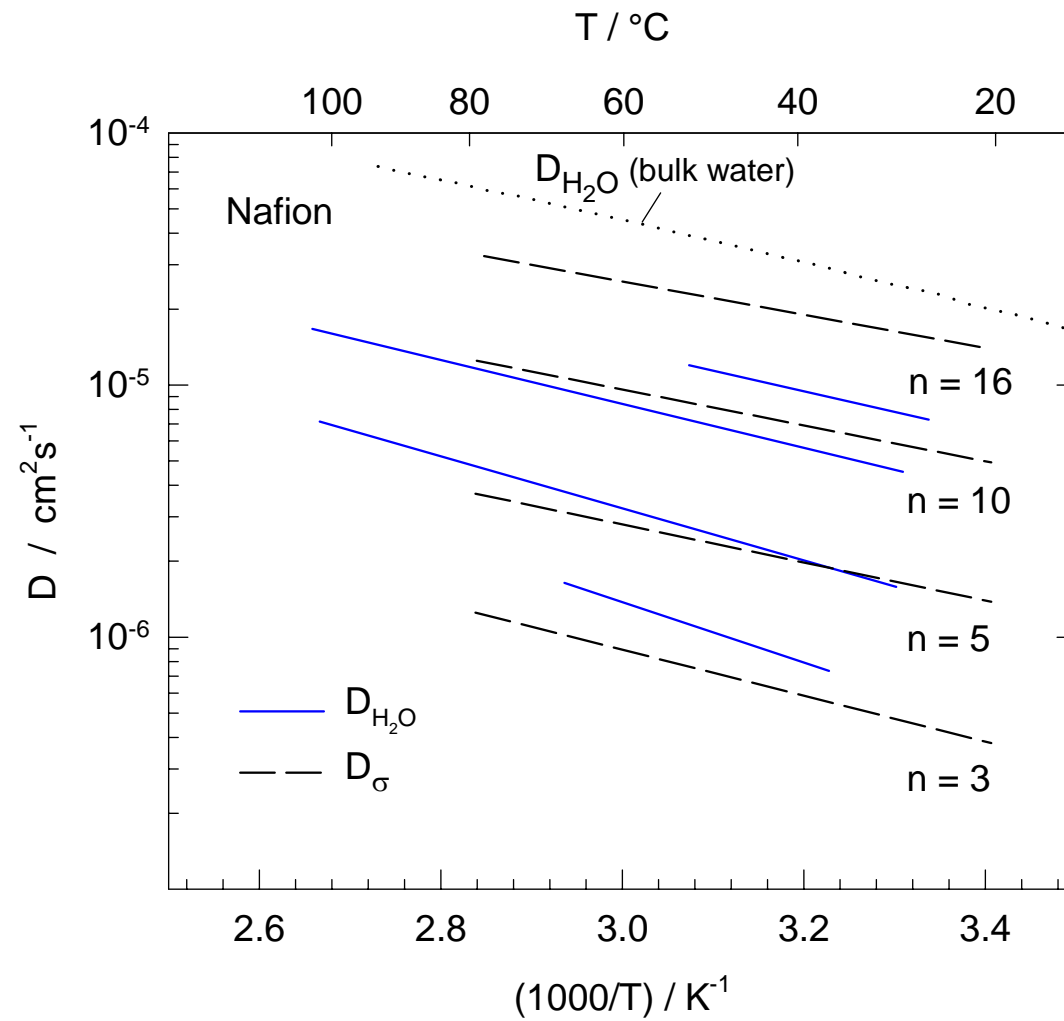
gas diffusion  
electrode  
(1 mg/cm<sup>2</sup> Pt on C)

membranes slices or  
rolls, constant T and  
solvent content due  
to sealed container,  
water and air-tight



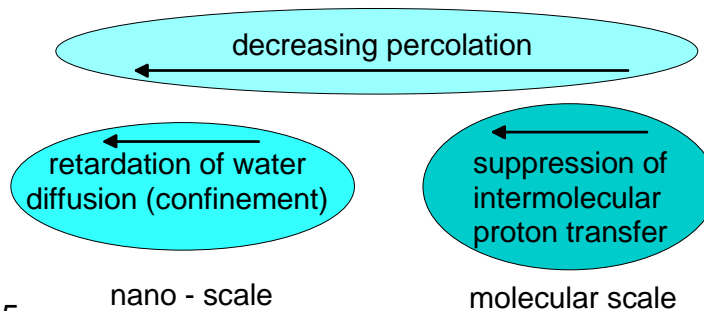
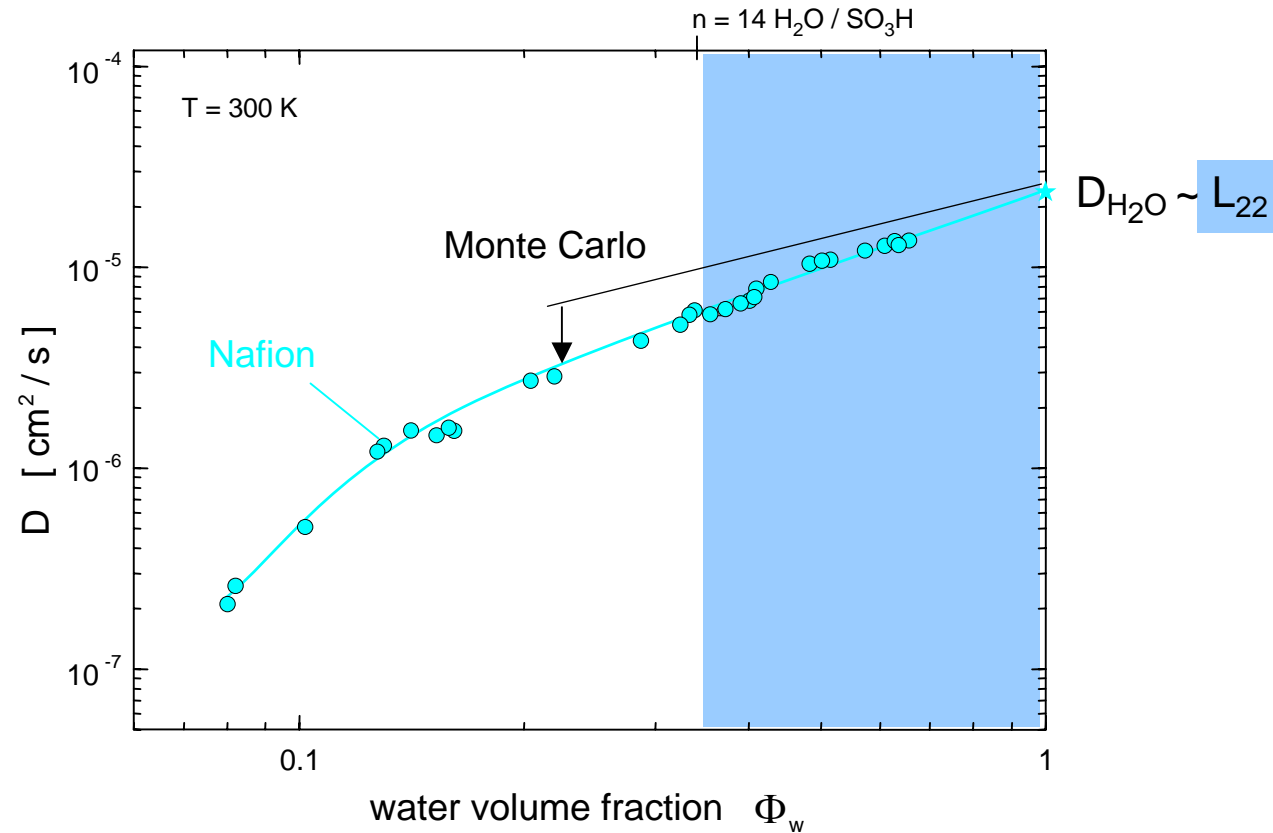


transport coefficients as a function of water content and temperature  
(proton mobility ( $L_{11}$ ) and water self-diffusion ( $L_{22}$ ))



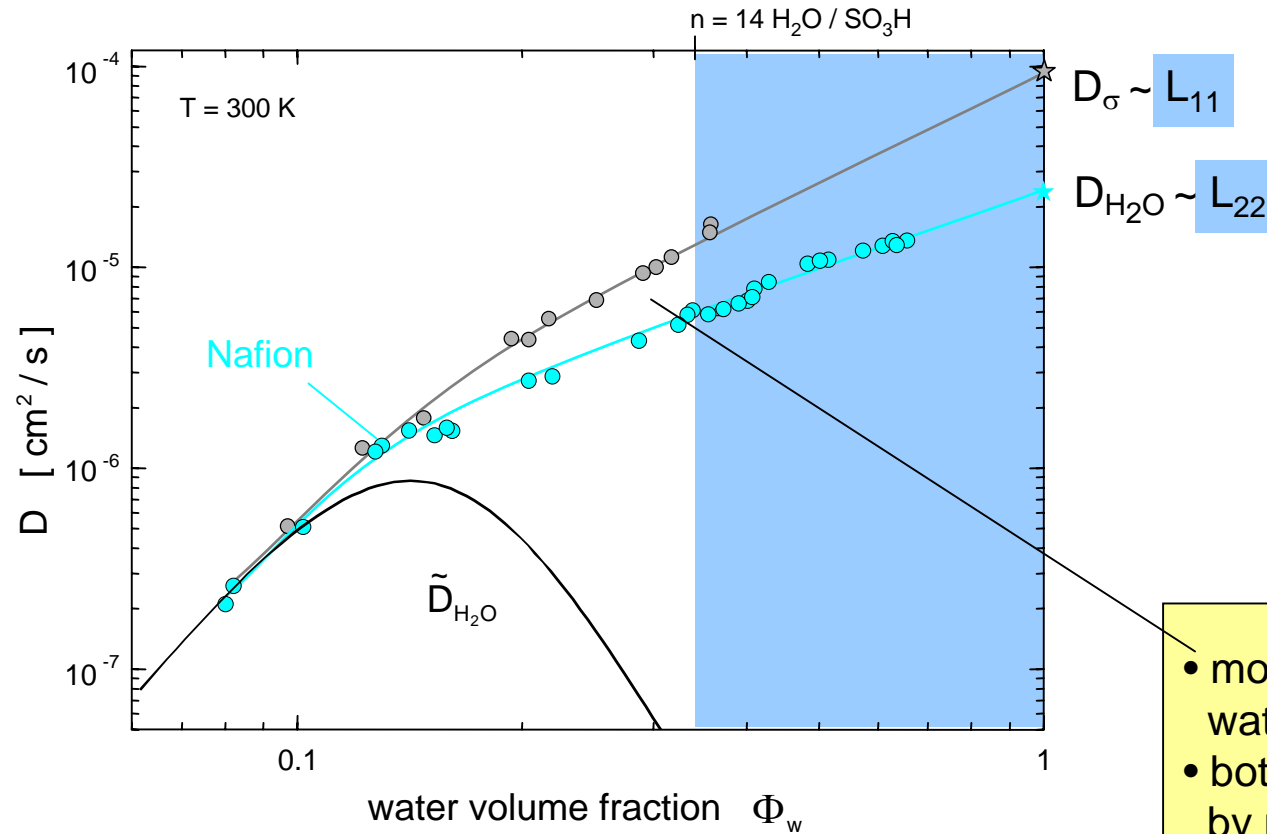


## transport coefficients as a function of water volume fraction (proton mobility ( $L_{11}$ ) and water self-diffusion ( $L_{22}$ ))

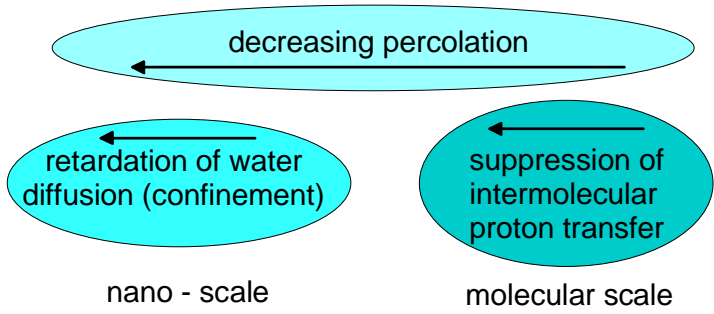




### transport coefficients as a function of water volume fraction (proton mobility ( $L_{11}$ ) and water self-diffusion ( $L_{22}$ ))

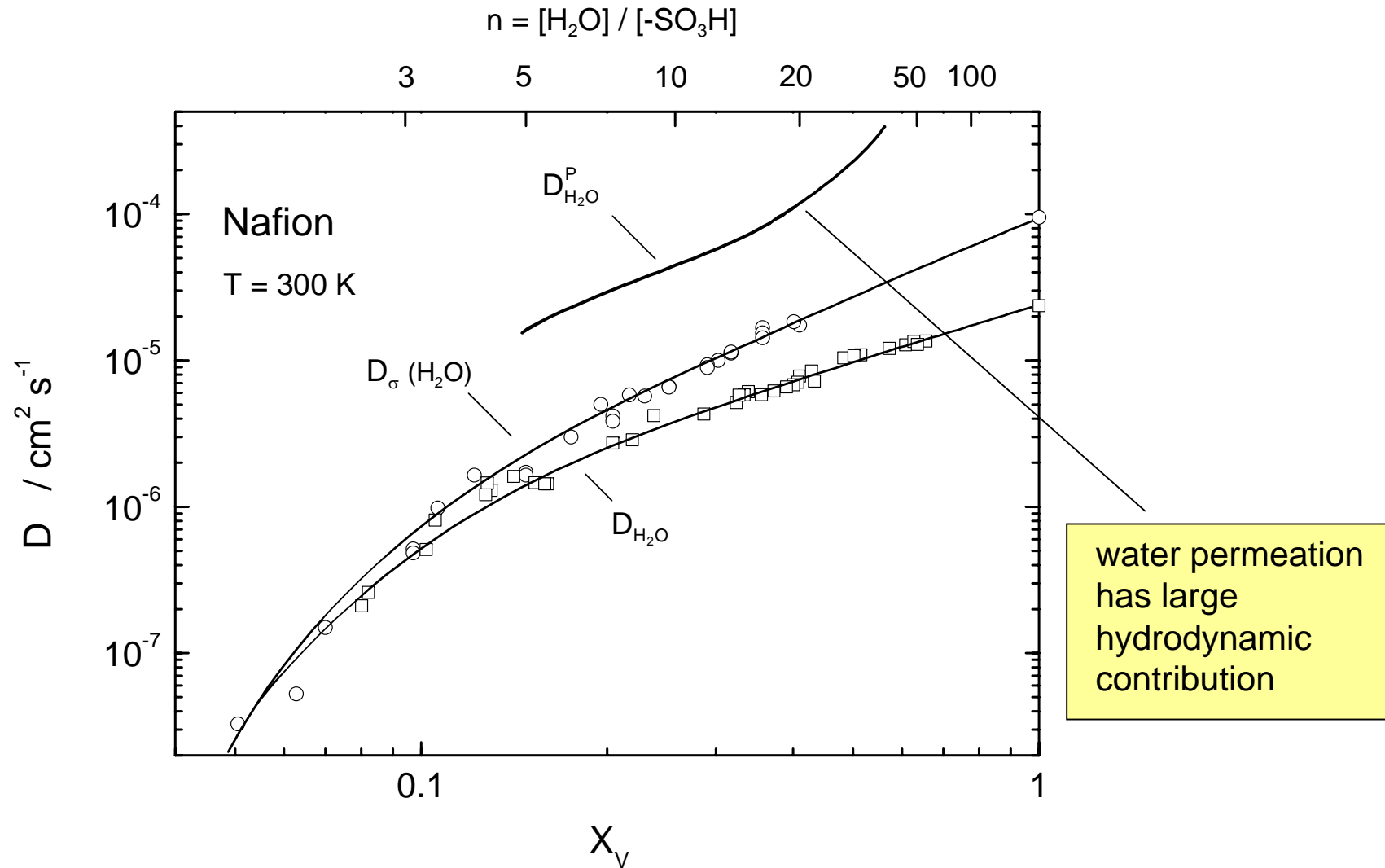


- mobility of protonic defects and water diffusion related
- both coefficients dominated by percolation (to some extent by water/polymer interaction)





### transport coefficients as a function of water volume fraction (water permeation ( $L_{34}$ ))

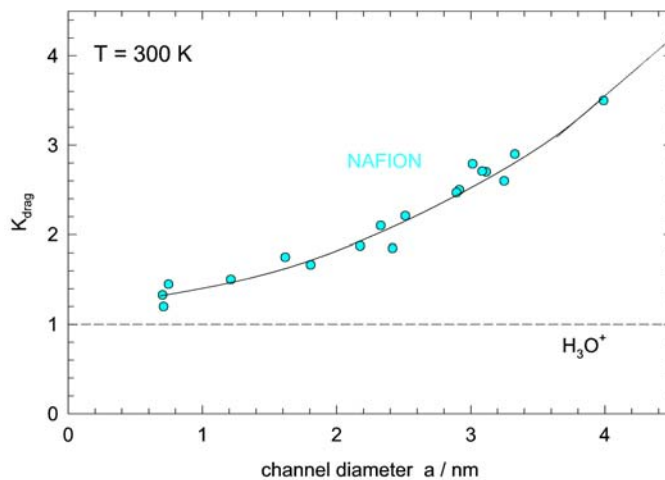
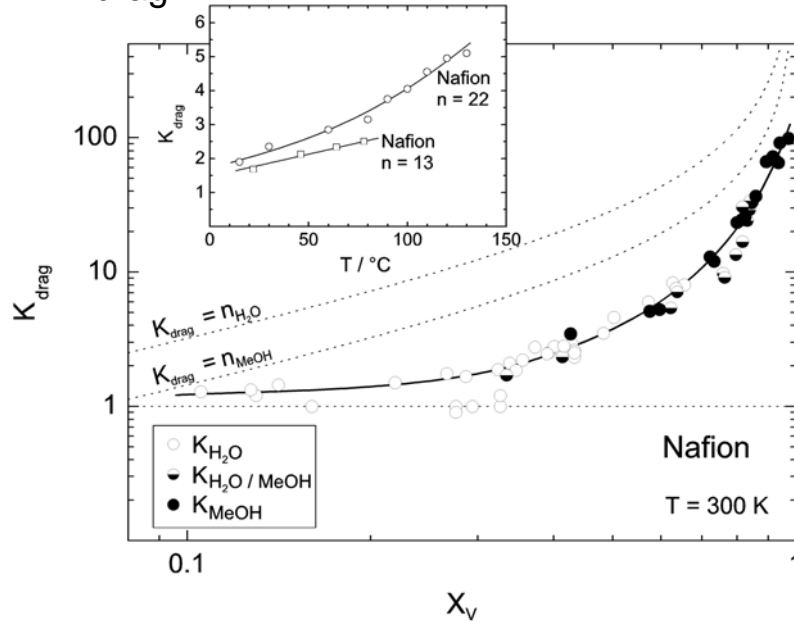




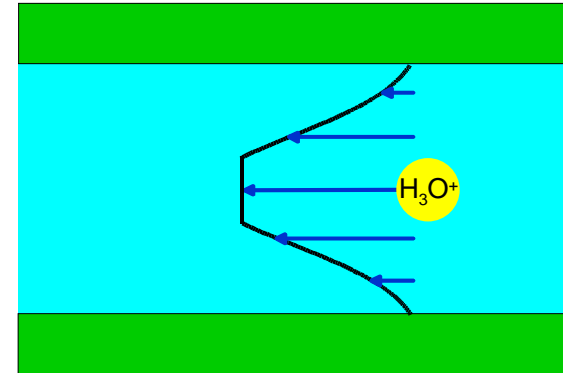


electroosmotic water/methanol  
 drag

$$\left( \frac{L_{12}}{L_{11}}, \frac{L_{13}}{L_{11}} \right)$$



electroosmotic drag:

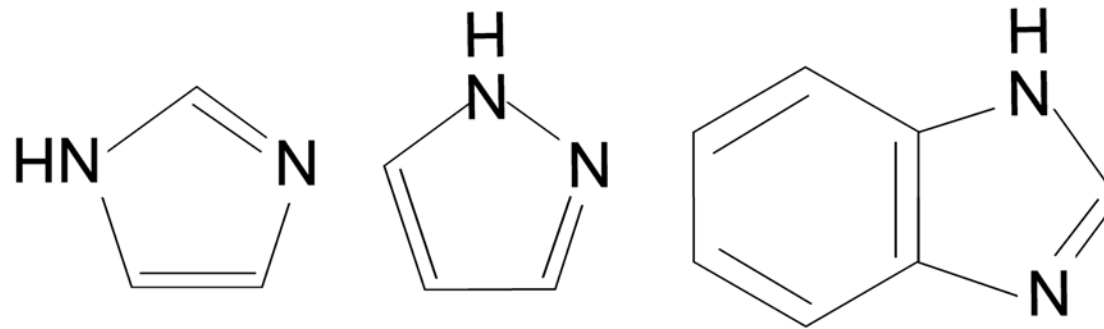


lower limit given by primary hydration of proton ( $H_3O^+$ )  
 otherwise electroosmotic drag may be described as hydrodynamic process controlled by *water/water* and *water/polymer interaction, microstructure and swelling*

→ ● increase water confinement



- Fully polymeric proton conductors based on heterocycles phosphonic acid as proton solvent



imidazole

pyrazole

benzimidazole

< 200°C

< 250°C

$T_m = 90^\circ\text{C}$

$T_m = 80^\circ\text{C}$

$T_m = 170^\circ\text{C}$



from similar hydrogen bond networks as water

transport coefficients similar to those of water  
for a given temperature relative to melting point

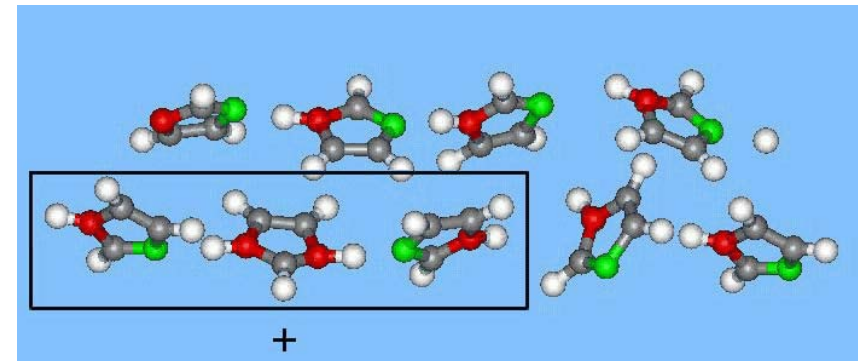
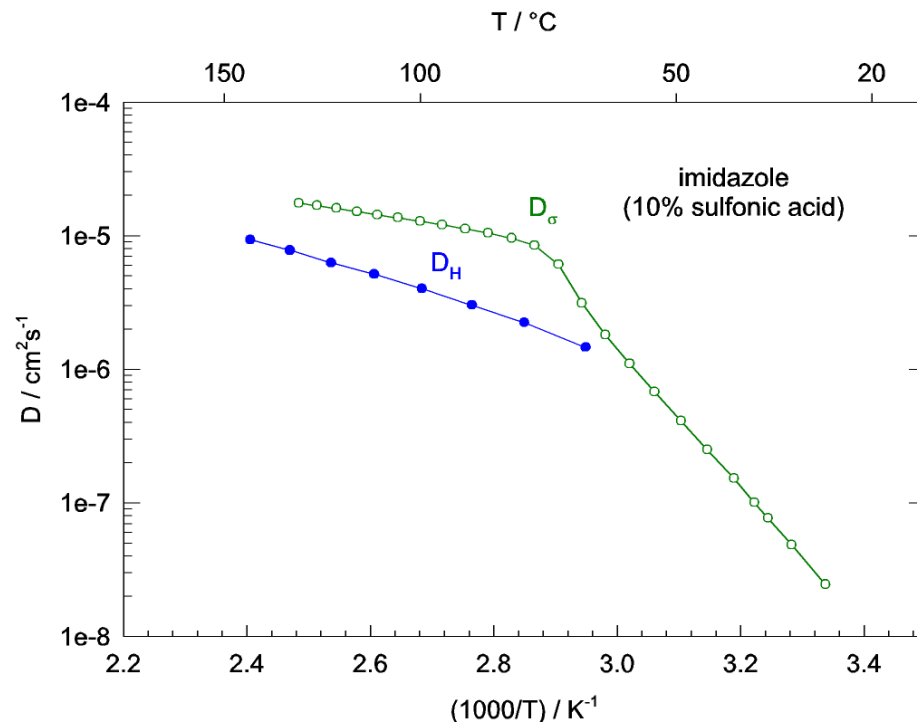
have proton donor and acceptor function ( $K_a$ ;  $K_b$  > amphoteric)



## structure diffusion in **liquid** imidazole

proton mobility and imidazole self-diffusion

ab - initio - MD



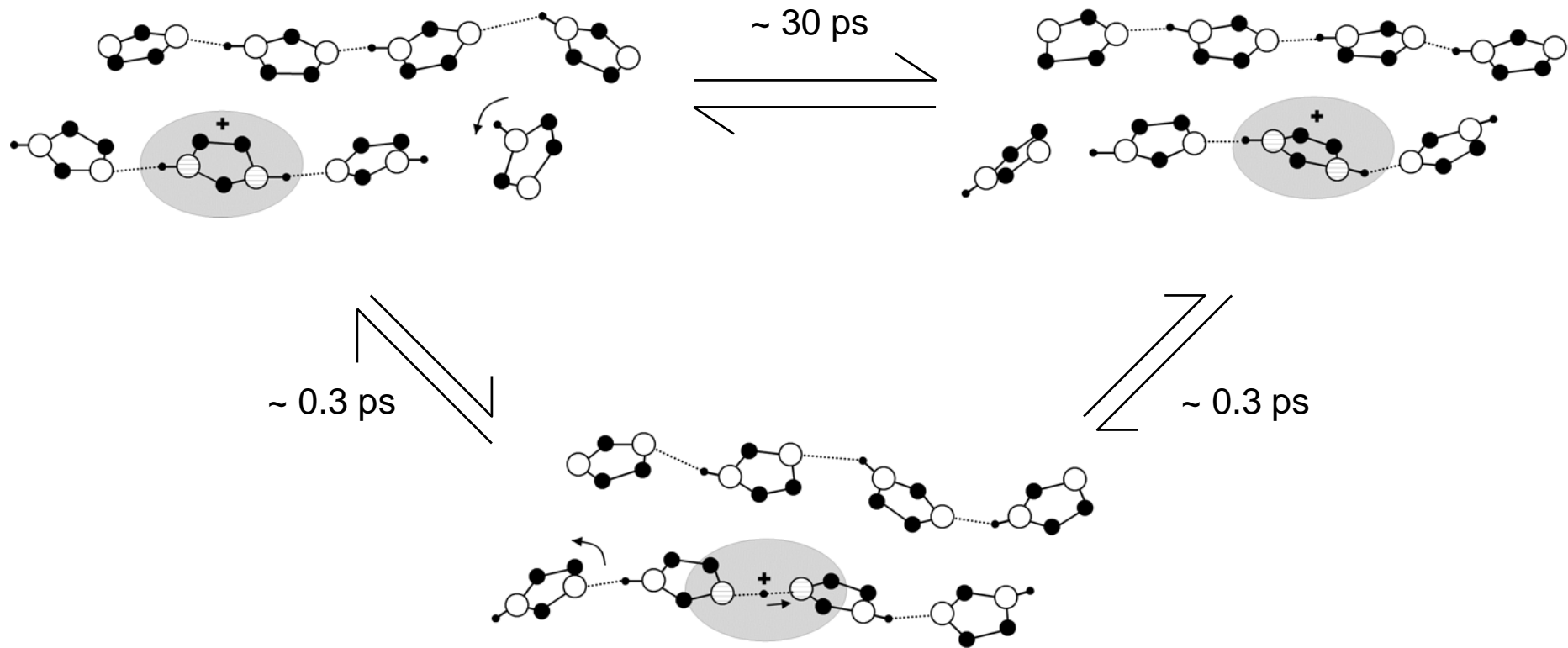
mechanism similar to that in water

K.D.Kreuer, A.Fuchs, M.Ise, M.Spaeth, J.Maier;  
Electrochim. Acta 43, 1281 (1998)

W.Münch, K.D.Kreuer, W.Silverstri, J.Maier, G.Seifert;  
Solid State Ionics 145, 295 (2001)



## structure diffusion of excess protons in **liquid** imidazole

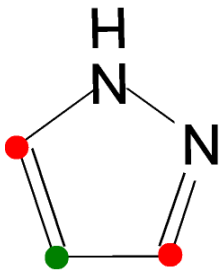
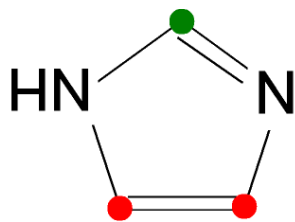


W. Münch, K.D. Kreuer, W. Silvestri, J. Maier, G. Seifert; *Solid State Ionics* **145**, 437 (2001)



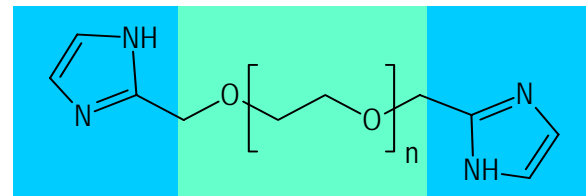
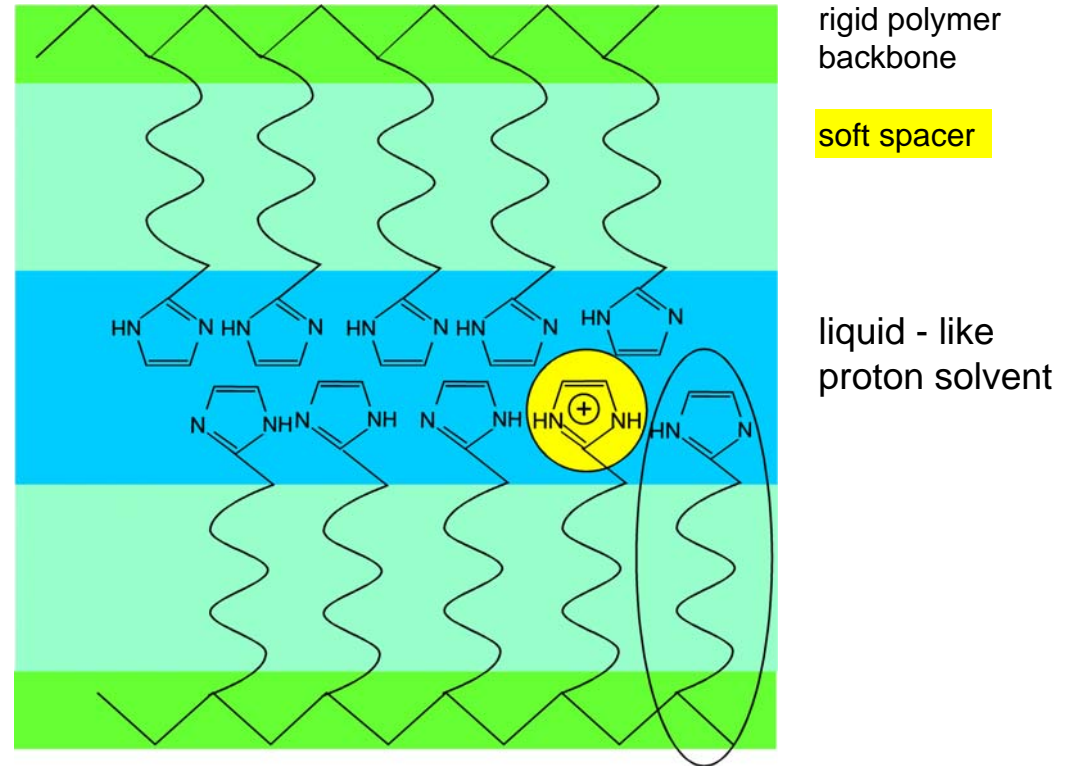
approach:

$\sigma$ -bond in symmetrical position



terminated soft side-chains

### hierachic architecture

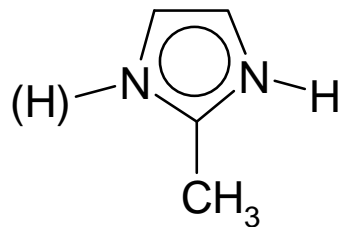


model for spacer  
Imi-n with  $n = 2, 3, 5$

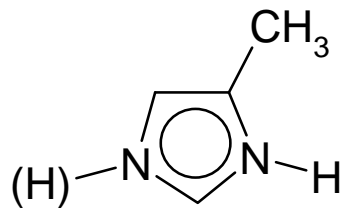


## how can heterocycles be immobilized without losing the local **liquid-like** dynamics assisting "structure diffusion" ?

effect of asymmetric bonding

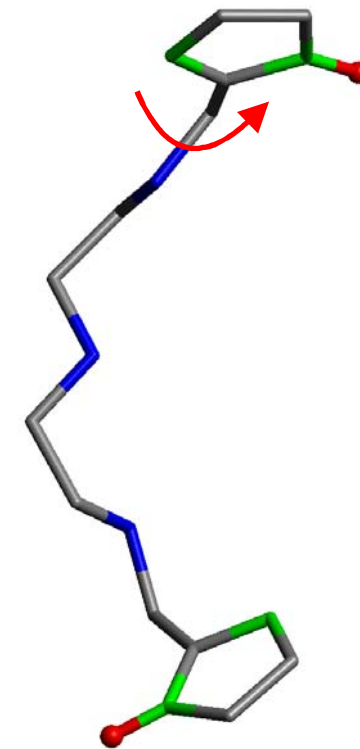


$$\Delta E = 0$$



$$\Delta E \sim 20 \text{ meV}$$

choice of spacer  
*energy variation with rotational coordinate*

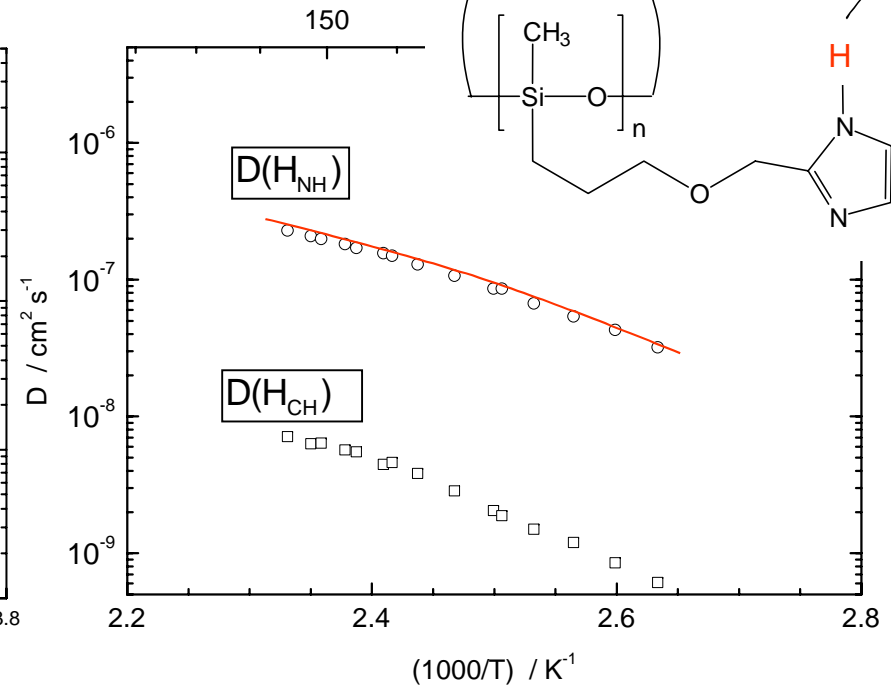
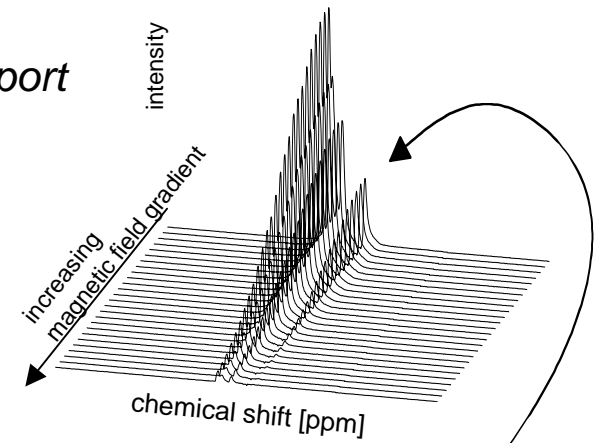
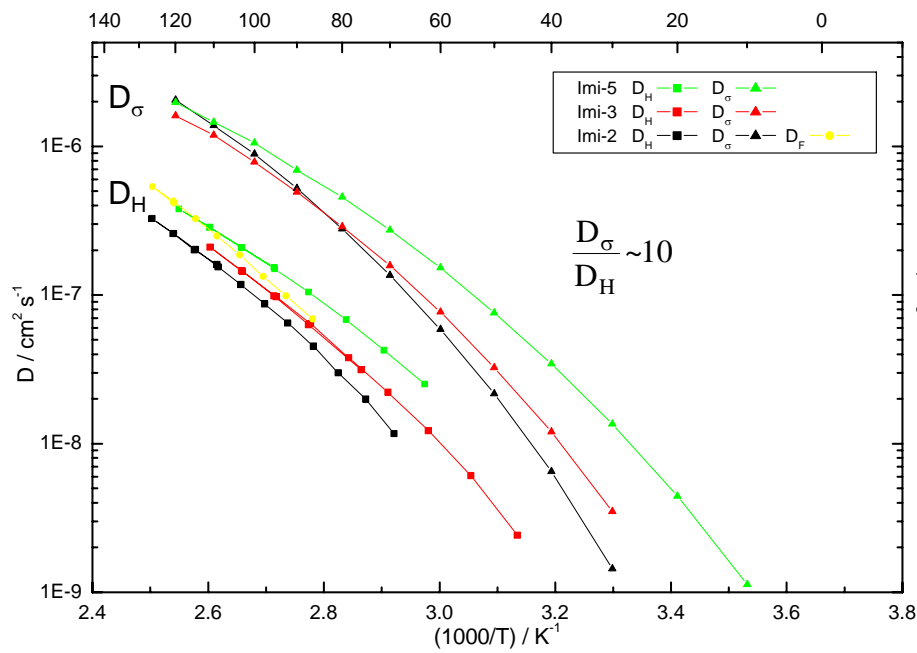
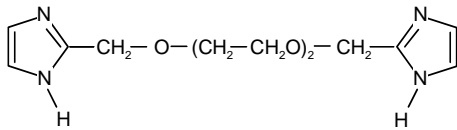


isolated chain



## decoupling of proton and oligomer transport (pure systems)

Imi2:



proton transport via structure diffusion

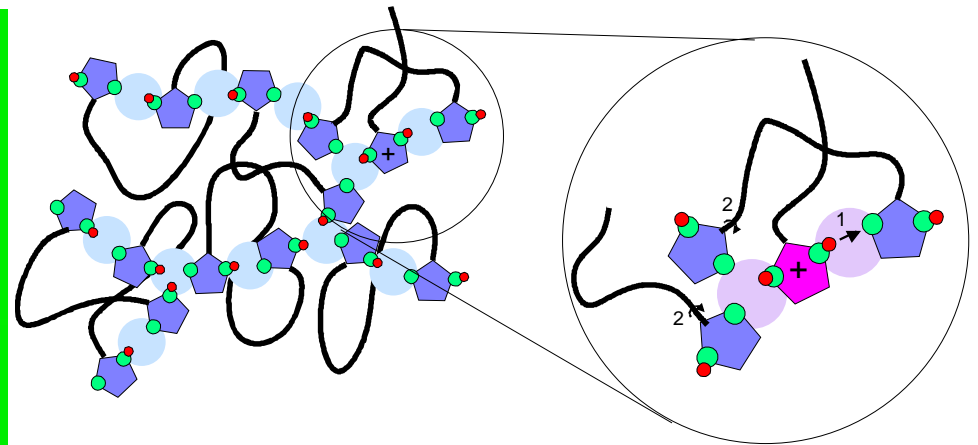
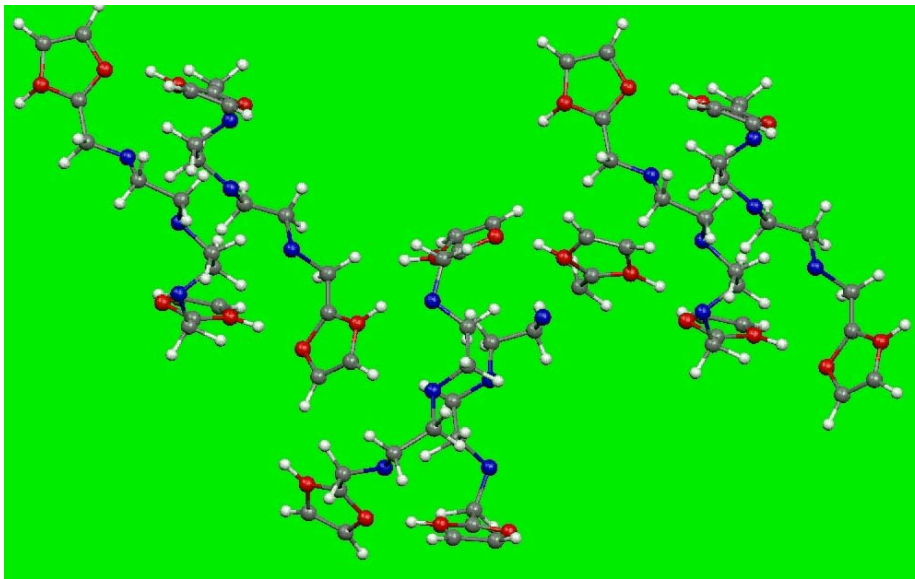


# proton conduction mechanism *aggregation and dynamic hydrogen bonding*



MD-simulation

$^1\text{H-NMR}$



W.Münch, K.D.Kreuer, J.Maier; Solid State Ionics, in preparation

G.R. Goward et al. J.Phys.Chem.B **106**, 9322 (2002)

K.D. Kreuer, 2005

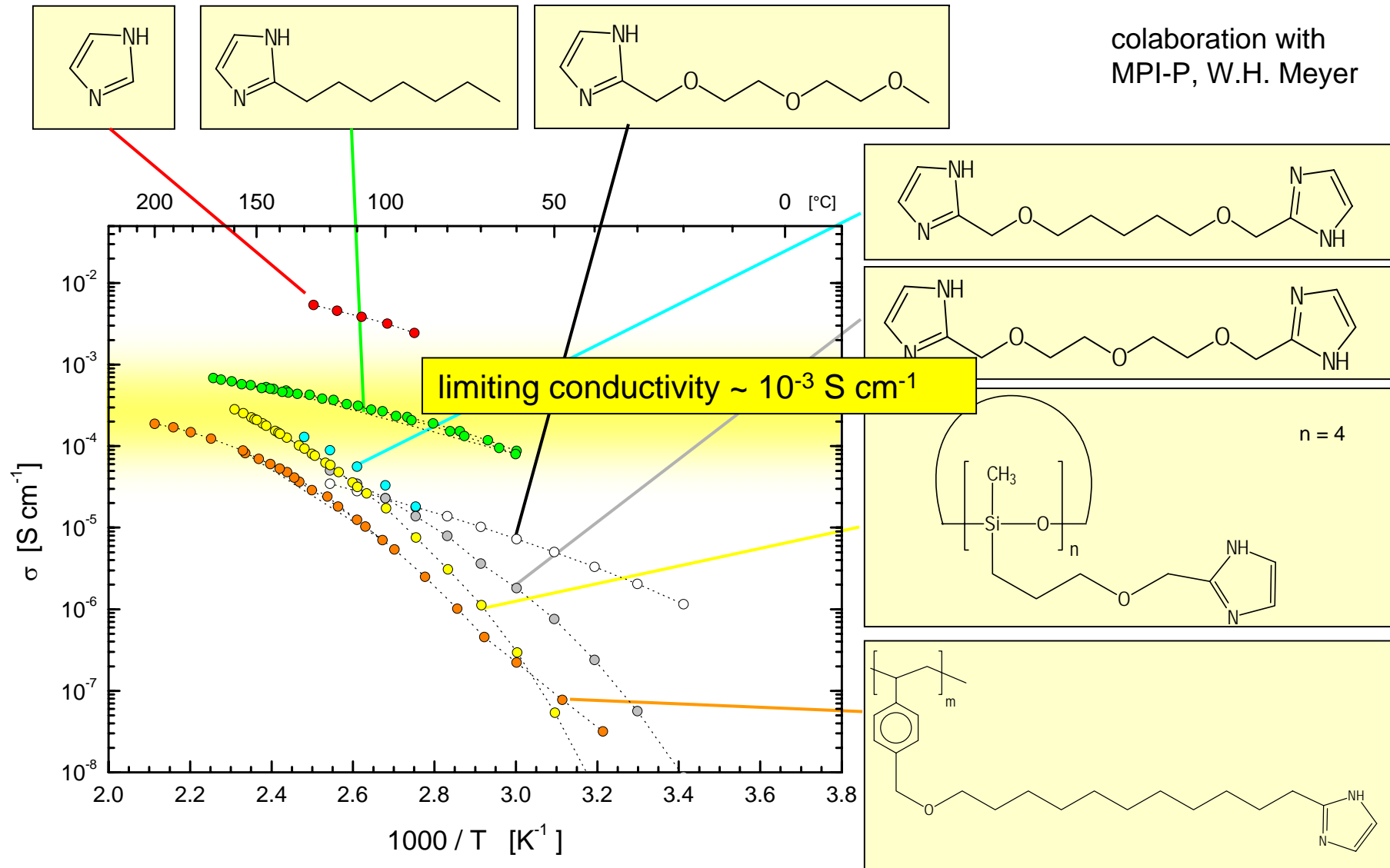




## conductivity limit (pure systems)

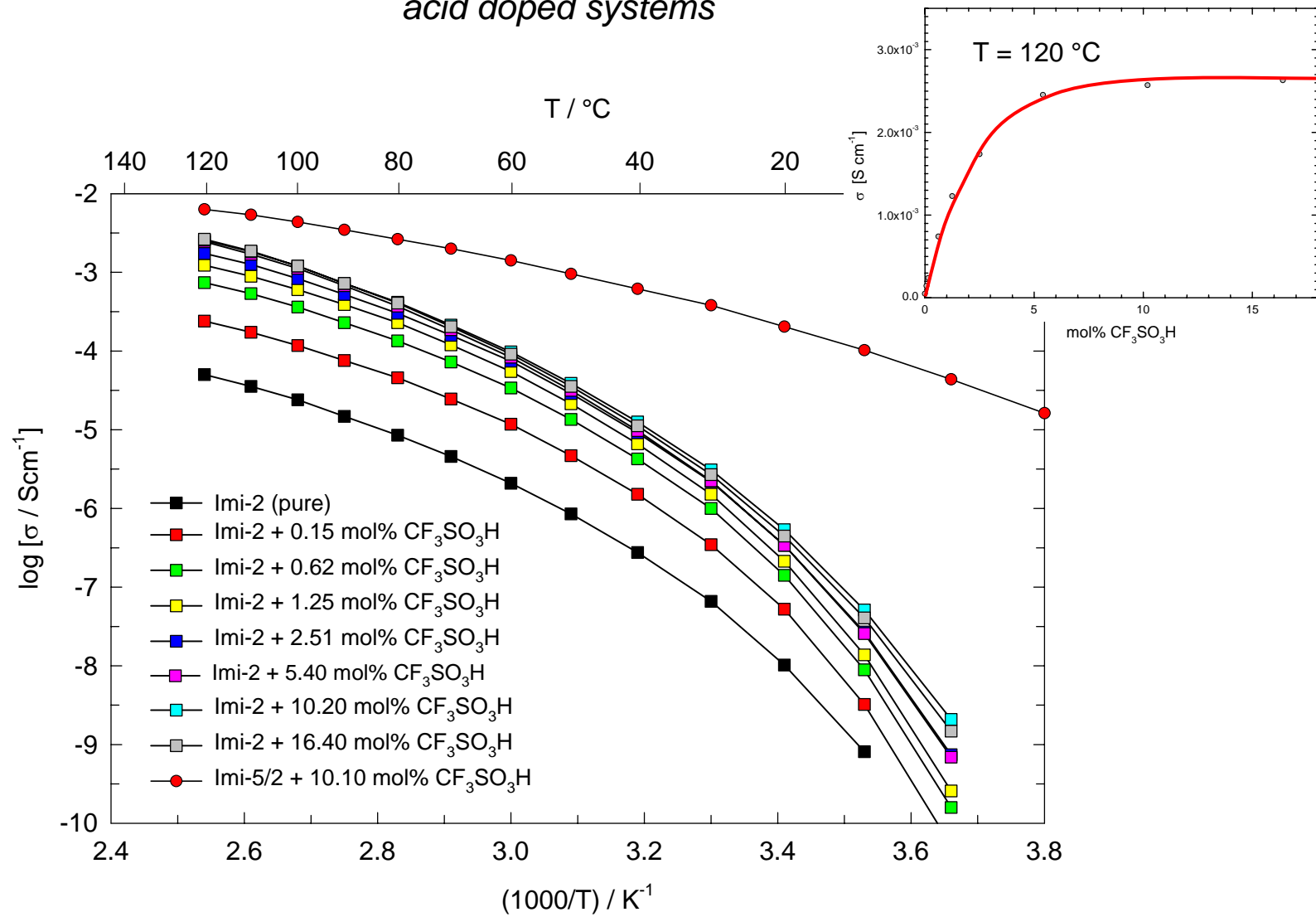
from **liquids** to **solids** with **liquid-like** properties

collaboration with  
MPI-P, W.H. Meyer



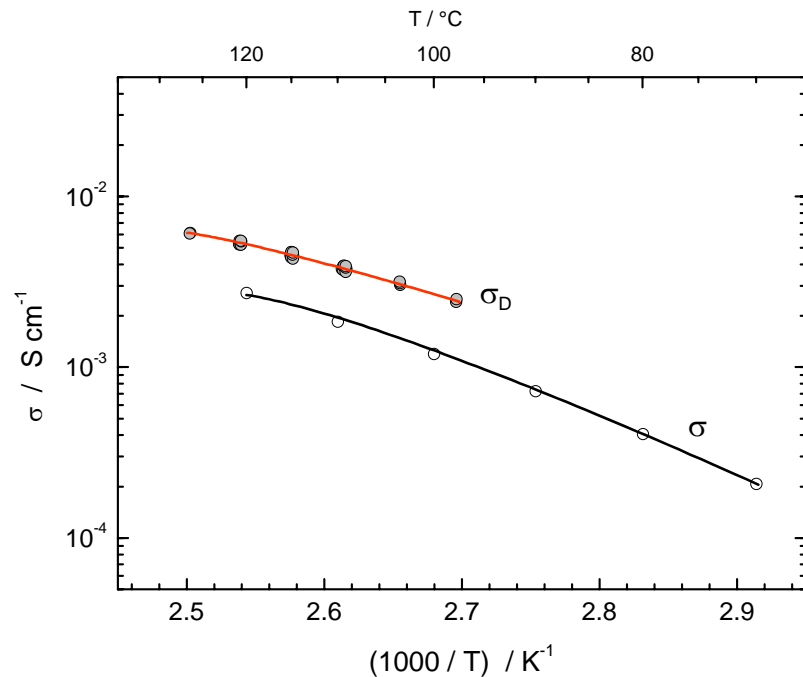


### acid doped systems





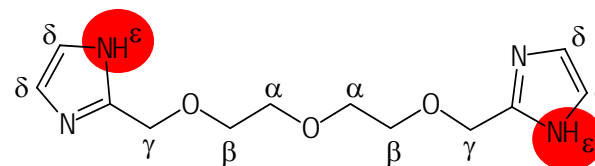
## cooperativity of proton transfer reactions



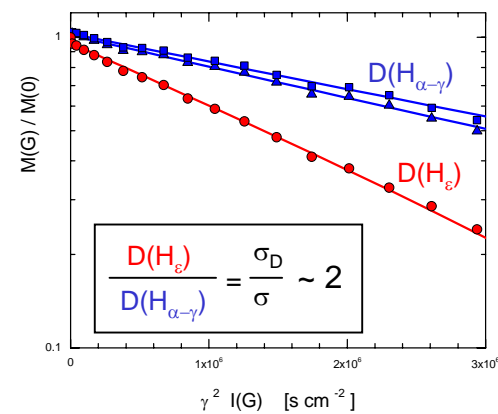
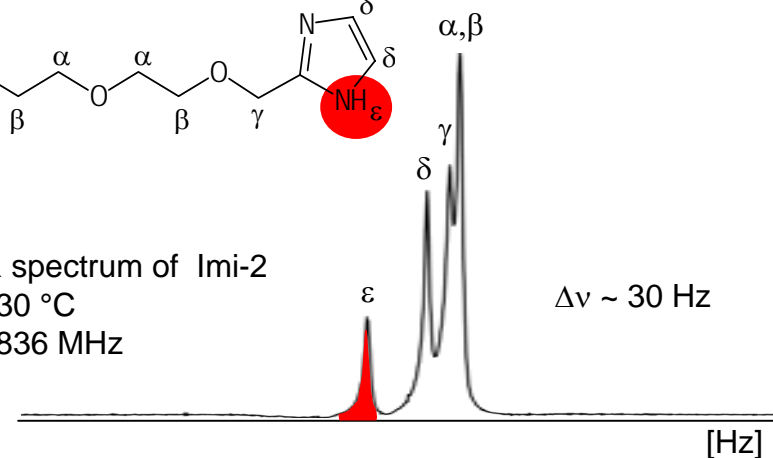
related observation:

compound	Haven ratio	
H <sub>3</sub> PO <sub>4</sub>	1.7	Dippel
NaOH	~ 100	Spaeth
Imi	~3-15	Schuster

## site-selective PFG-NMR

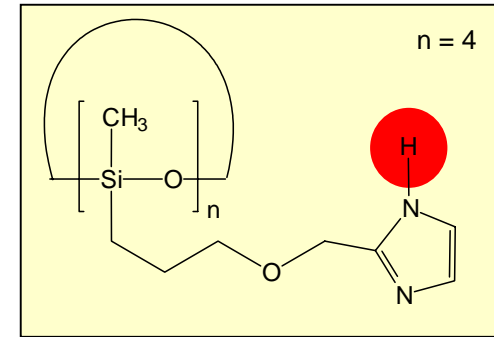
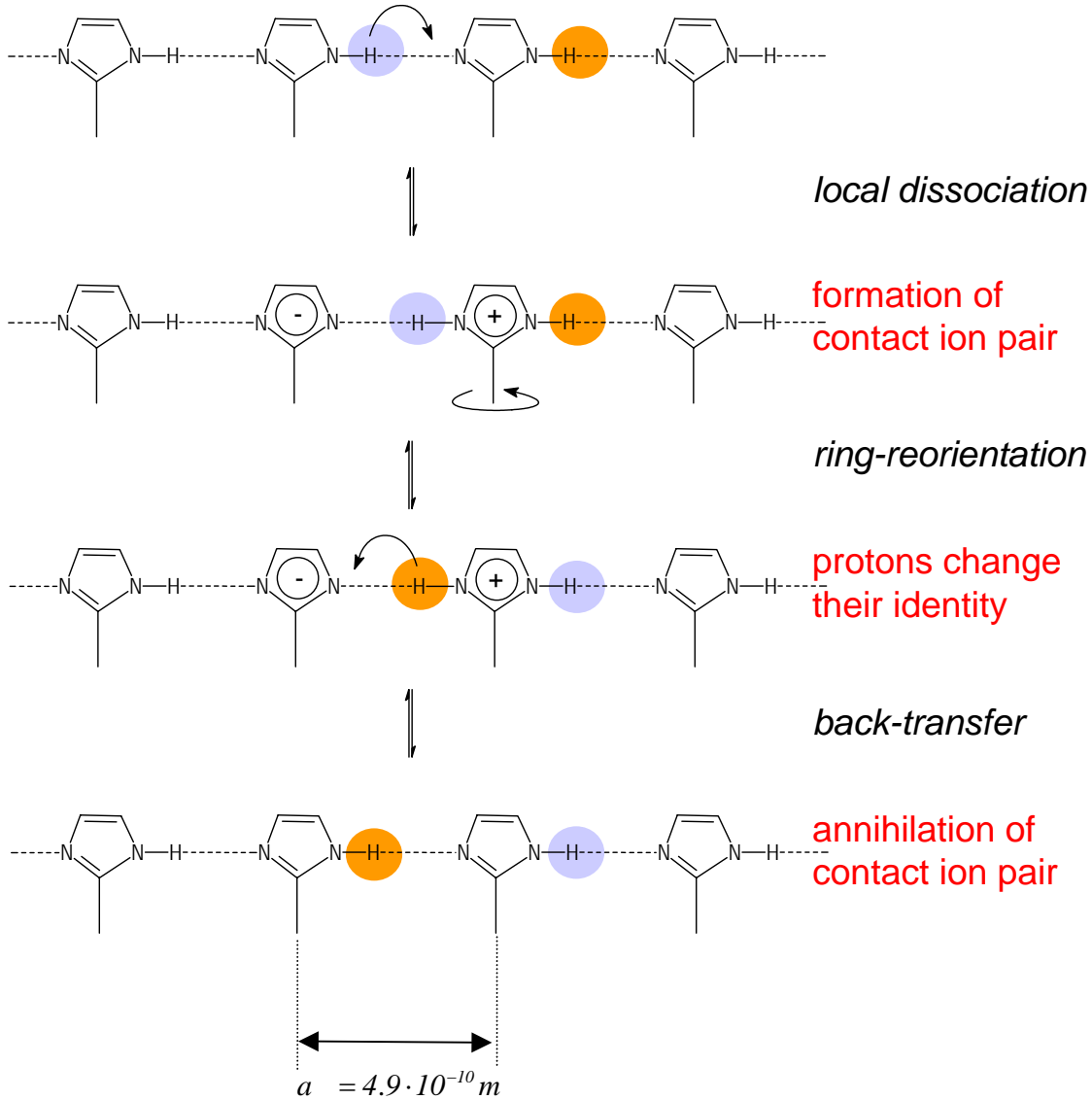


<sup>1</sup>H NMR spectrum of Imi-2  
at T = 130 °C  
ν<sub>0</sub> = 49.836 MHz

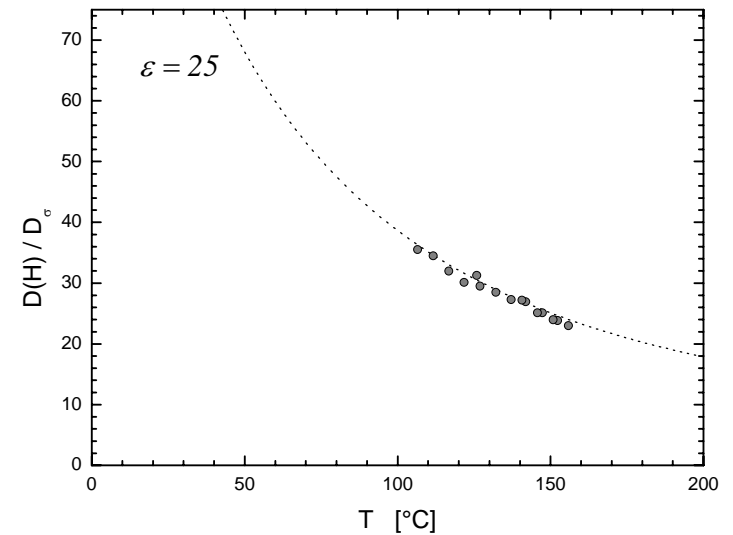




### proton diffusion without charge separation



rate ratio  $\exp\left\{\frac{e^2}{4\pi\epsilon\epsilon^0 akT}\right\}$



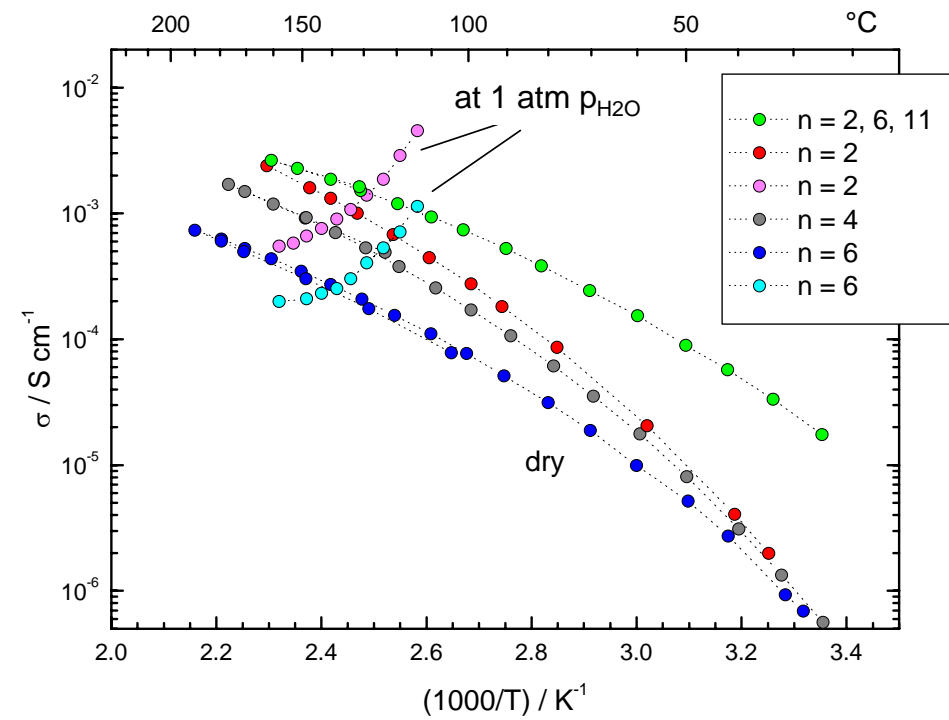
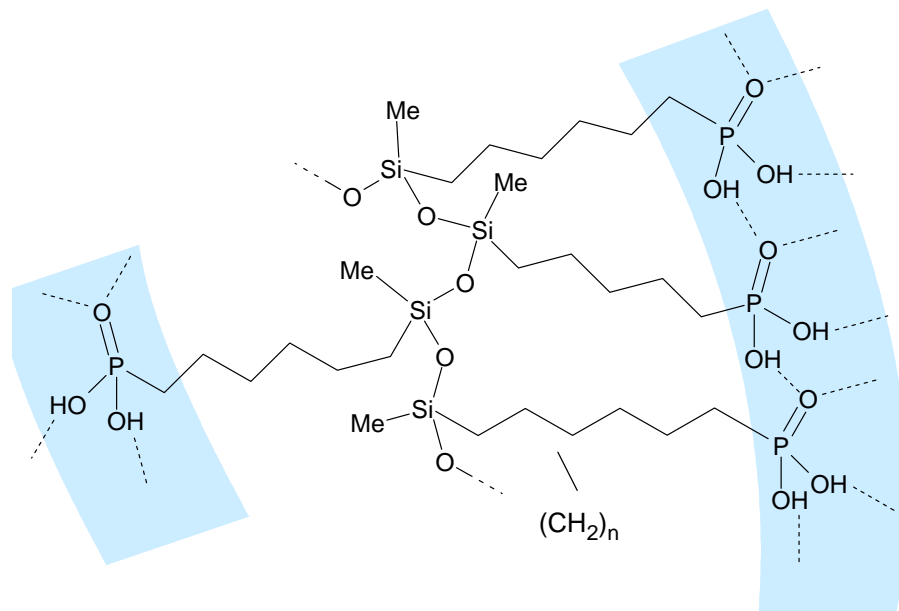
reorientation rate > separation rate



- increase of **amphoteric character**
- increase of **local dielectric constant**
- optimization of polymer architecture with respect to dynamical hydrogen bonding:
  - aggregation by hydrogen bonding
  - fast hydrogen bond breaking and forming processes (Umlagerung)



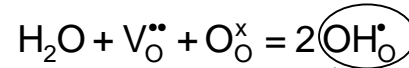
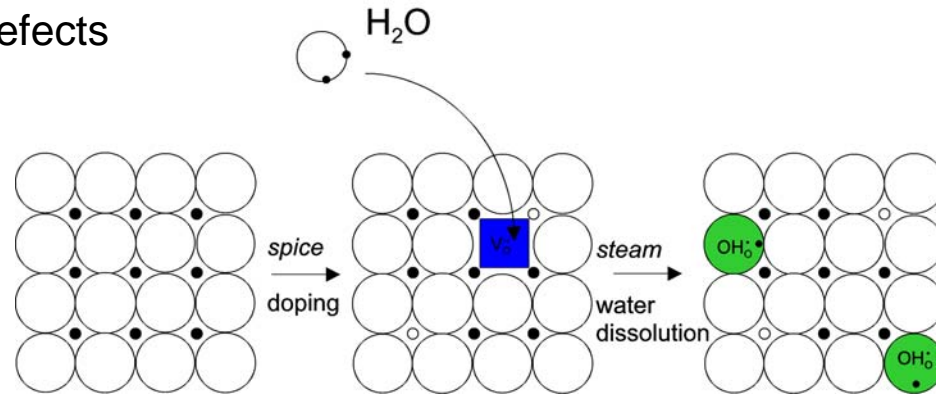
## phosphonic acid functionalized polymers



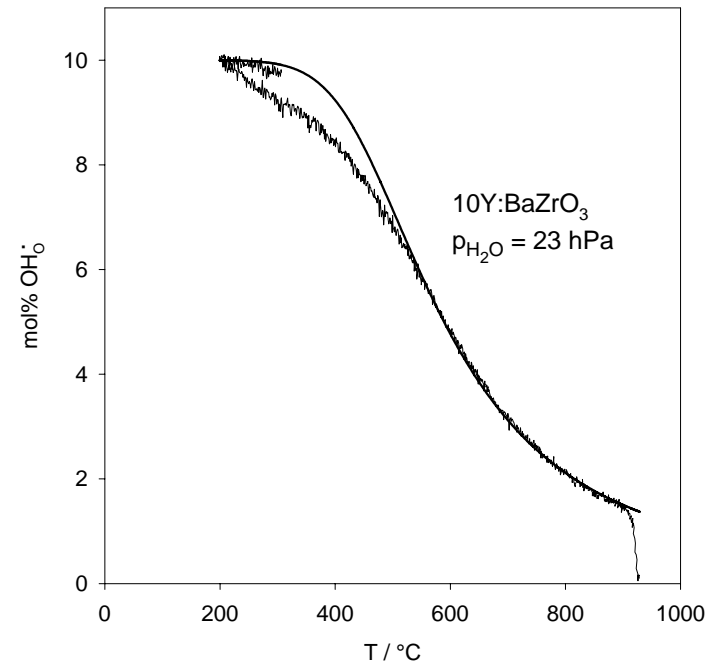
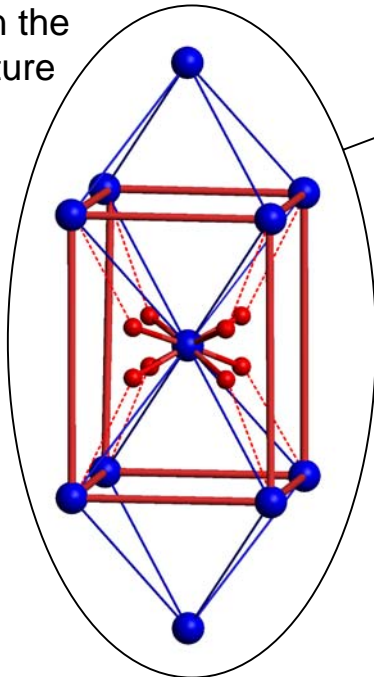


• proton conducting oxides

formation of protonic defects



protonic defects in the perovskite structure

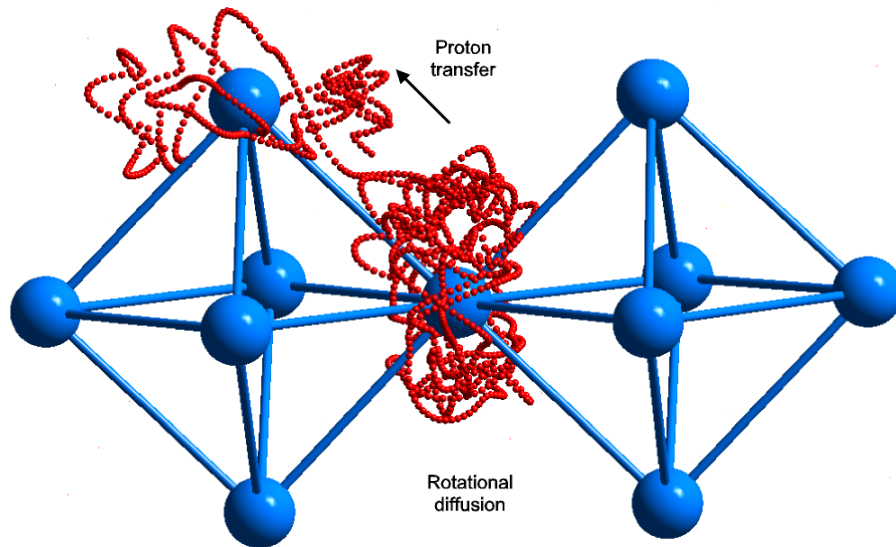




## mobility of protonic defects

rapid rotational diffusion of  $\text{OH}_0^\bullet$

strong hydrogen bonds

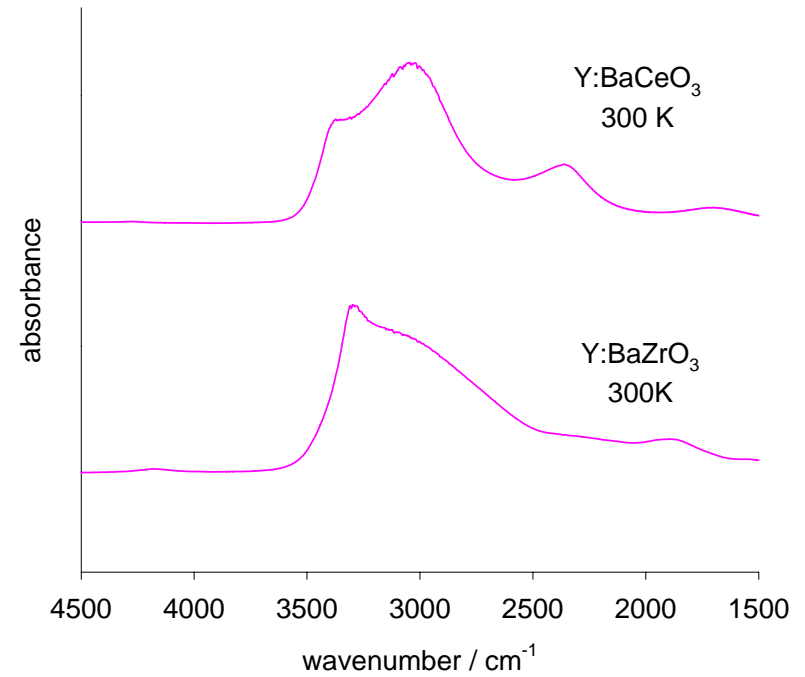


QNS

$\mu$ SR

quantum-MD

IR spectra of single crystals

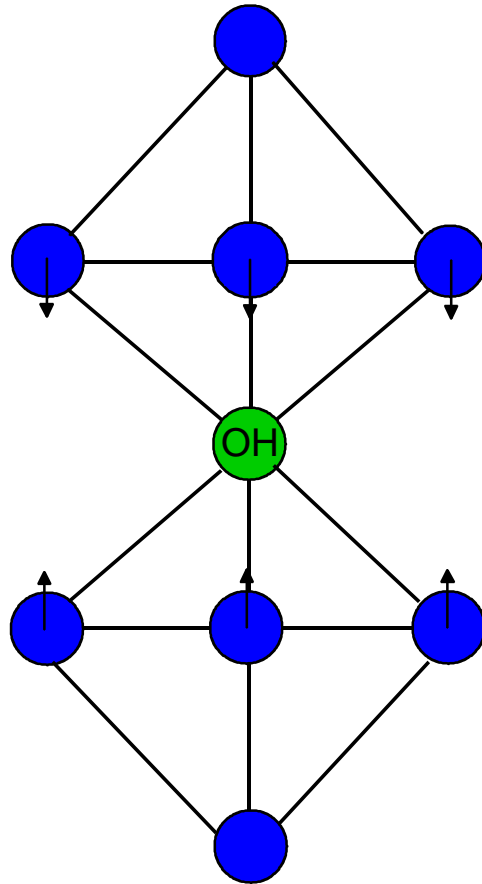


nature of hydrogen bonding?

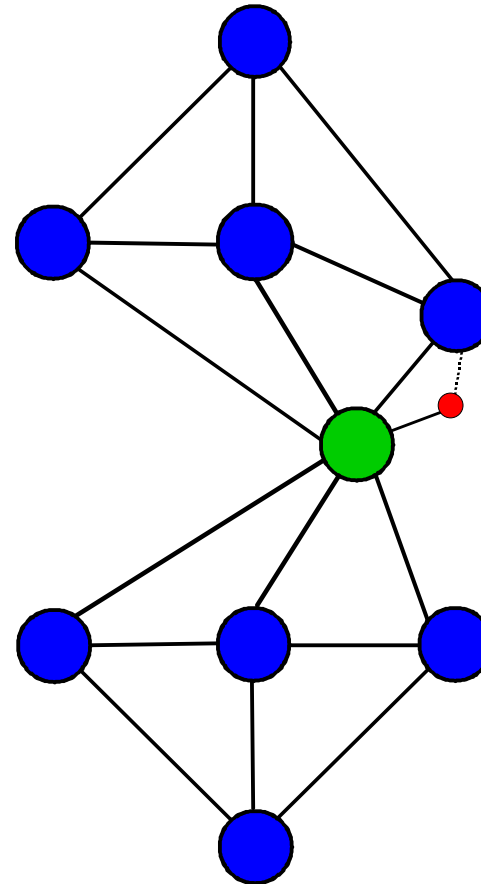




### formation of dynamical hydrogen bonds with all 8 nearest neighbours



average configuration

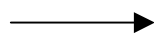
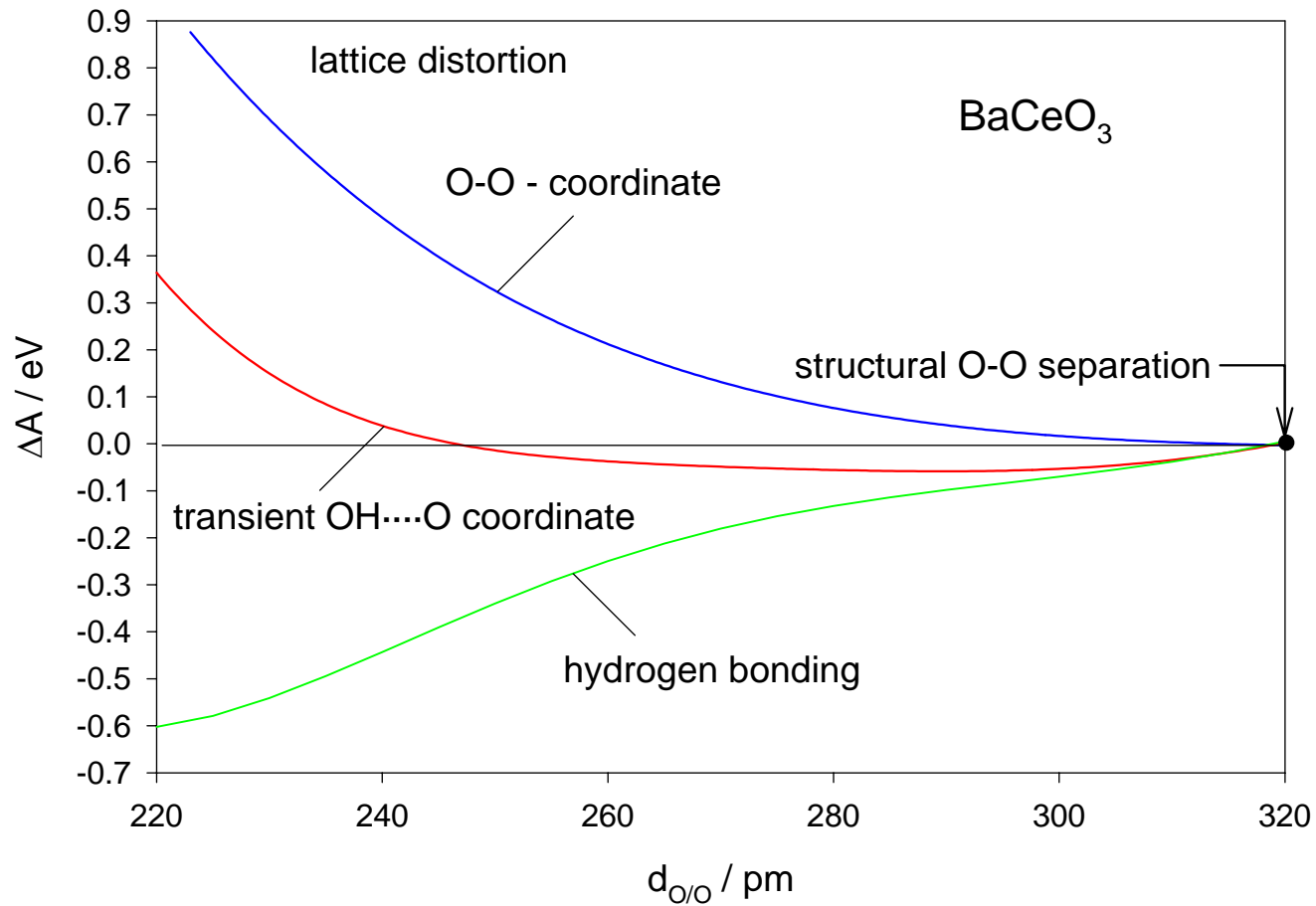


transition hydrogen bond (schematic)

- strong bend hydrogen bonds
- lattice distortion



## thermodynamics of hydrogen bond formation

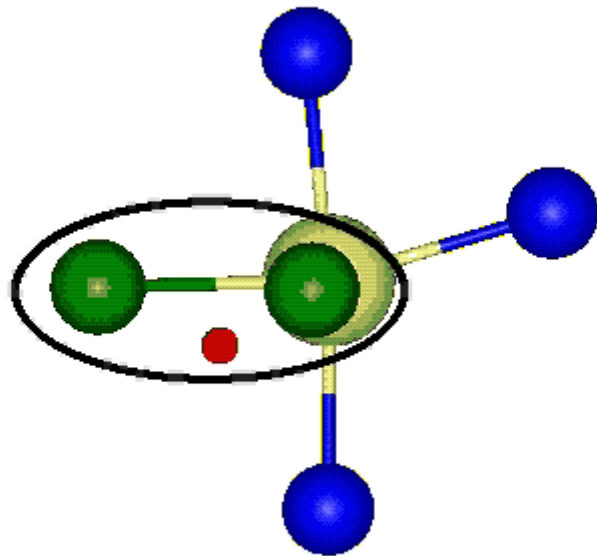


extended variations of OH / O separation (local lattice softening)

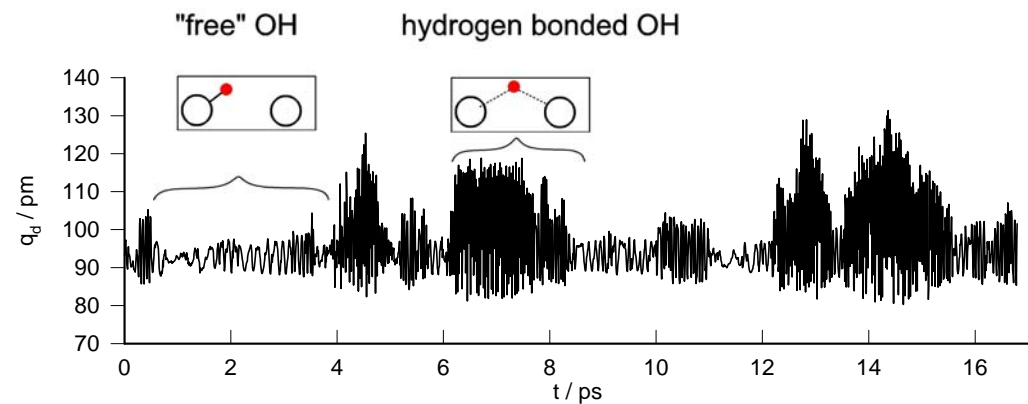


## dynamical hydrogen bond

### fluctuating hydrogen bond



$\text{SrTiO}_3$  ( $T=1800\text{K}$ )



variation of hydrogen bond strength leads to configurations which favors bond breaking and situations which favors proton transfer  
**"liquid-like dynamics"**

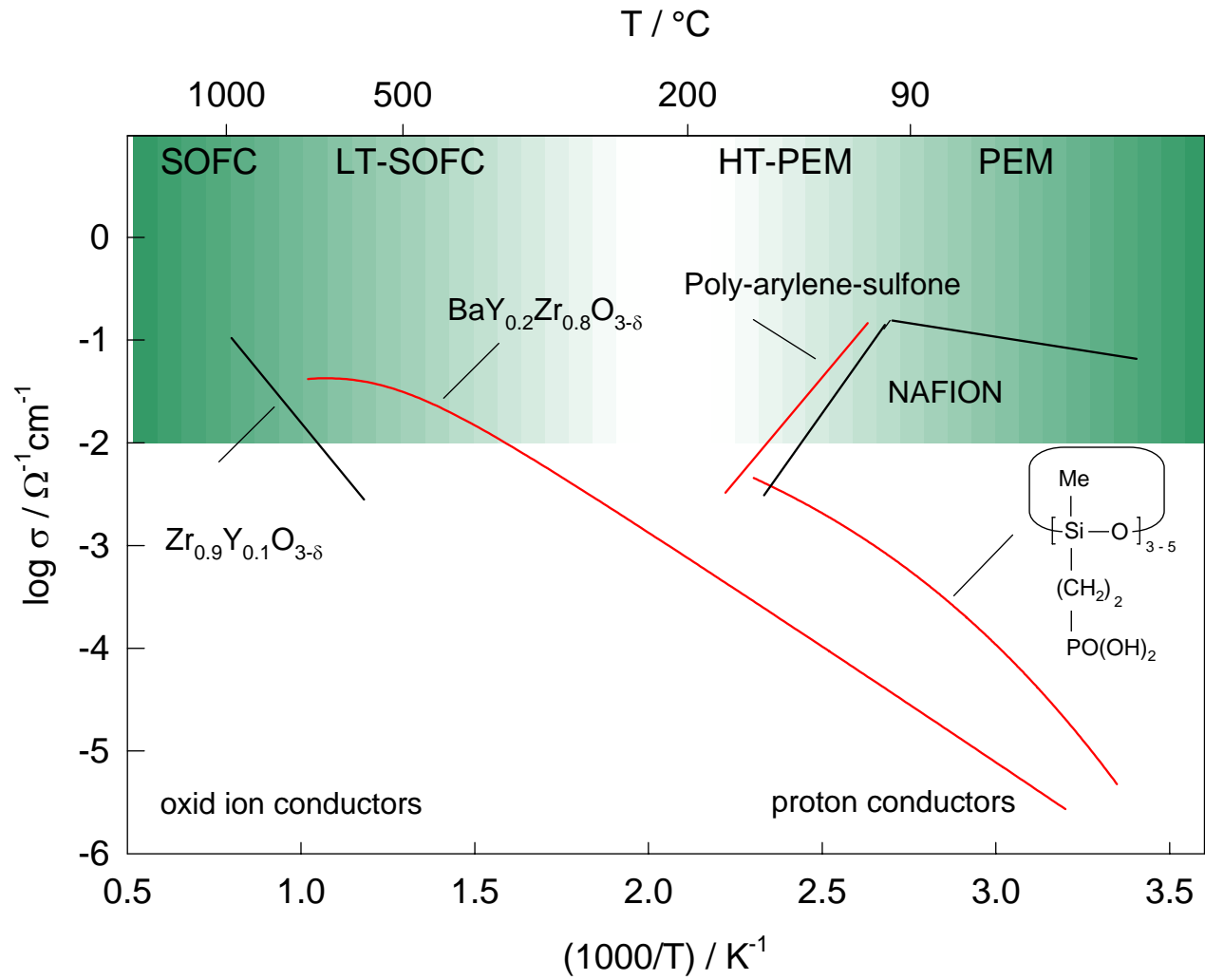


- balance hydrogen bond and covalent interaction
- maximize local symmetry



## Instead of a Summary I

closing the T-gap with new materials





Max-Planck-Institut für Festkörperforschung, Stuttgart

*Max-Planck-Institute for Solid State Research*

## Instead of a Summary II

- **dynamical hydrogen bonding:** the clue to the understanding of proton conductivity in the **liquid-** and **solid state**
- typical feature of bulky material



Max-Planck-Institut für Festkörperforschung, Stuttgart

Max-Planck-Institute for Solid State Research

**MPI - FKF**

A. Fuchs

U. Traub

M. Ise

M. Schuster

H.G. Herz

A. Noda

T. Rager

W. Münch

J. Maier (head of department)



**financial support**

G. Frank, Hoechst

R. Bauer, FuMaTech

M. Waidhas, Siemens

DFG

BMBF

Energiestiftung BW

**MPI -P**

W.H. Meyer

M.F. Schuster

G. Scharfenberger

**Uni Göttingen**

St. Adams

**Uni Dresden**

G. Seifert

**Motorola**

S.J. Paddison

**MPI - MF**

hosting nmr

