PROTON BEHAVIOR AT GLASS/WATER INTERFACES: IMPLICATIONS ON REACTIONS AND PROTON TRANSPORT

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OUTLINE

- Motivation
- Dissociative Water Potential
- Interactions between Water and Silica Surfaces
- Proton Transport in Water
- Proton Adsorption Sites and Lifetimes on SiO_2

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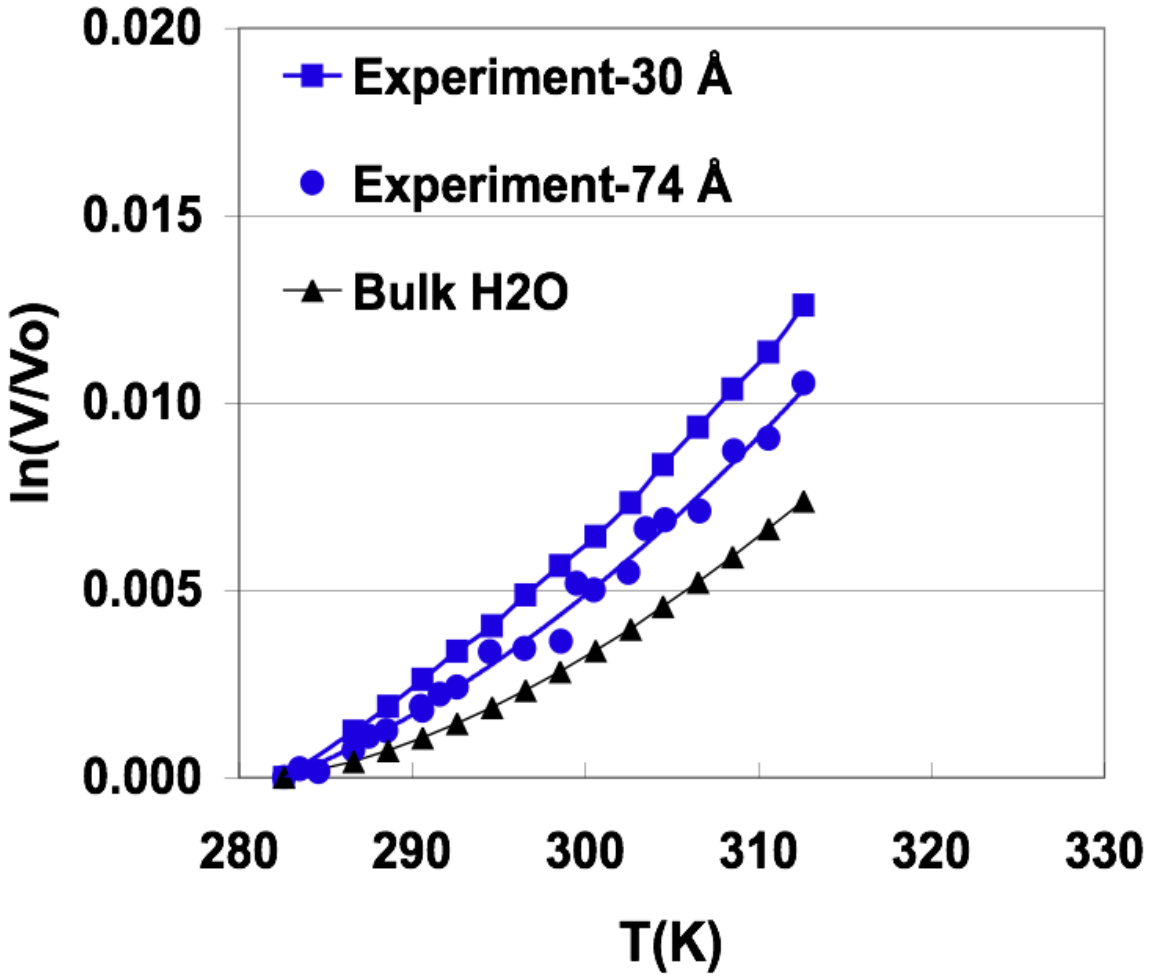
Motivation:

Experimental results regarding the surprisingly high thermal expansion of nanoconfined water.

But a second one developed based on our results that might be relevant to the electrochemical studies of Nogami, Abe, etc. showing high proton conductivity in nanoporous silica exposed to water.

ANOMALOUS EXPANSION OF NANOCONFINED WATER



Xu and Scherer, MRS Proc. Vol 790 2004

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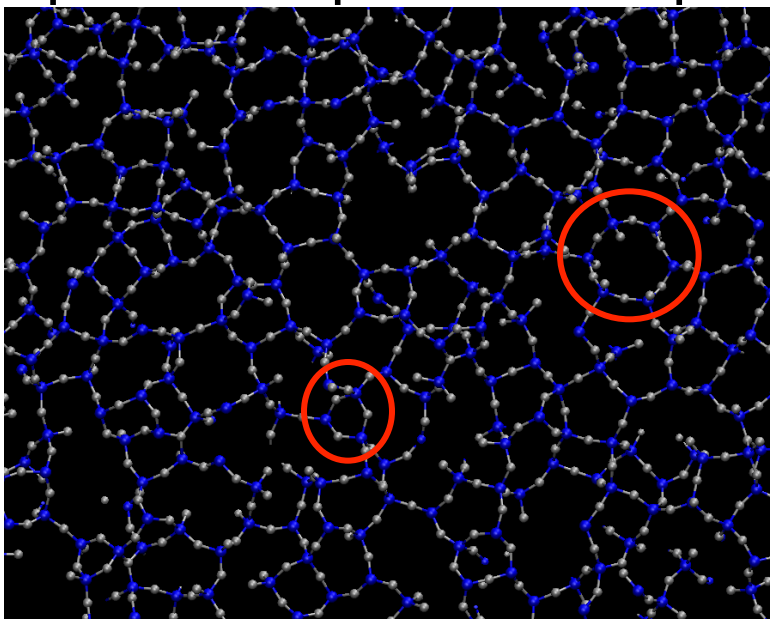
PREVIOUS SIMULATIONS OF WATER CONFINED IN SILICA PORES USED:

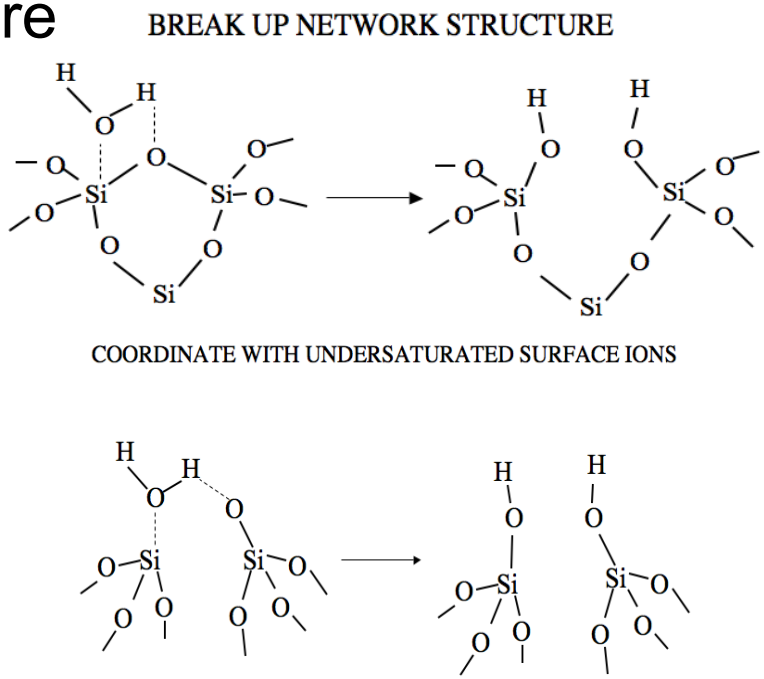
RIGID WATER MODELS (SPC/E, TIP4P, etc)

RIGID SILICA (glassy or crystalline)

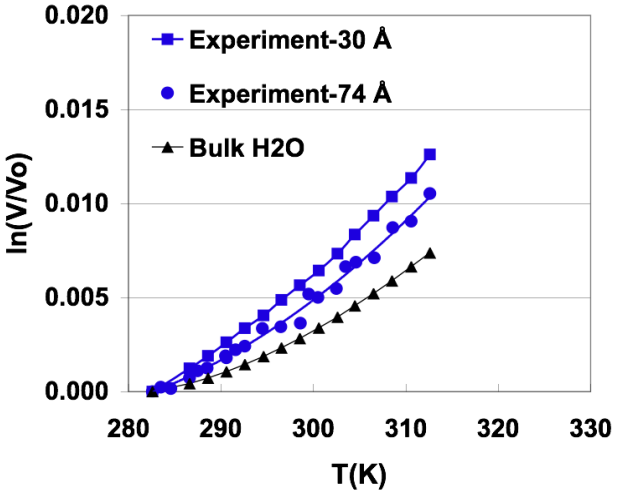
Milischuk et al. JCP(2012)
Shaik et al. JCP (2010)
Thompson et al JPC B (2007)
Giovambattista et al Phys Rev E (2006)
Wensink et al Langmuir (2000)
Ricci et al J Phys Cond Mat. (2000)
Spohr et al J. Molec Liq (1999)
Gallo et al Phil Mag (1999)

SiO_2 network ring surface structure (important in proton transport…)





NEED MORE REALISTIC POTENTIALS



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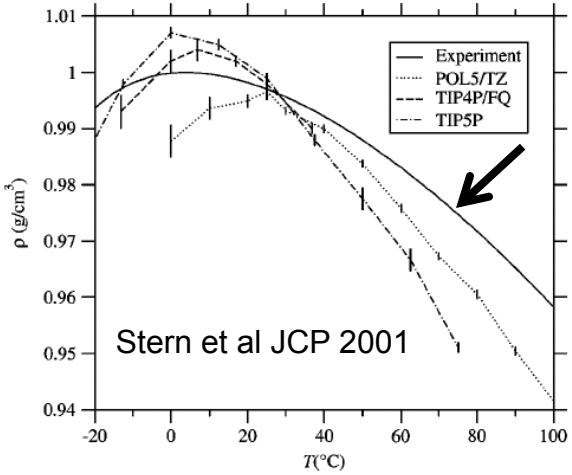
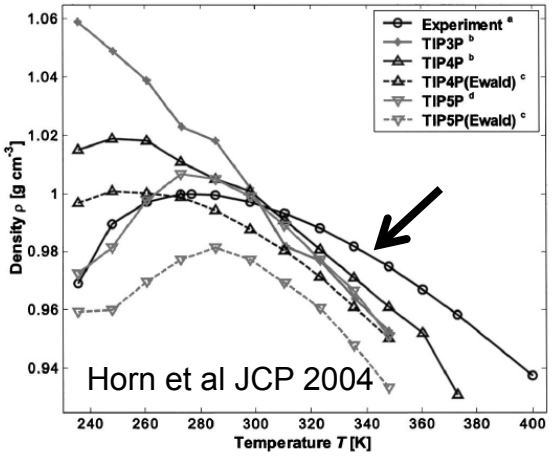
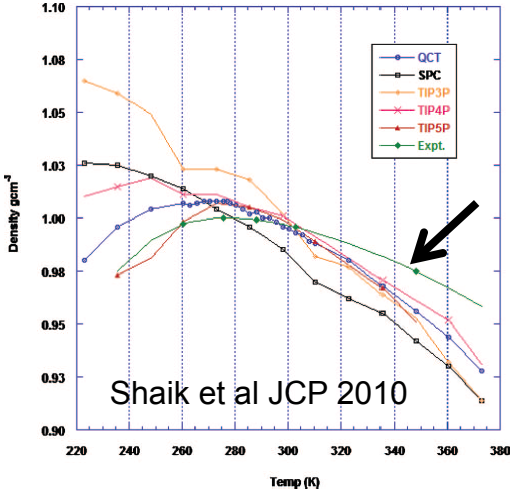
Spohr et al J. Molec Liq (1999)
Gallo et al Phil Mag (1999)

However, these popular models do not match liquid equation of state.







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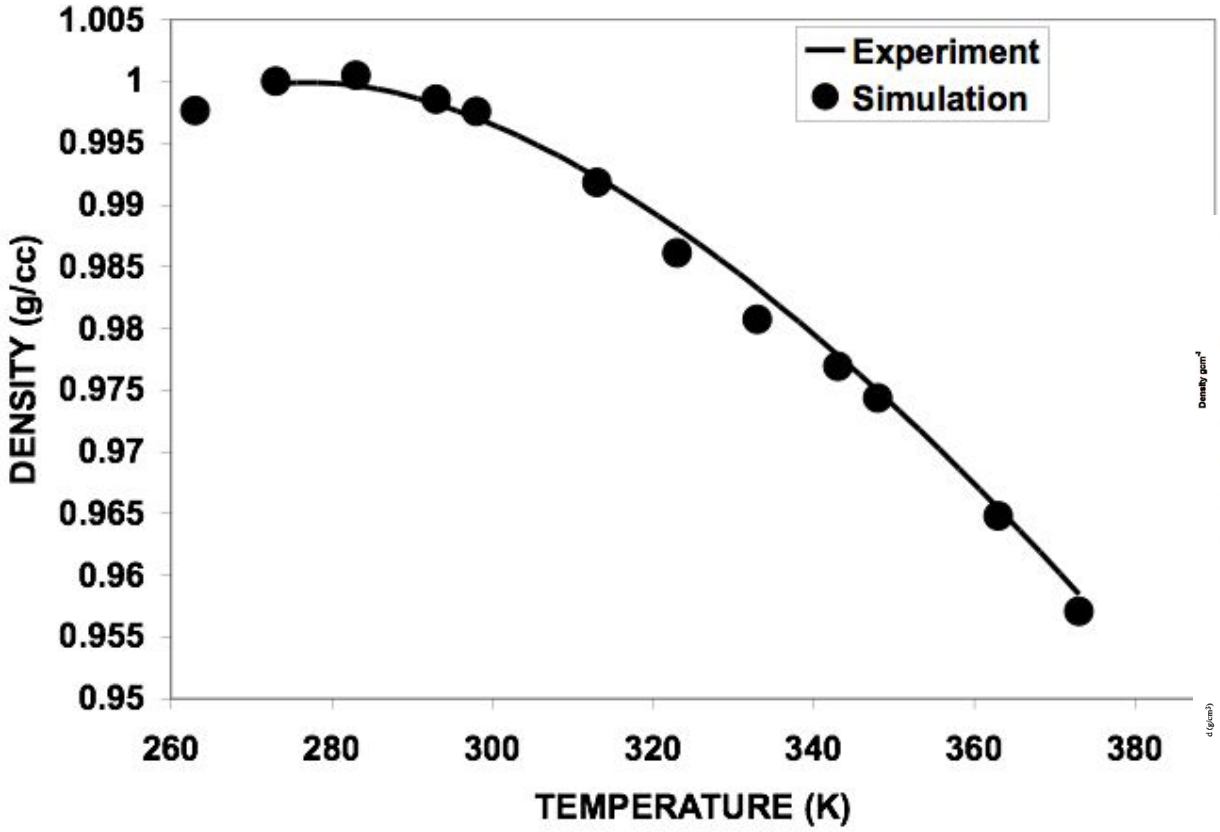
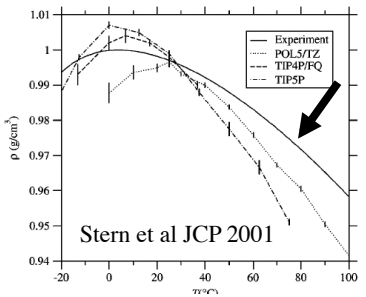
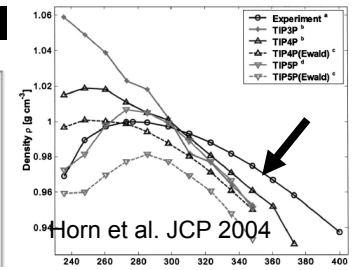
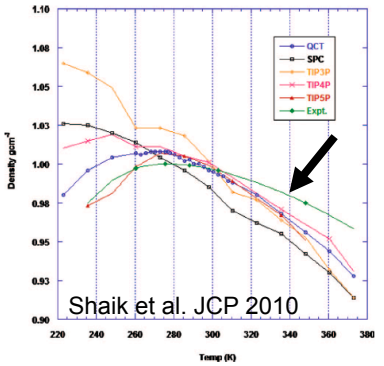
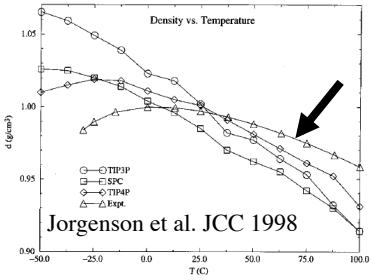
New Multibody Dissociative Water Potential











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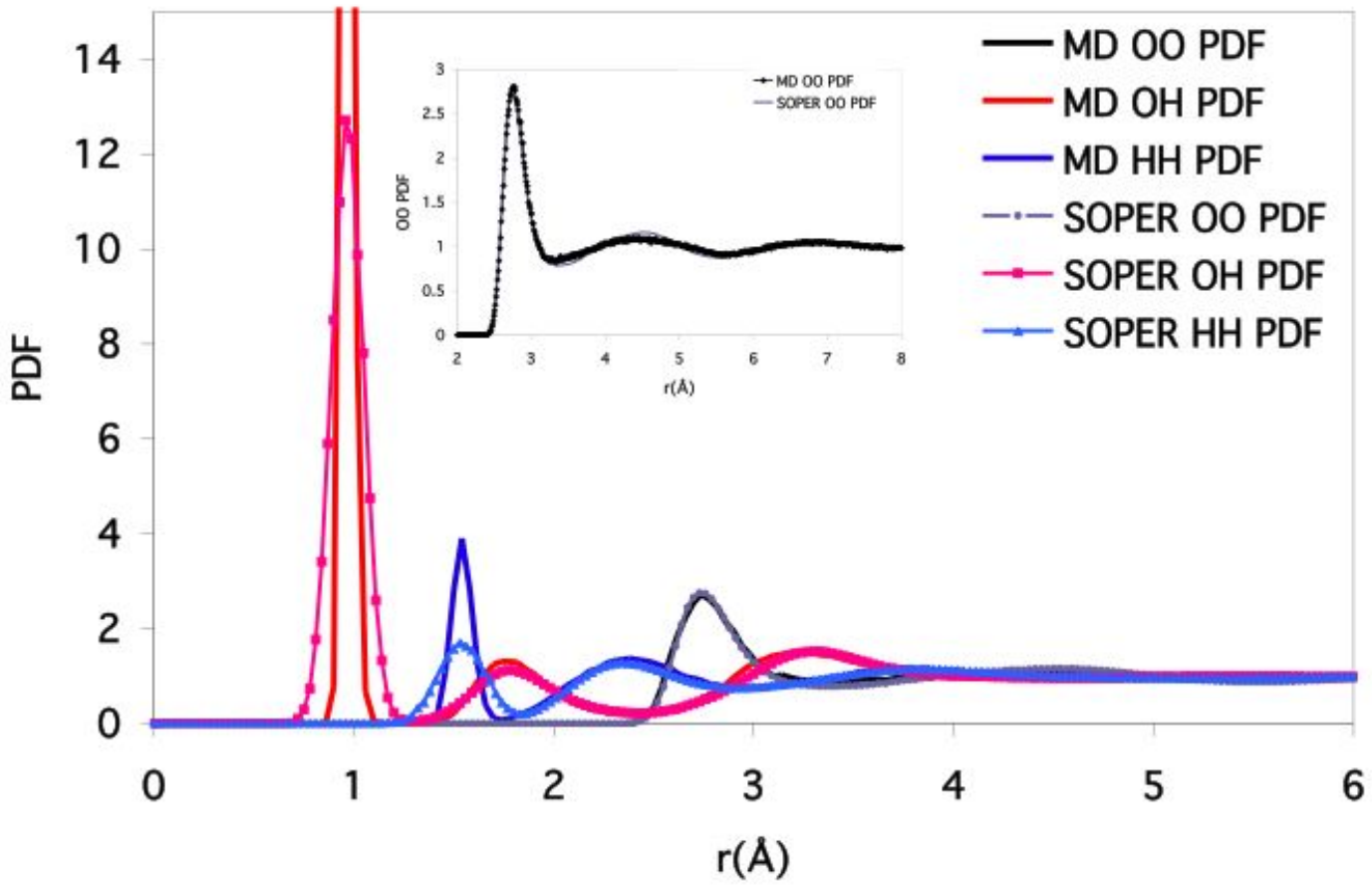

Soper, ChemPhys(2000)

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OTHER BULK WATER PROPERTIES
Our MD simulations vs other MD and experiment

	MD (here)	MD*	EXP
ΔH_{vap}^{exp} (kcal/mole)	10.5	10.0	10.5
μ (D)	2.6	2.1- 3.0	2.6
D (x10^{-5} cm^2/s) 298K	2.45	1.1- 5.0	2.3

* TIP4P, SPC/E and other models

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NEW WATER POTENTIAL MATCHES EXPERIMENTAL DATA:

LIQUID DENSITY-TEMPERATURE CURVE
STRUCTURE
FREQUENCY SPECTRUM
HEAT OF VAPORIZATION
DIPOLE MOMENT
DIFFUSION CONSTANT

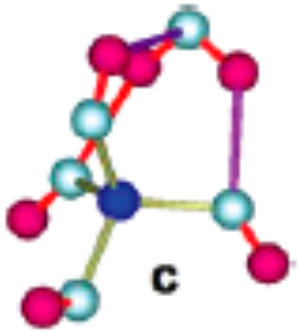
Mahadevan and Garofalini J Phys Chem B 111(2007)8919

Interactions between silicic acid molecule and a water molecule

Interaction energy

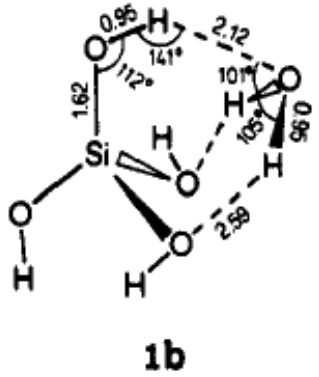
MD simulation

10.6 kcal/mole



ab-initio calculations*

9.0-11.6 kcalmole



•Pelmenschikov et al, JPC 96 (1992) 7422

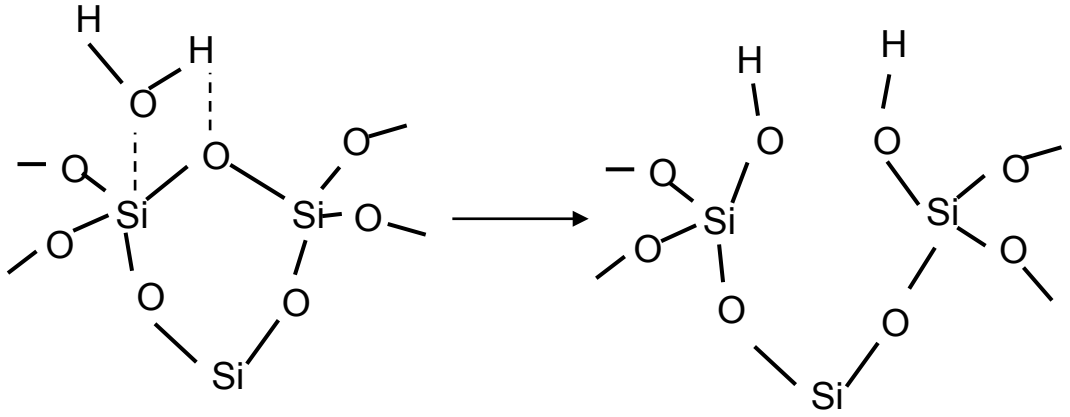
MO calc. gaussian, w and w/o MP2

Before we look at nanoconfined water,

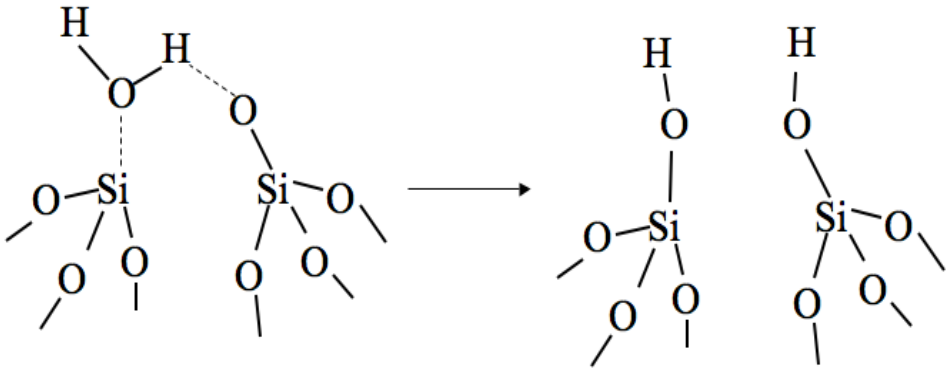
Expose silica glass surface to water vapor

Simulations show expected mechanisms commonly considered

BREAK UP NETWORK STRUCTURE



COORDINATE WITH UNDERSATURATED SURFACE IONS



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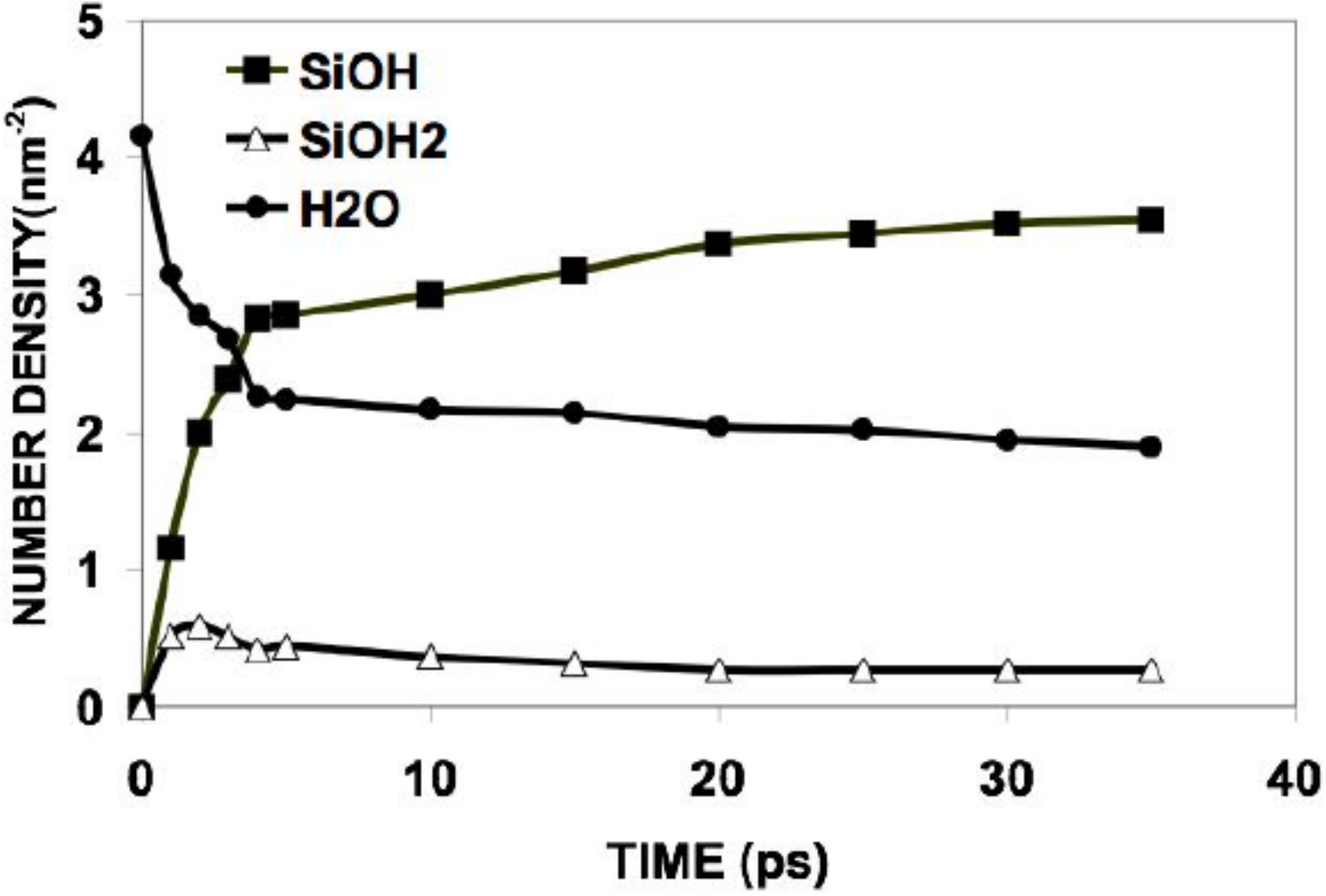
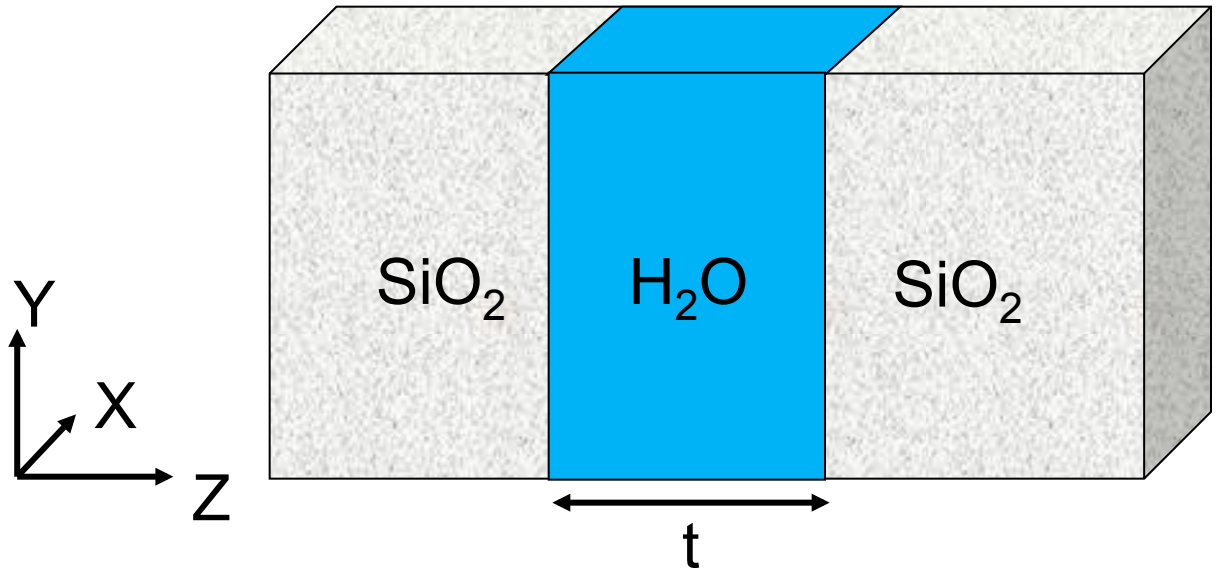
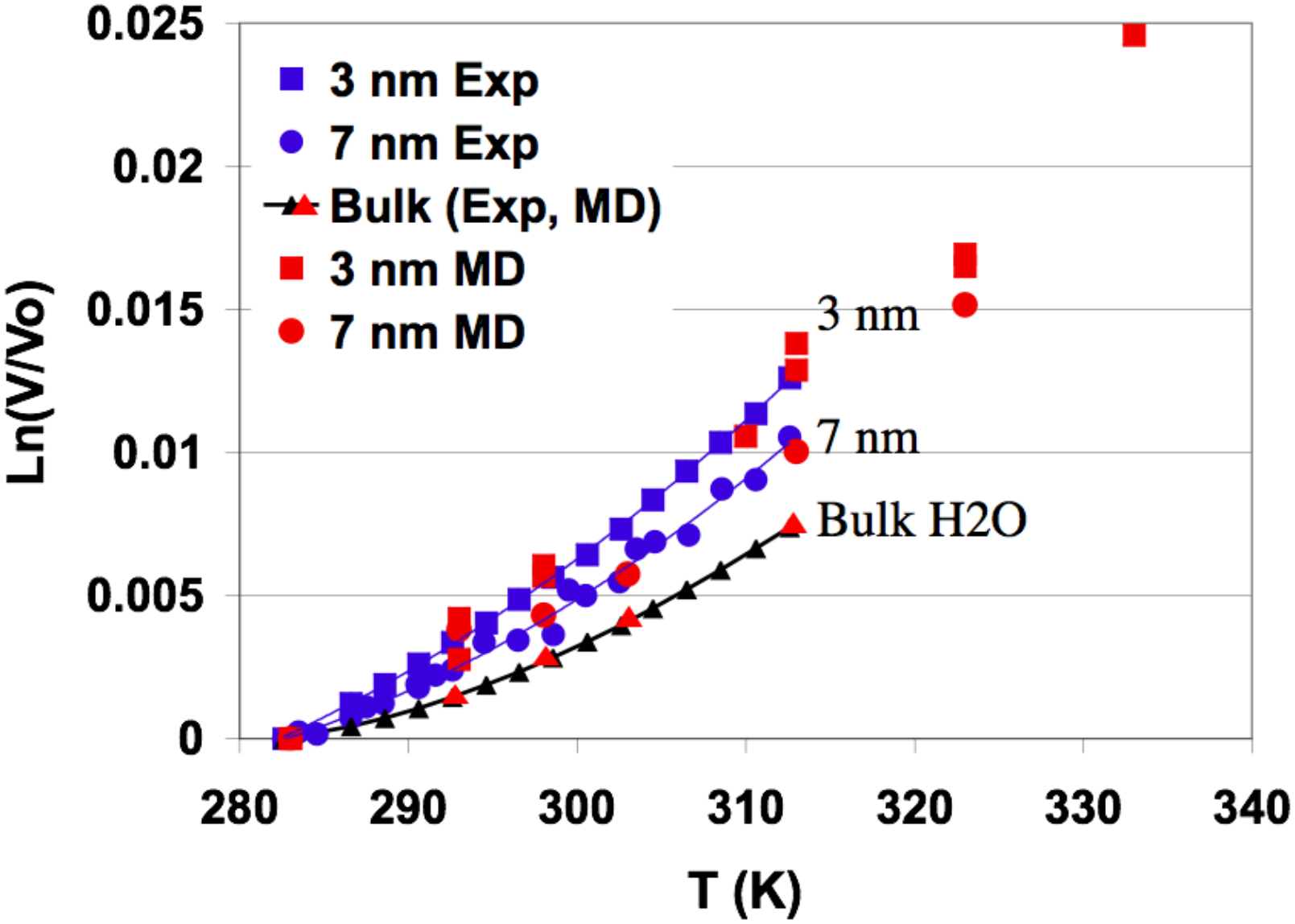
Silanol concentrations as a f(time) approach experimental results



Put water between silica slabs (t=3nm and t=7nm)
Heat to various Temperatures under 1 atm pressure





Garofalini et al ChemPhysChem2008, Xu et al Langmuir 2009.

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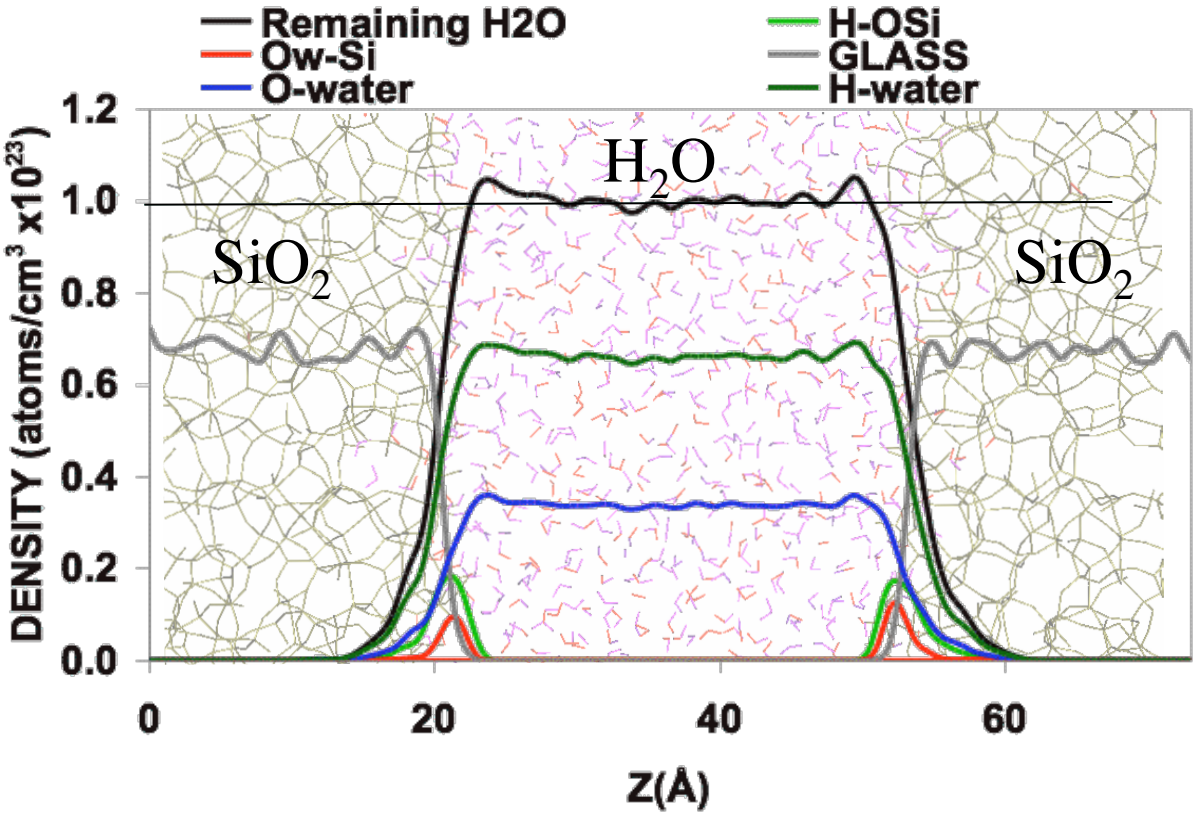

Garofalini et al ChemPhysChem 9 (2008), Xu et al Langmuir (2009).

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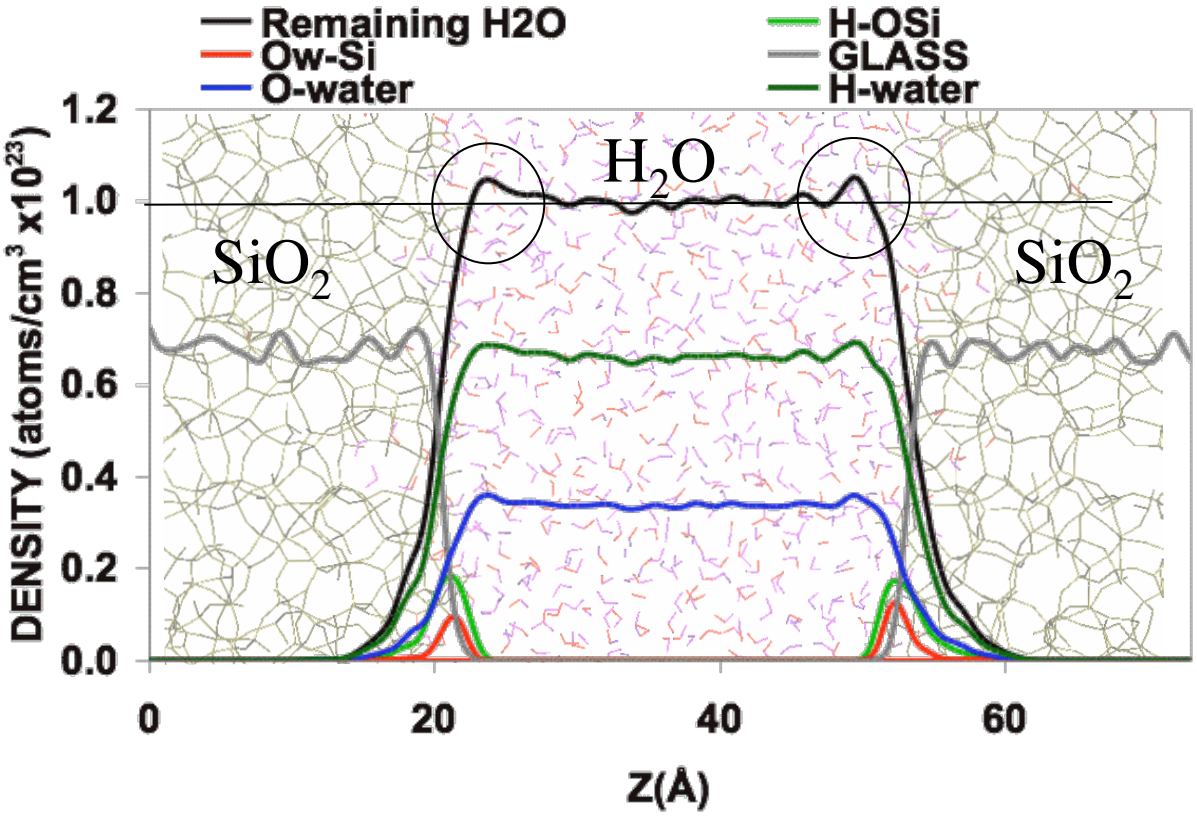
Density near interface plays significant role in expansion behavior



Garofalini et al ChemPhysChem 9 (2008), Xu et al Langmuir (2009).

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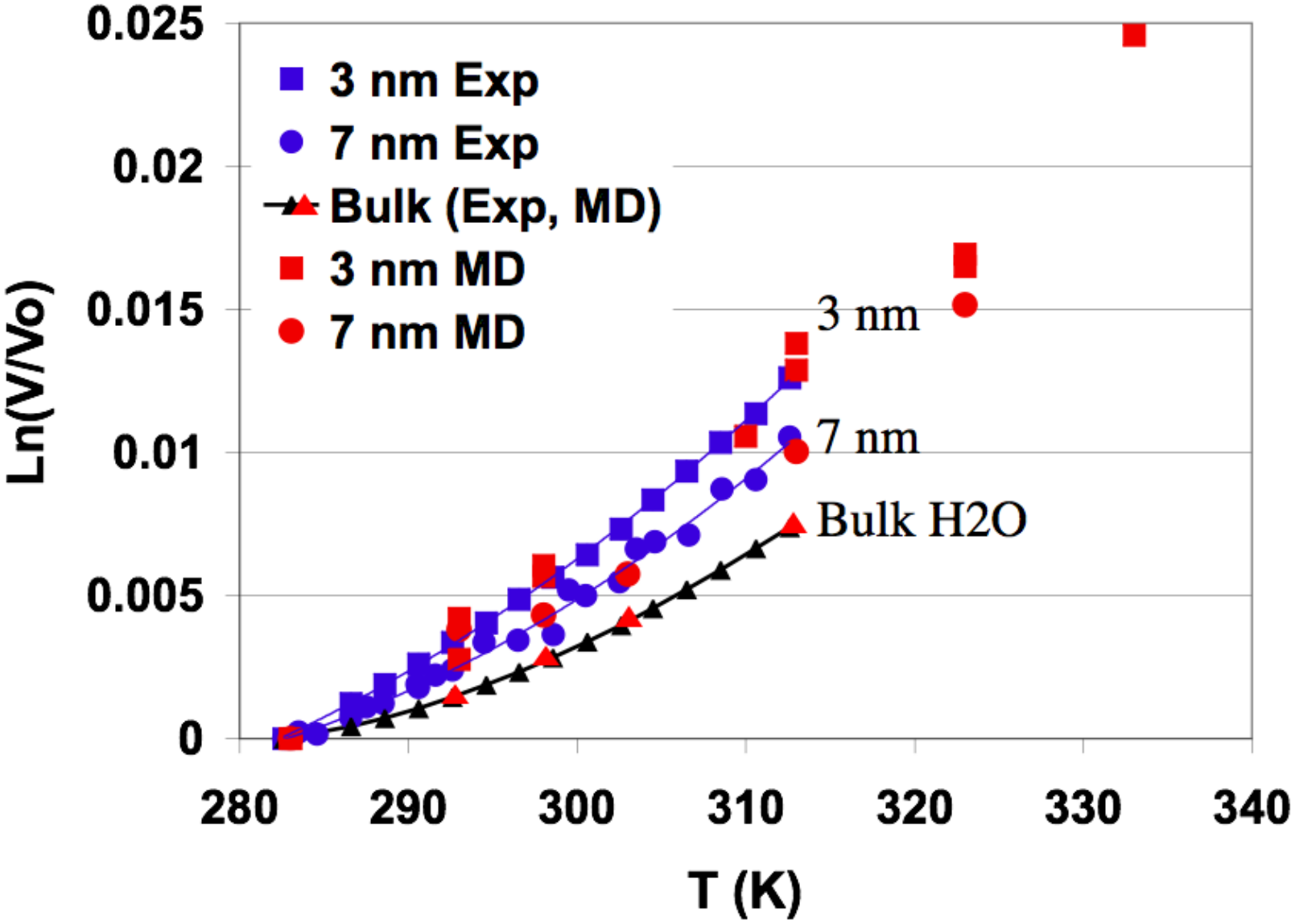
Minassian et al* showed that the CTE of bulk water increases as Pressure (density) increases.

Increase Density, Increase CTE

*Minassian et al JCP 75 (1981) 3064



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NEW WATER POTENTIAL MATCHES EXPERIMENTAL DATA:

LIQUID DENSITY-TEMPERATURE CURVE
STRUCTURE
FREQUENCY SPECTRUM
HEAT OF VAPORIZATION
DIPOLE MOMENT
DIFFUSION CONSTANT

and

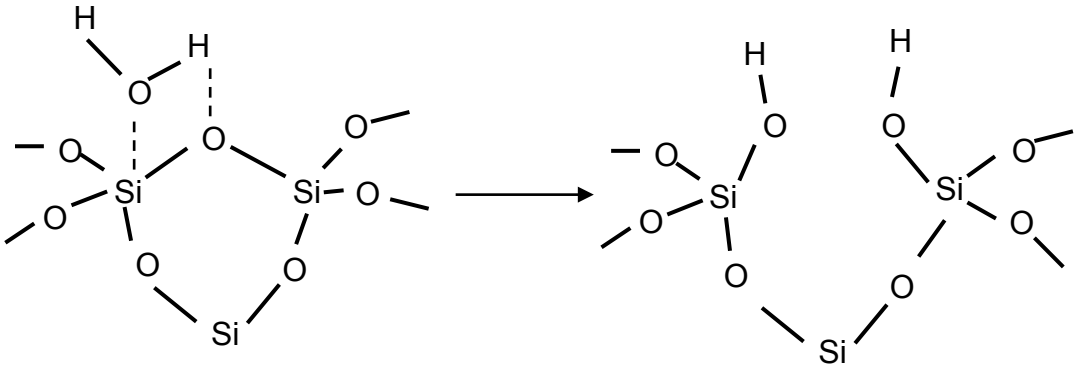
TRANSFERABLE TO NANOCONFINED WATER

Simulations reproduce many features seen experimentally for bulk water and is transferable to nanoconfined water.

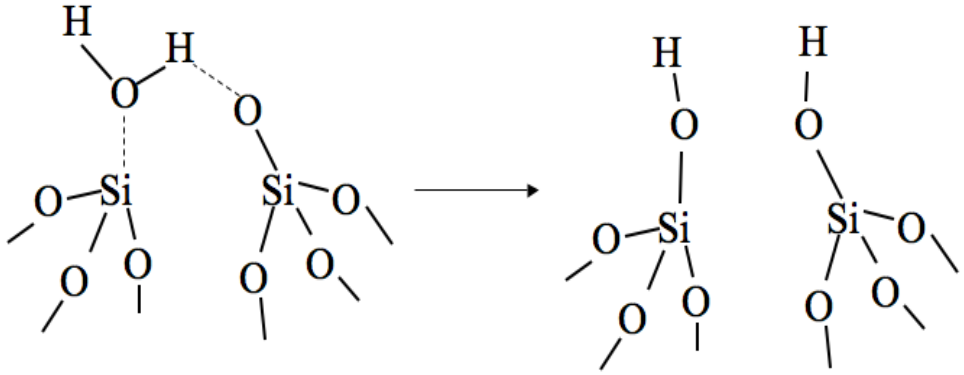
However, what are the molecular mechanisms of the reactions occurring in the simulations causing the silanol sites and how does this affect proton transport?

Simulations also show additional reaction mechanisms beyond these obvious ones

BREAK UP NETWORK STRUCTURE



COORDINATE WITH UNDERSATURATED SURFACE IONS



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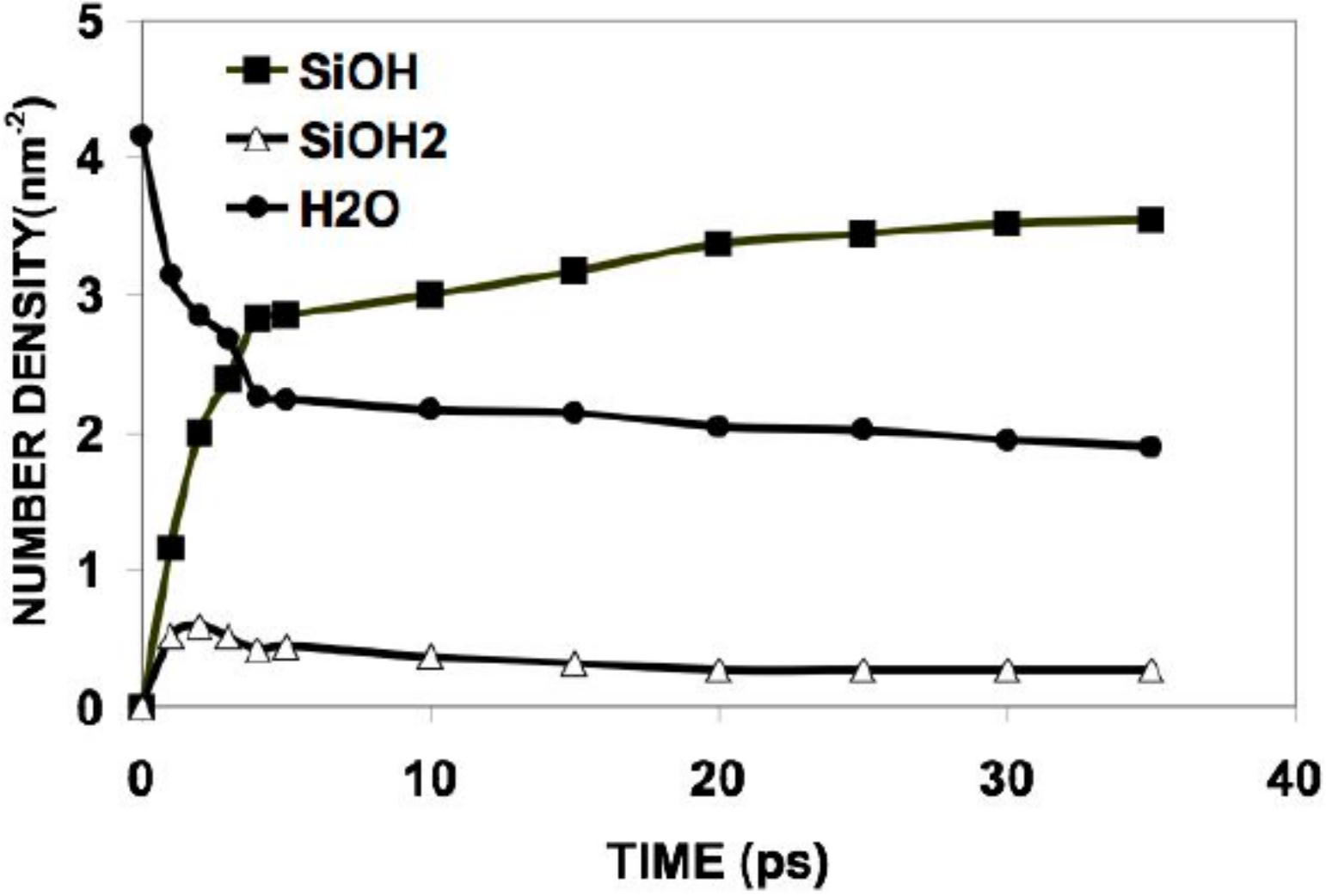
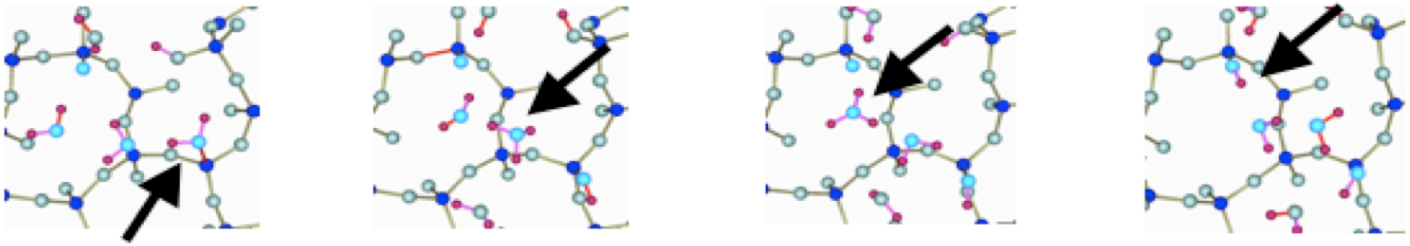
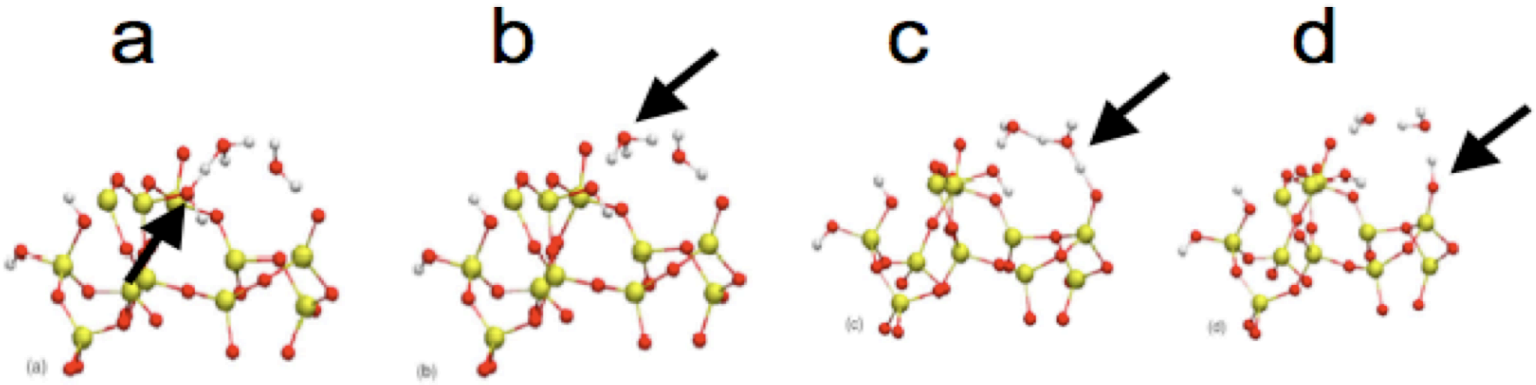


H_3O formation at silica surface

MD



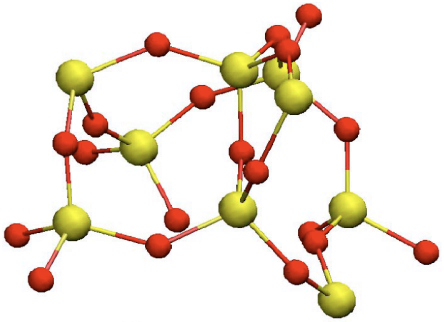
AIMD



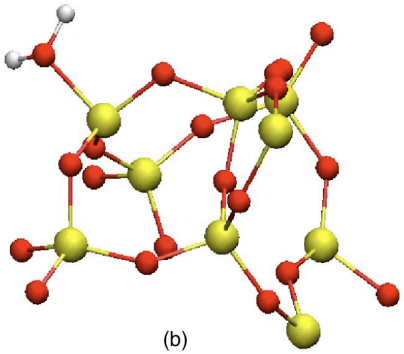
Each takes ~150 fs

MD simulations match AIMD simulations

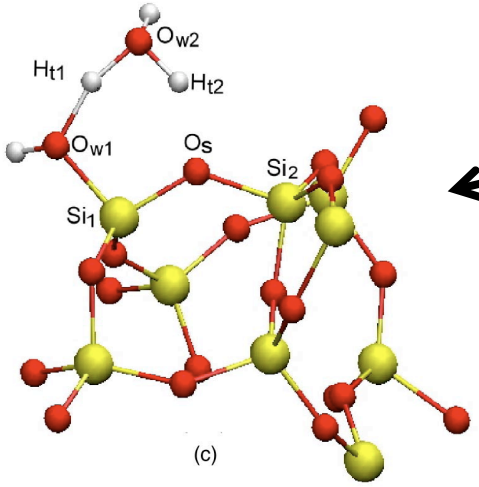
MD Mahadevan and Garofalini, JPCC 2008
AIMD Ma et al, JCP2005



(a)



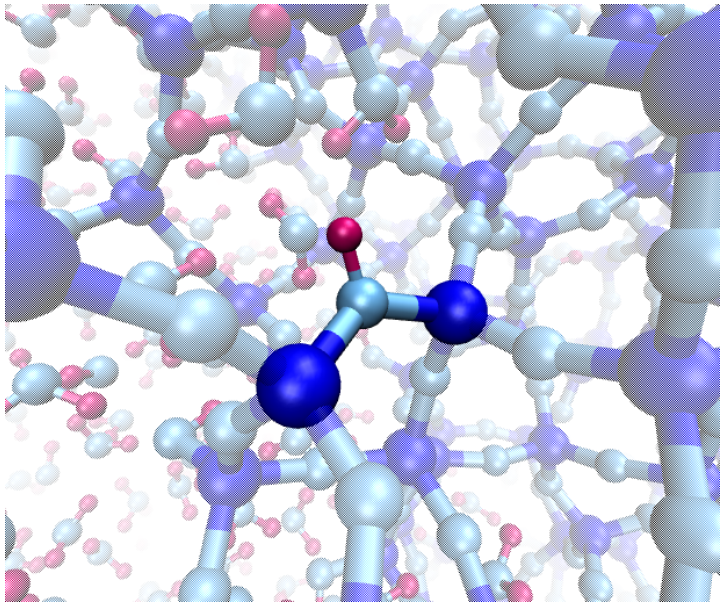
(b)

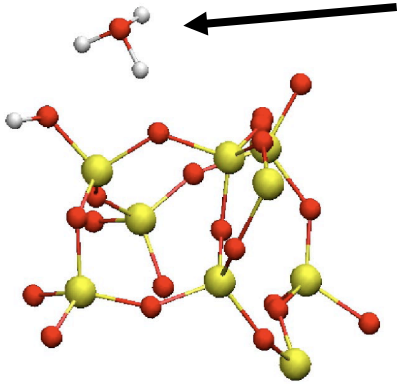


(c)

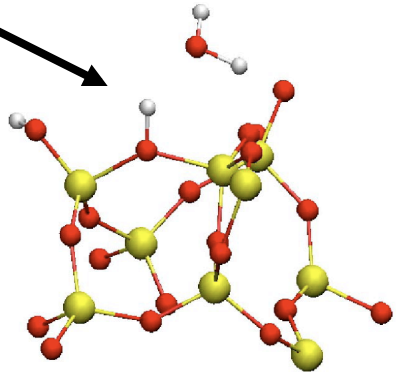
AIMD

MD





(d)



(e)

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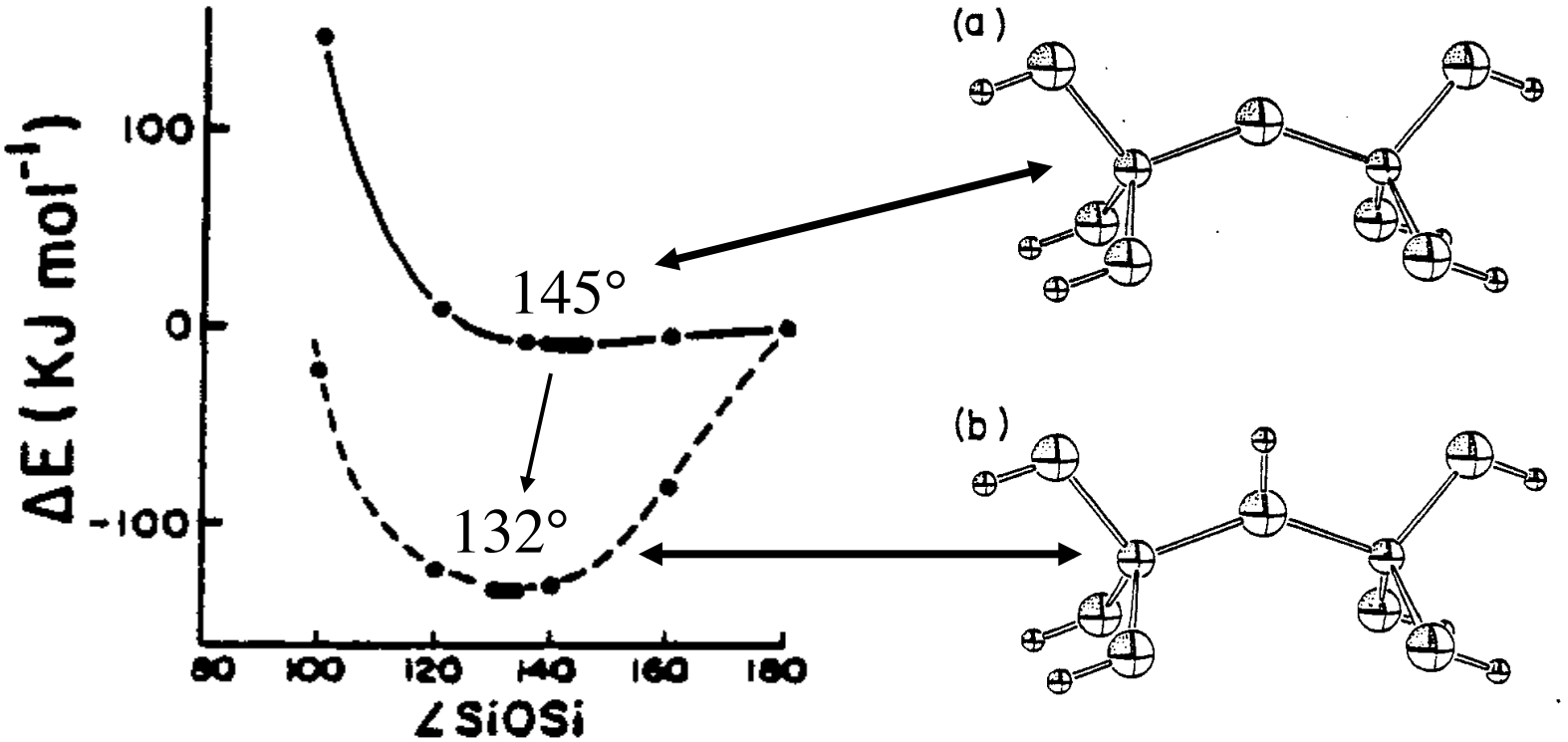

Geisinger, Gibbs, Navrotsky PhysChemMiner 11(1985)266
Van Heusden et al, IEEE Trans. Nucl. Sci. 46 (1999) 1562

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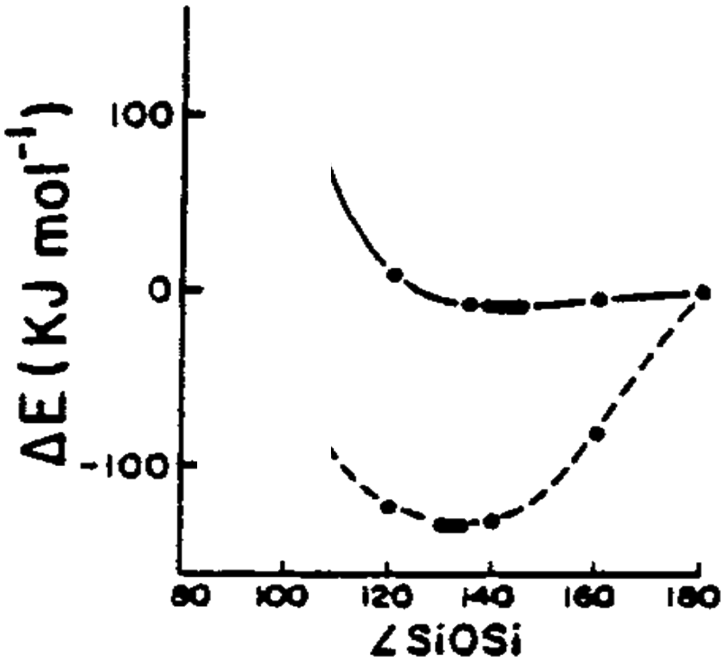
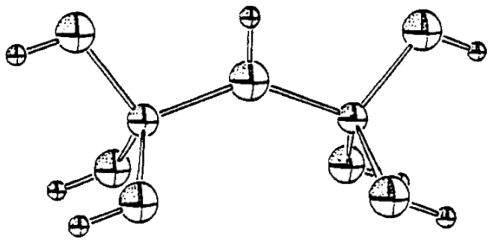
Energy vs. Angle

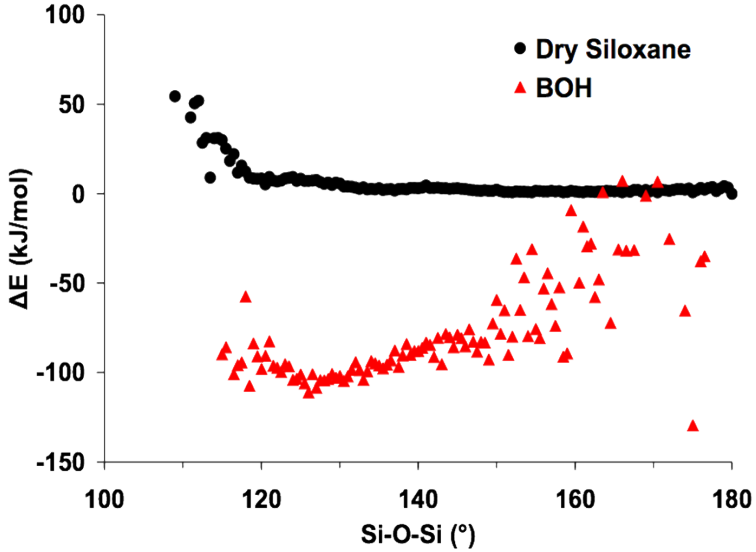
Molecular Orbital (QM)

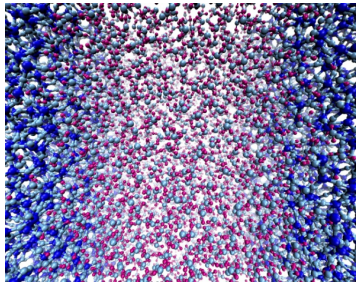




Geisinger et al., Phys. Chem. Miner. 11 (1985) 266.

Our MD





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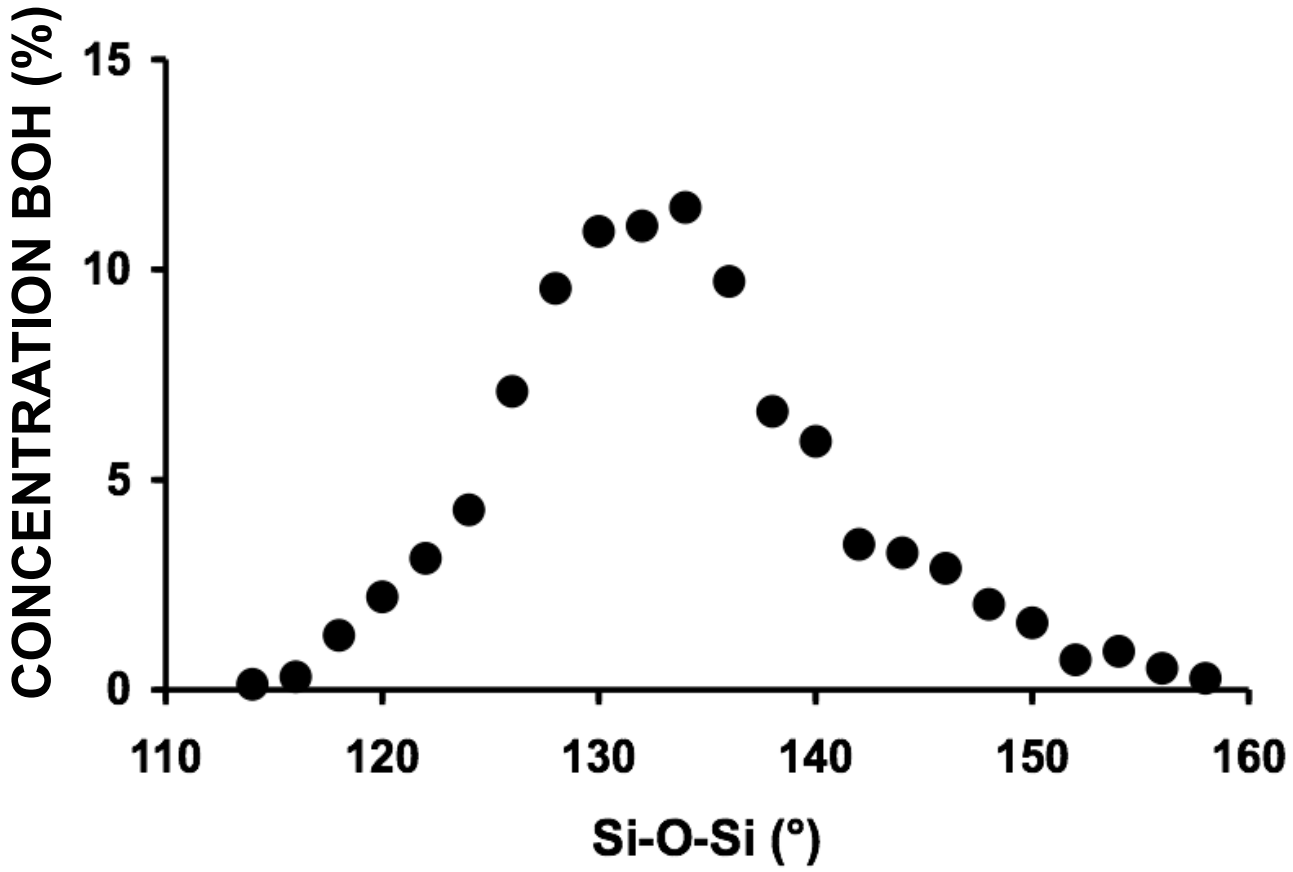


Soooo…

We have protons on bridging oxygen sites,

protons on $SiOH_2$ sites,

and protons on SiOH sites

And excess H_3O ions near the interface.

We need to know how well the simulations reproduce proton transport (PT) in bulk water.

Therefore, we need to add an H_3O ion to bulk water…

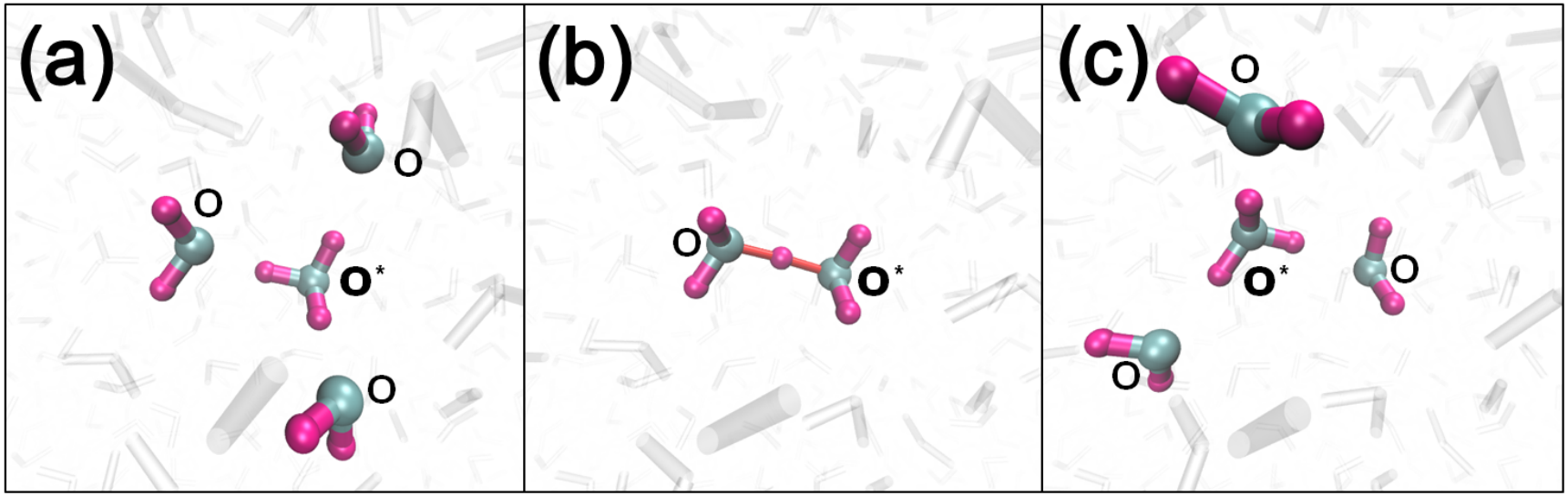
But we first need some background regarding PT in water

Lot's of background regarding Proton Transfer in water

But real molecular data comes from ab-initio MD simulations (AIMD) and classical simulations specifically designed for studying proton transport, the most advanced being MS-EVB models

So, we'll compare to those.

PROTON TRANSPORT IN WATER

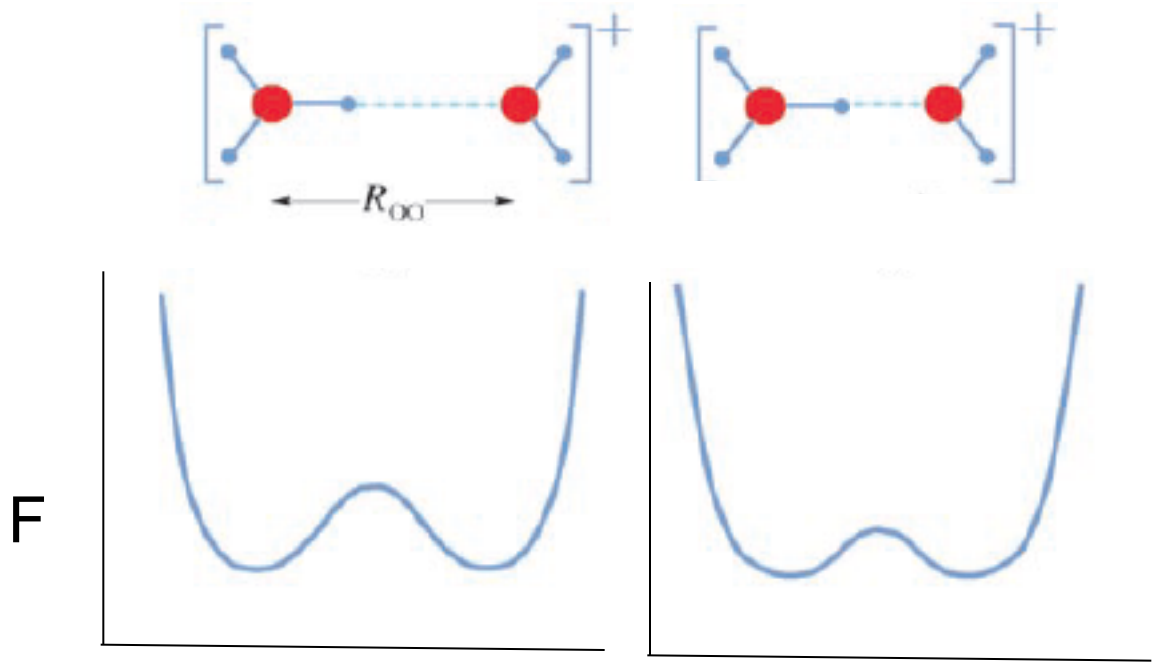


Eigen
$H_9O_4^+$

Zundel
$H_5O_2^+$

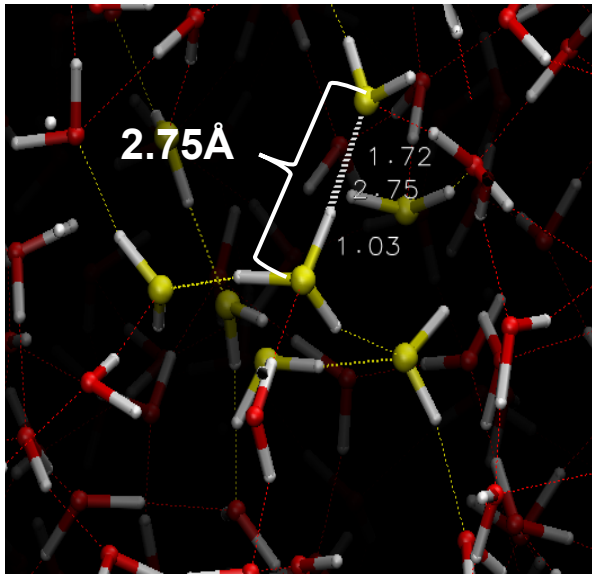
Eigen
$H_9O_4^+$

Free Energy decreases with decreasing O-O separation distance

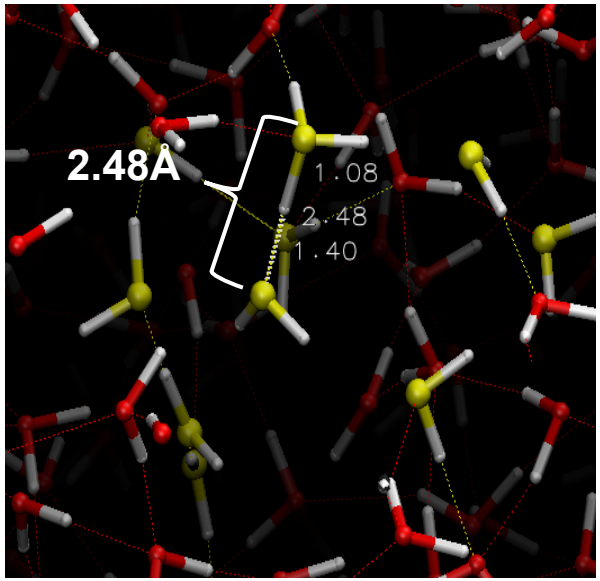


Marx CPC 2008

Our MD Simulations
H_3O^+ IN BULK WATER



Eigen



Zundel

MATCHES PROTON TRANSPORT VIA EIGEN AND ZUNDEL COMPLEXES

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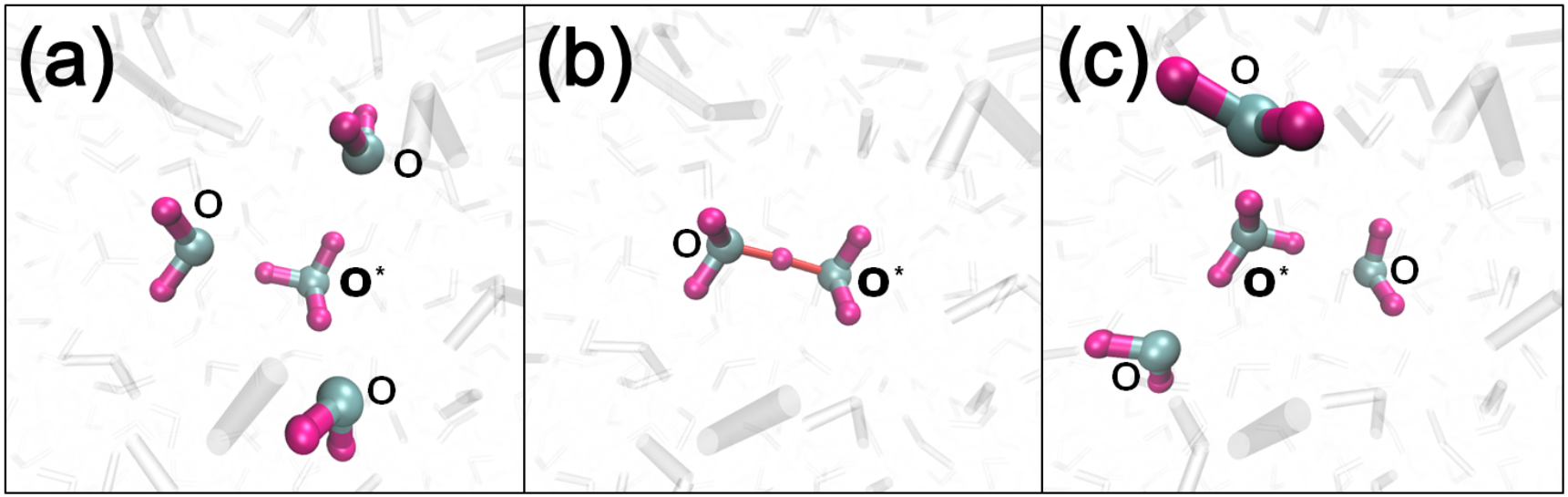
What causes a 1st shell water to get close to the Hydronium ion to form the Zundel complex?

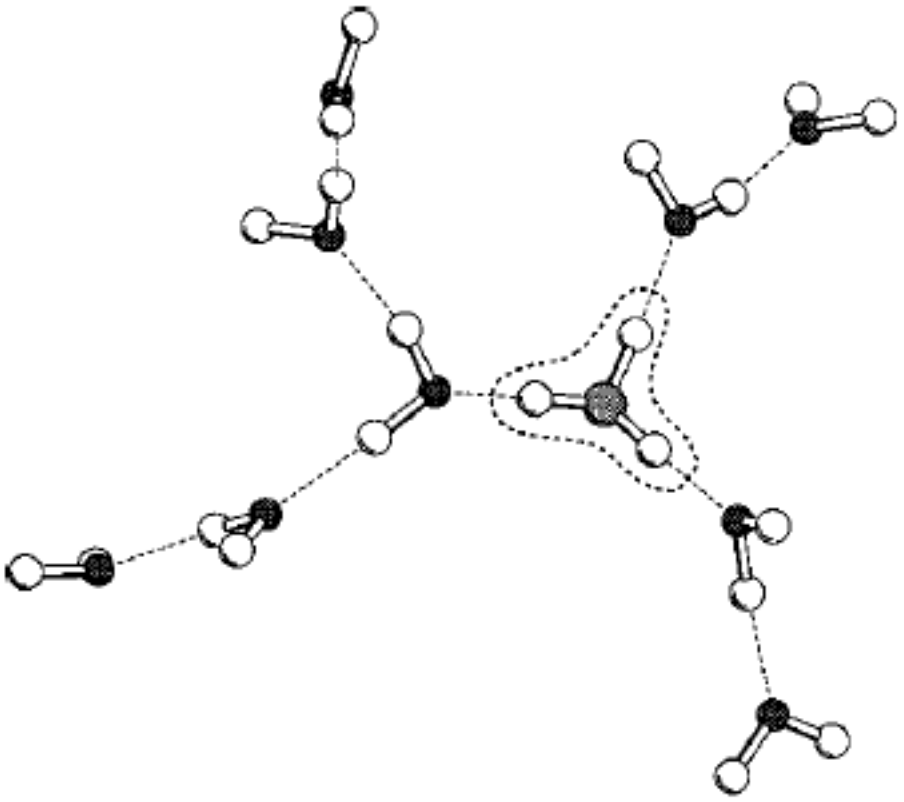


Eigen
$H_9O_4^+$

Zundel
$H_5O_2^+$

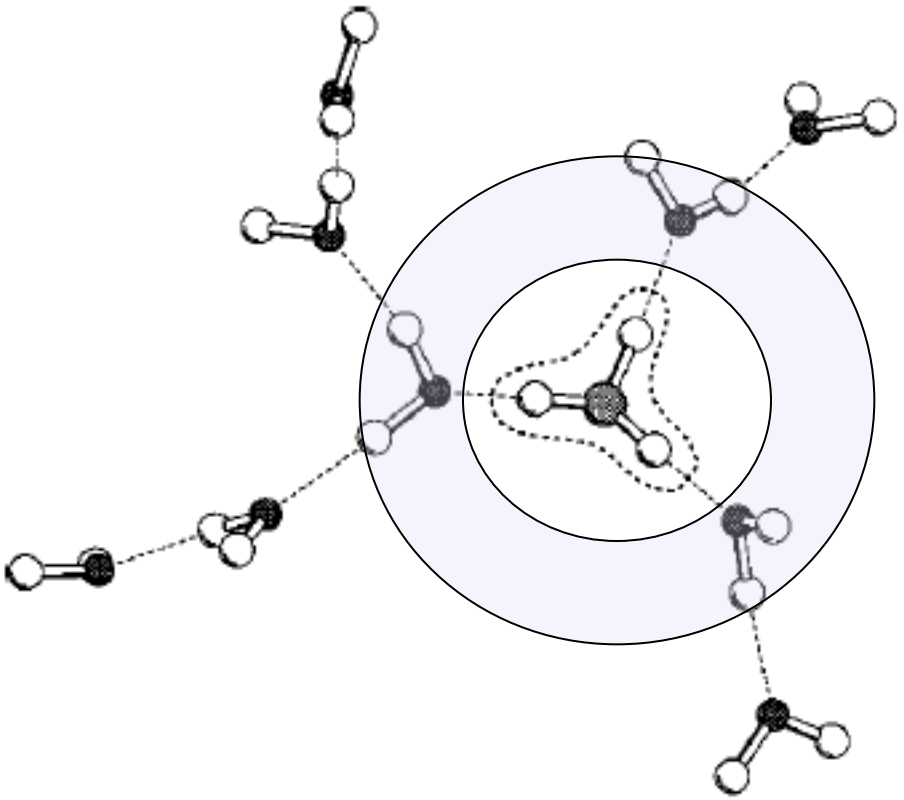
Eigen
$H_9O_4^+$

FIRST AND SECOND SHELL WATERS AROUND H_3O^+ ION



Schmitt JCP1999

FIRST AND SECOND SHELL WATERS AROUND H_3O^+ ION



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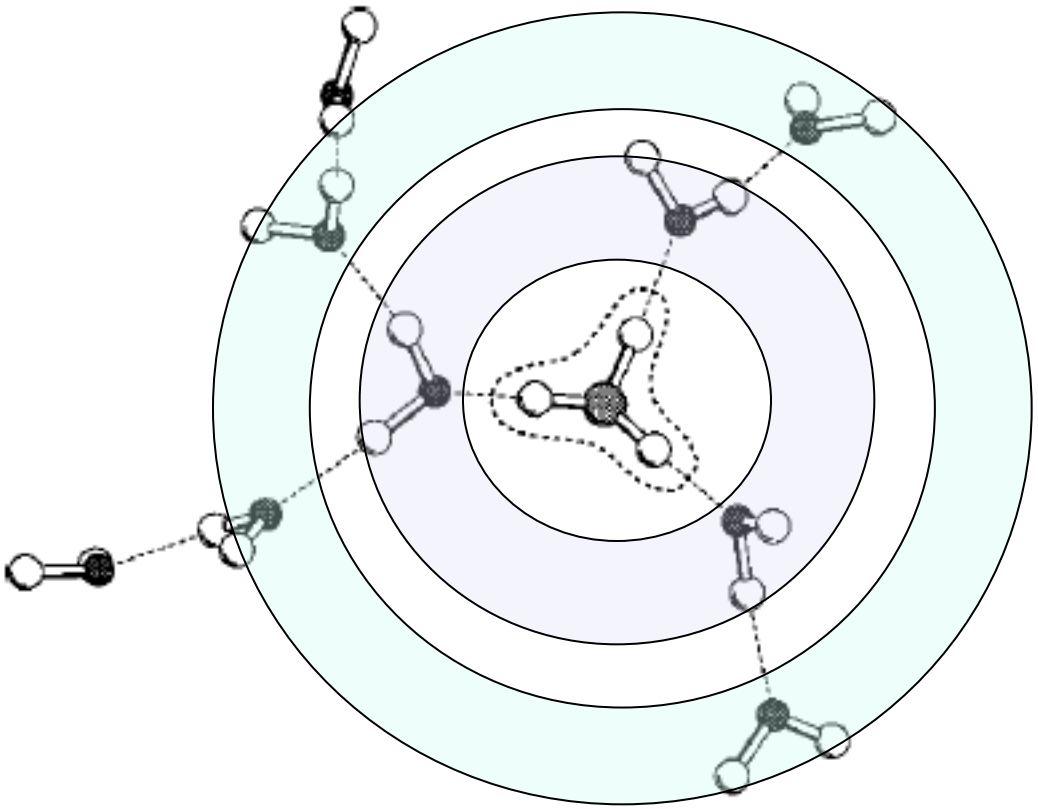
FIRST AND SECOND SHELL WATERS AROUND H_3O^+ ION



Change in 2nd shell waters HB to 1st shell affects a 1st shell water, enabling formation of the Zundel and proton transfer (see next slide).

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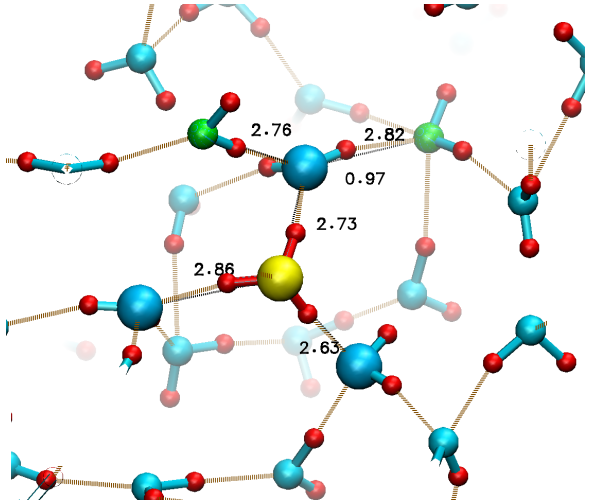
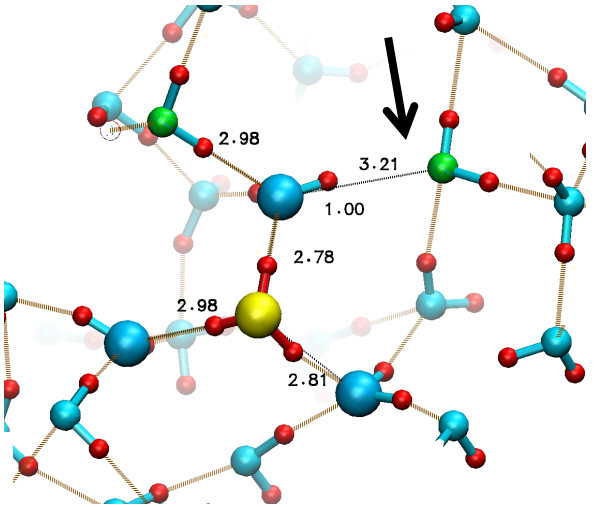
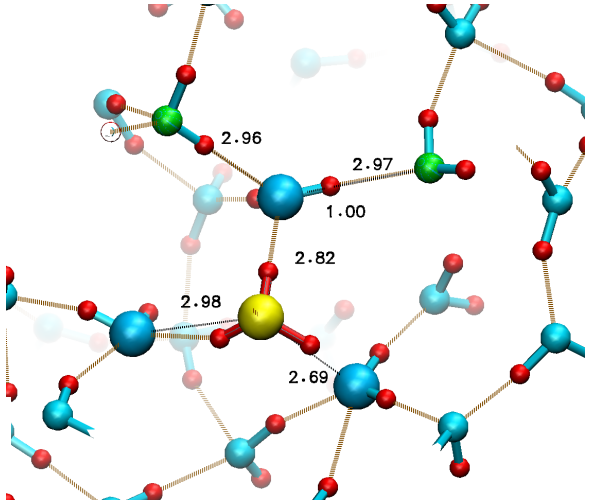
MD result showing 1st shell waters (blue O) around H_3O ion (yellow) and two 2nd shell waters (green), with arrow pointing to HB change in (b), but more dynamic than just HB rupture causing Zundel and PT in (d).



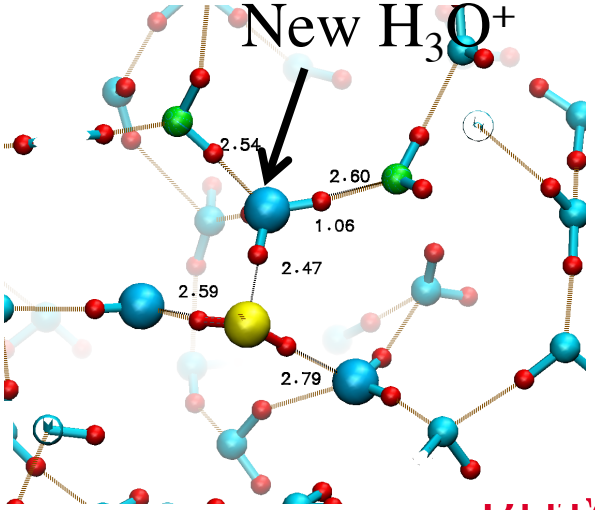
(a)



(b)



(c)



(d)

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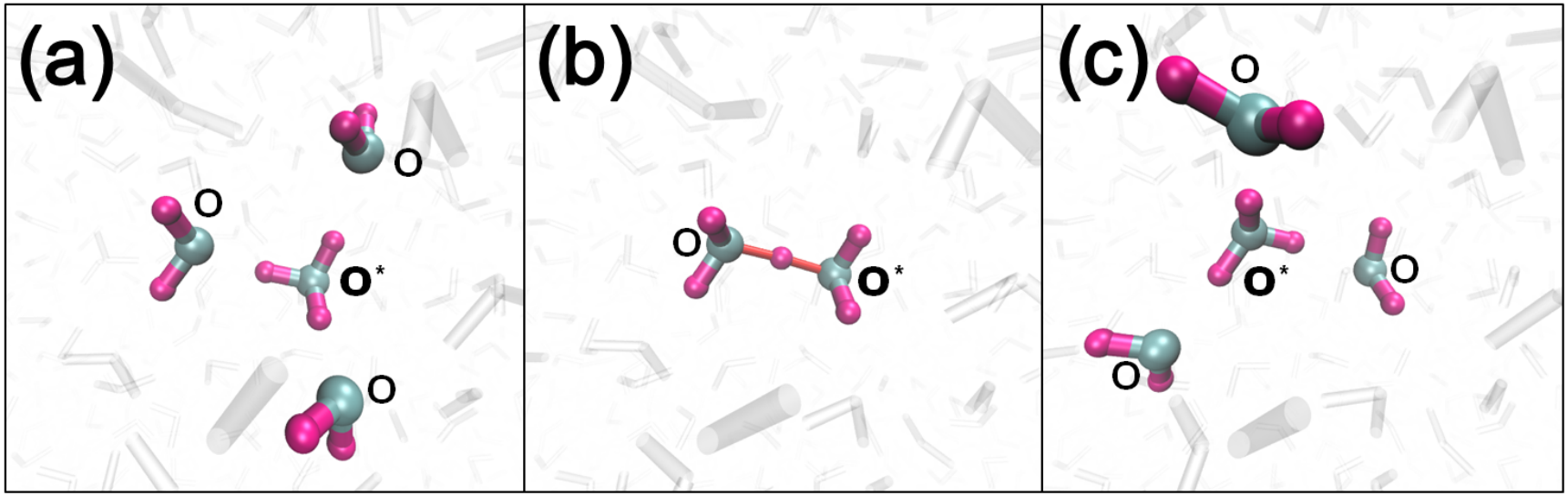
PROTON TRANSPORT IN WATER
MD SIMULATION



Eigen Zundel Eigen

LIFETIME AUTOCORRELATION FUNCTIONS

Probability that hydronium O* (that formed at time 0) will be O* at some other time t

$$c_c(t) = \frac{< h(0)H(t) >}{< h >}$$

Continuous c(t): continuously protonated from 0 to t

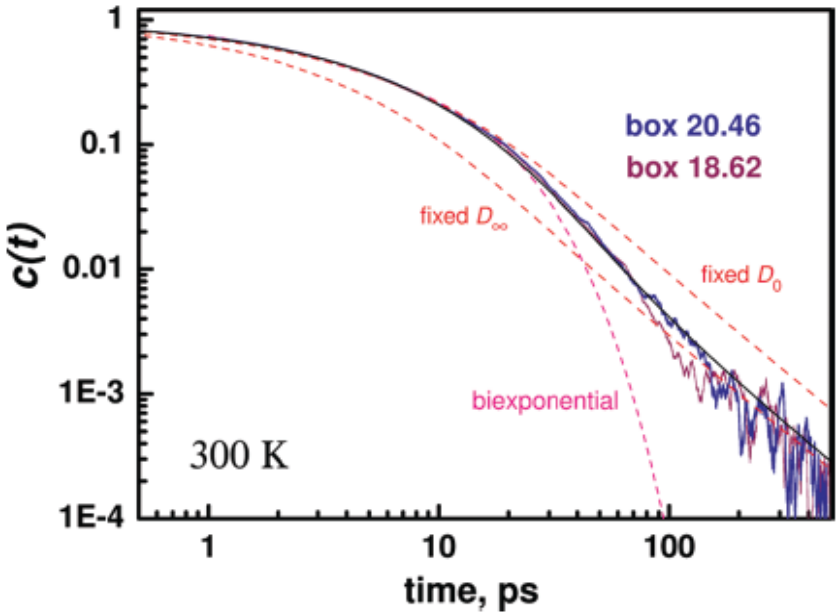
$$c_i(t) = \frac{< h(0)h(t) >}{< h >}$$

Intermittent c(t): protonated at 0 and t, regardless of protonation state between 0 and t

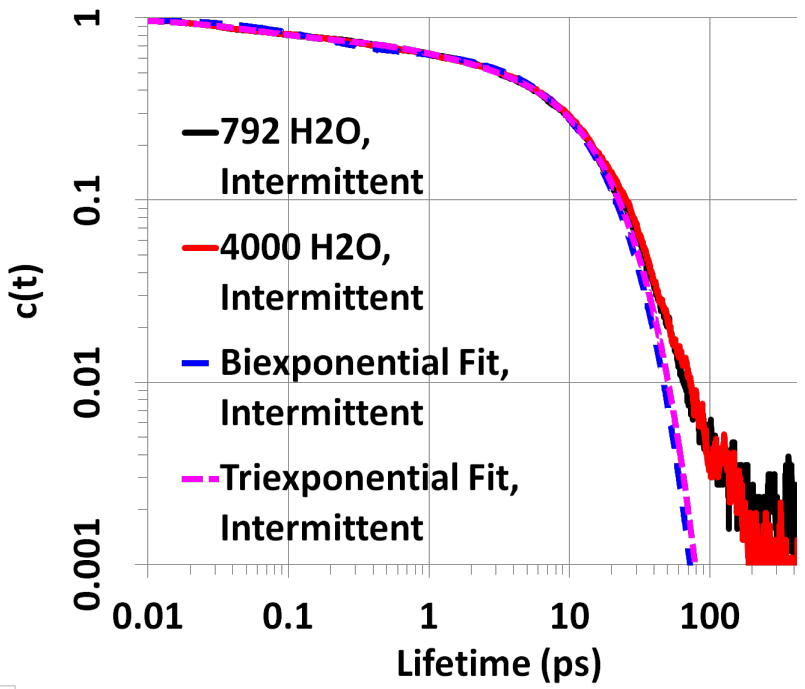
RESULTS OF ONE H_3O IN BULK WATER AND H_3O LIFETIMES

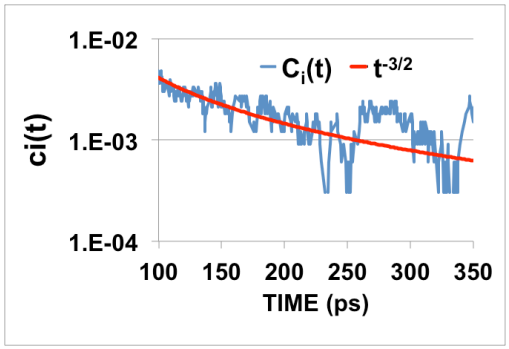
Chen and Voth MS-EVB3

J. Phys. Chem. B, Vol. 114, No. 1, 2010



Our MD





AT LONG TIMES:
$t^{-3/2}$ BEHAVIOR

Our MD results similar to the highly developed MS-EVB3 model for exponential behavior and long time $t^{-3/2}$ behavior

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Table 2. Comparison of the Diffusion Coefficient D in Å^2/ps of the Center of Excess Charge Resulting from Different Approaches

Excess Proton		
Garofalini 283 K (NpT)	0.25	this work
Garofalini 283 K (NVE)	0.26	this work
Garofalini 296 K (NpT)	0.39	this work
Garofalini 298 K (NVE)	0.38	this work
Garofalini 323 K (NpT)	0.61	this work
Garofalini 325 K (NVE)	0.67	this work
MS-EVB2 298K	0.29	36
MS-EVB 298K	0.35	34
MS-EVB3 298K	0.36	36
aMS-EVB3 298K	0.41	37
qMS-EVB3 298K	0.50	36
MS-EVB 298K	0.77	33
MS-EVB 298K	0.83	35
experimental	0.93	58, 59

Hofer et al. J Chem. Theory Comp, 2012

SUMMARY

Exceedingly robust dissociative water potential for MD simulations.

Uniquely reproduces the trend of increased CTE of nanoconfined water as a function of pore size similar to experiment

Provides mechanism for high CTE of nanoconfined water

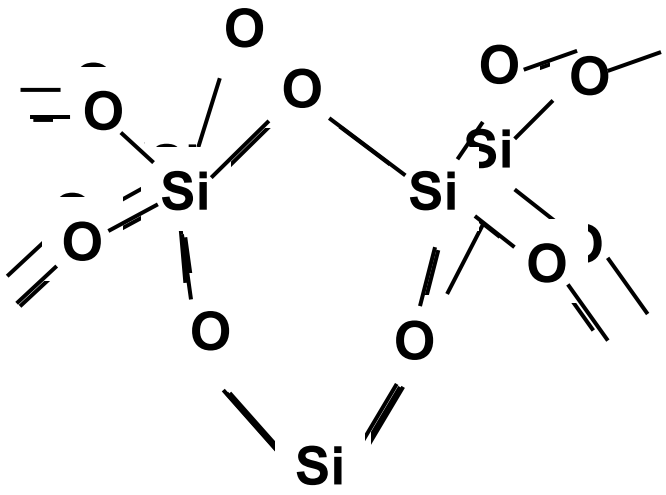
Shows appropriate reactions on silica surfaces

Shows proton transport in water via Eigen and Zundel complexes

Shows enhanced hydronium ion formation at silica surfaces, with reactions similar to AIMD

Shows lifetimes for protons in water similar to AIMD and MS-EVB, but at much less computational cost

Reactions between moisture and silica during irradiation



O

High energy PKA disrupts structure

But re-formation of bonds…'self-healing'…can occur

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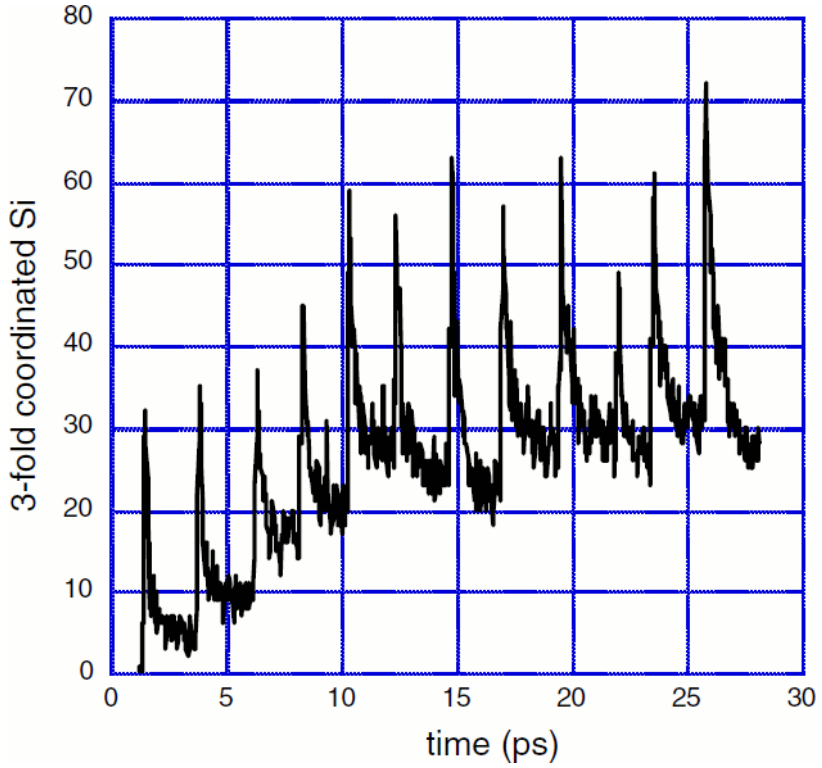
IRRADIATION OF DRY SILICA GLASS



Kubota et al. Nucl. Instr. Meth. Phys. B, 202 (2003)

However, no atomistic models have included water

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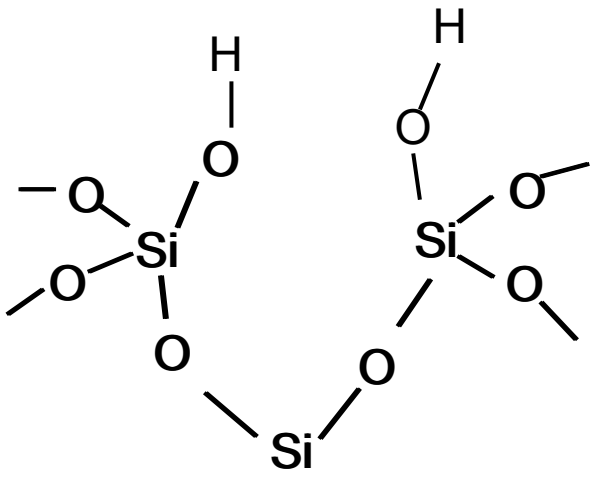
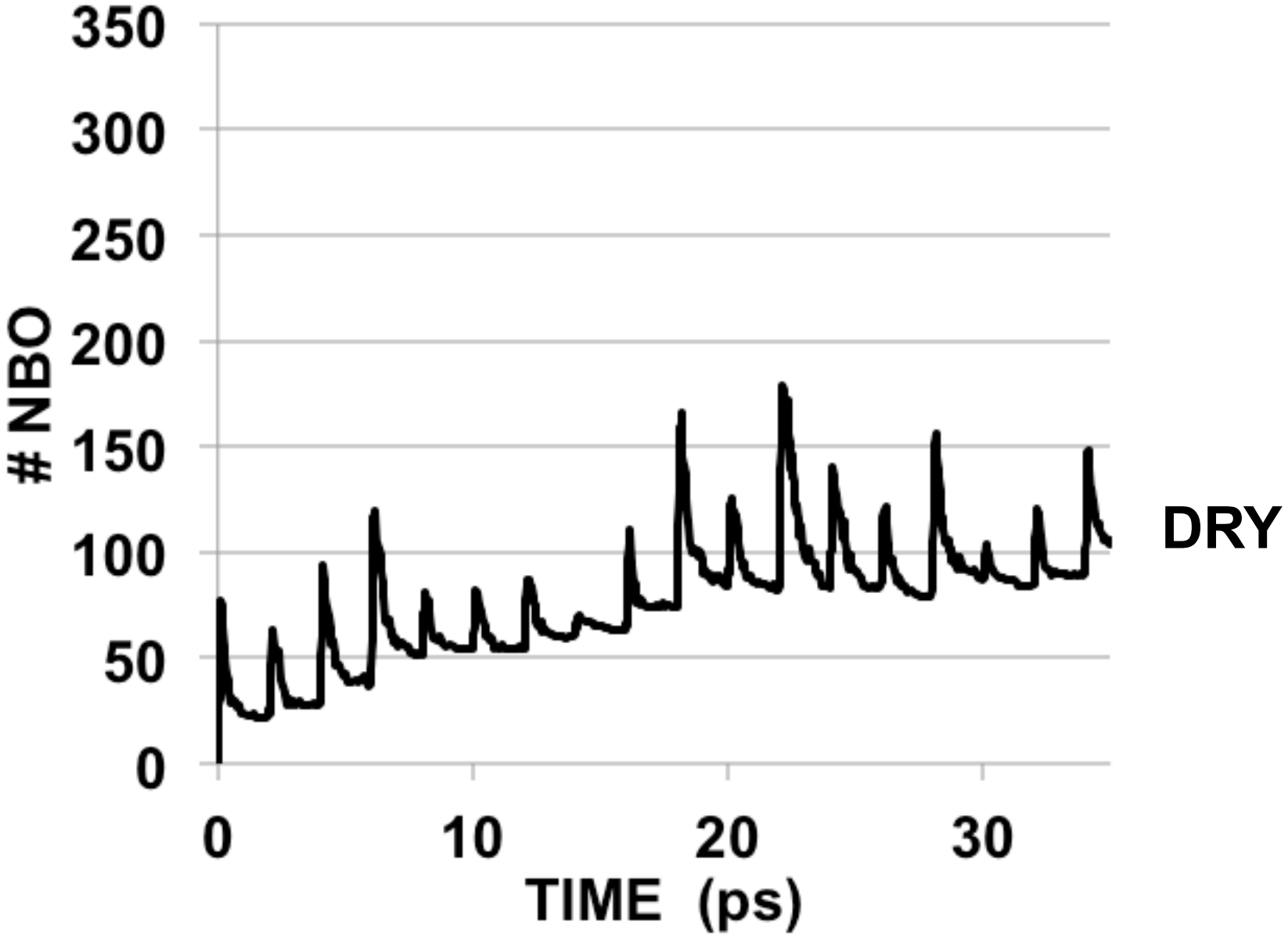
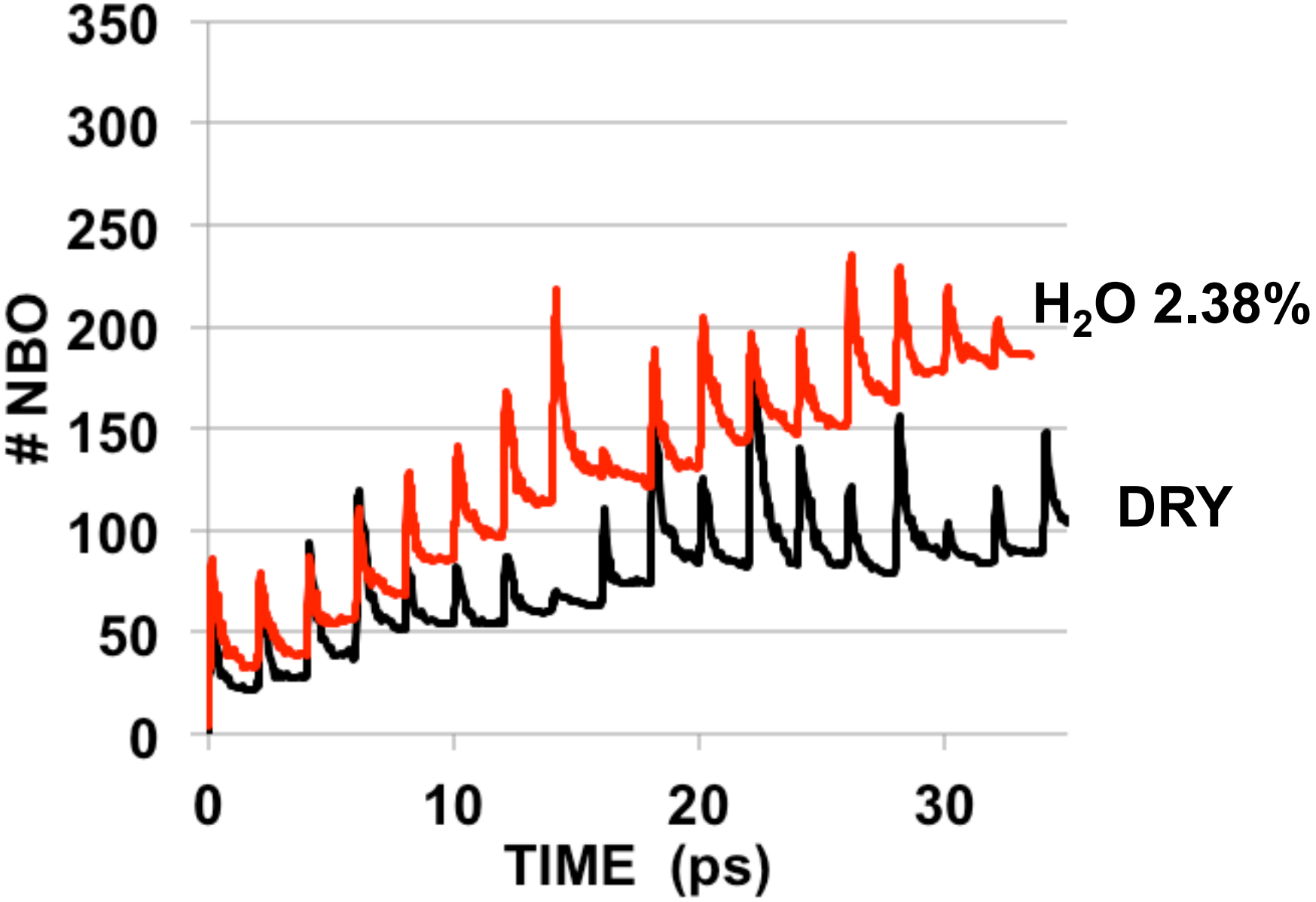
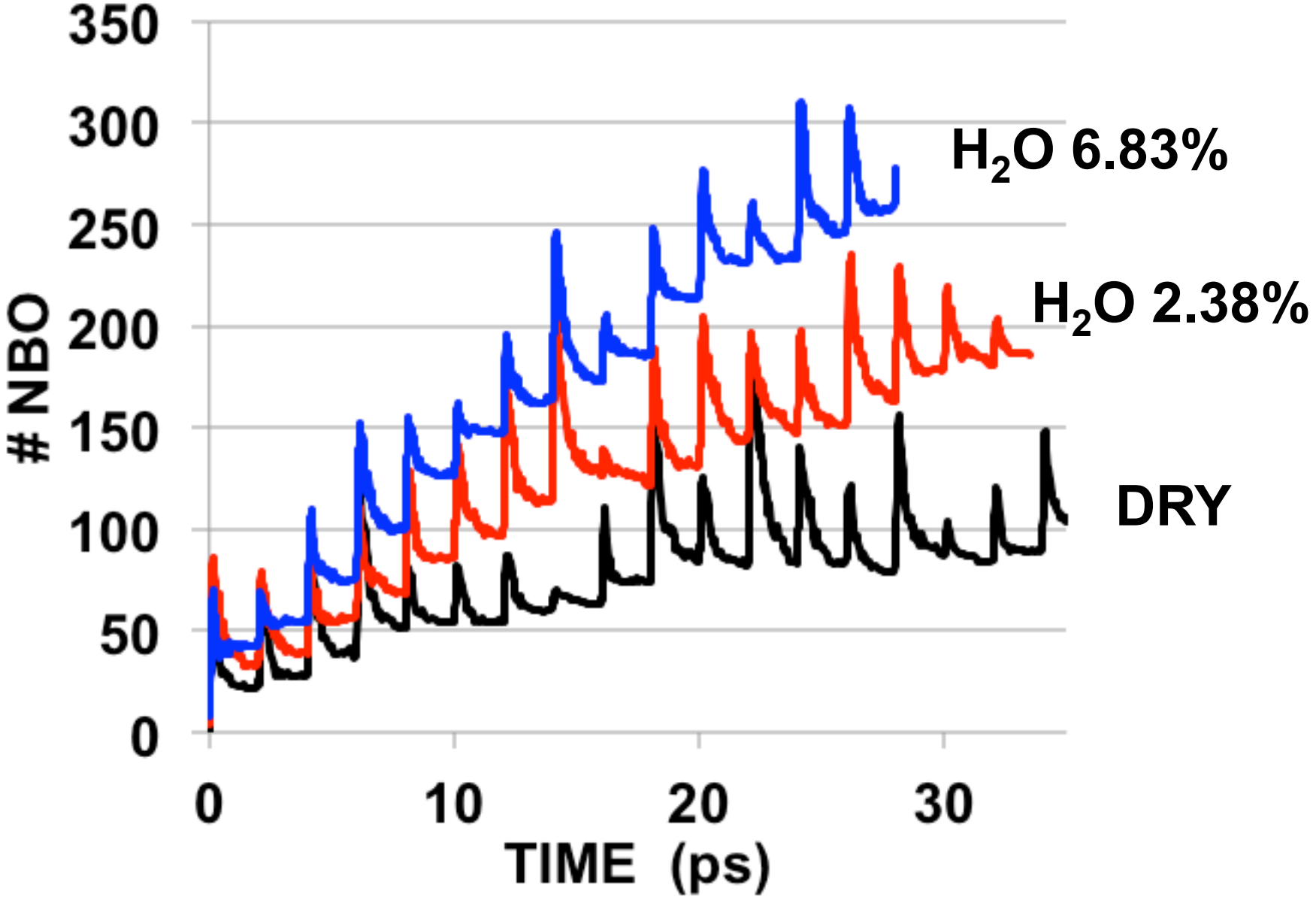
Presence of H_2O can inhibit bond re-formation



Insert either intact H_2O molecules within the silica structure or as already dissociated molecules (H^+ and OH^-) – then irradiate – Results are the same

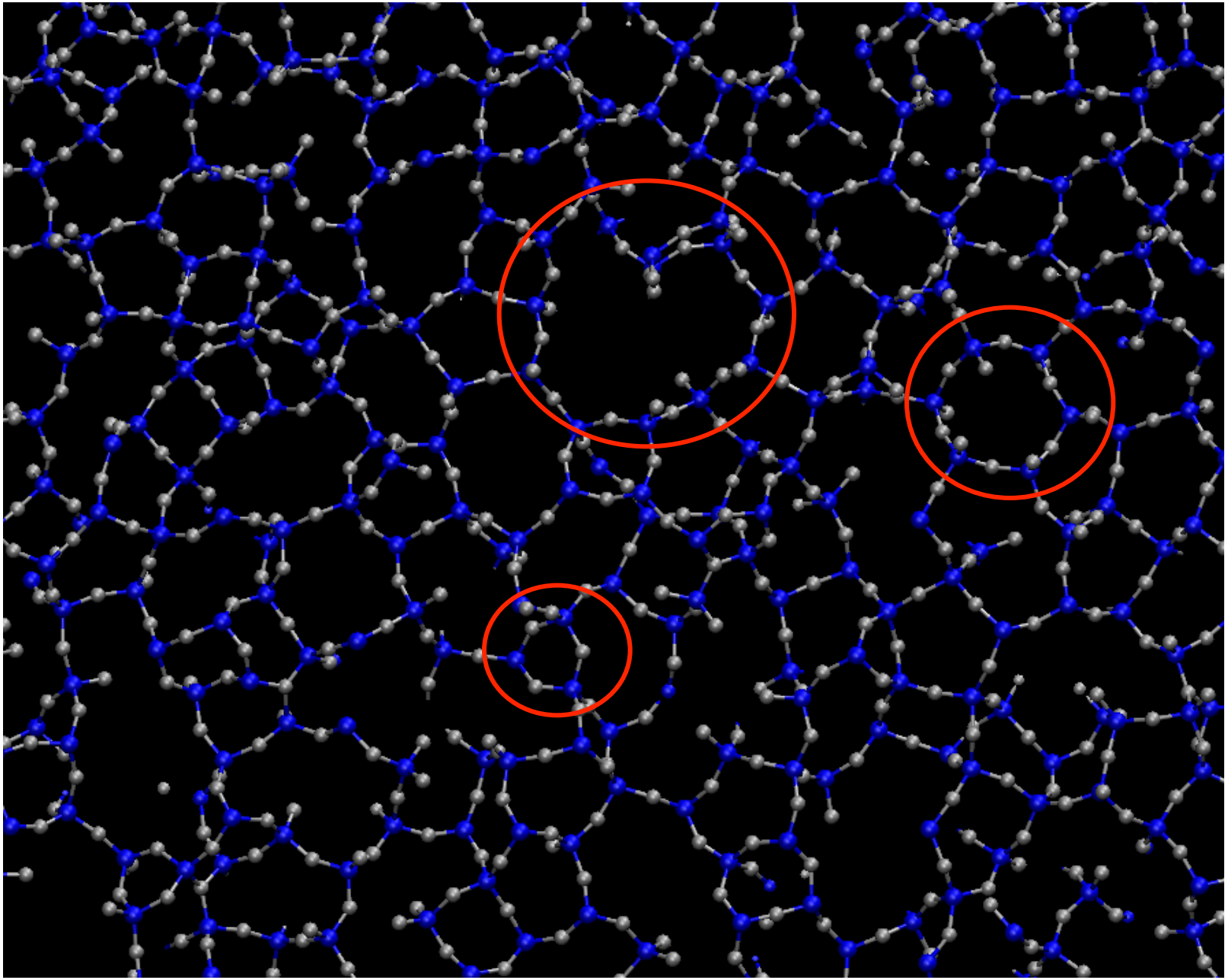

350
300
250
200
150
100
50
0
NBO
0
10
20
30
TIME (ps)
DRY


350
300
250
200
150
100
50
0
NBO
0
10
20
30
TIME (ps)
H2O 2.38%
DRY



Lockwood and Garofalini J Nucl Matl 400 (2010) 73

RUTGERS



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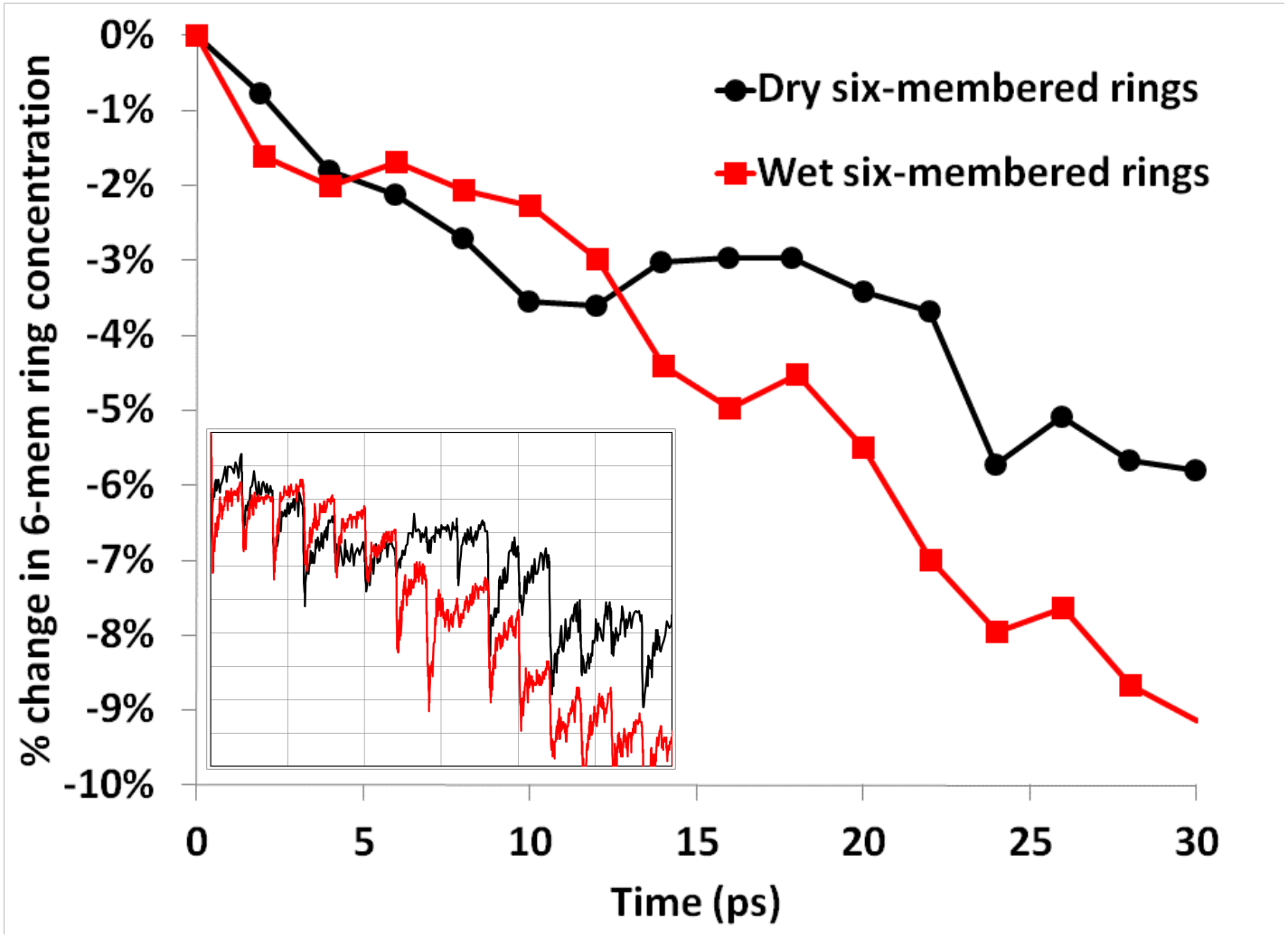
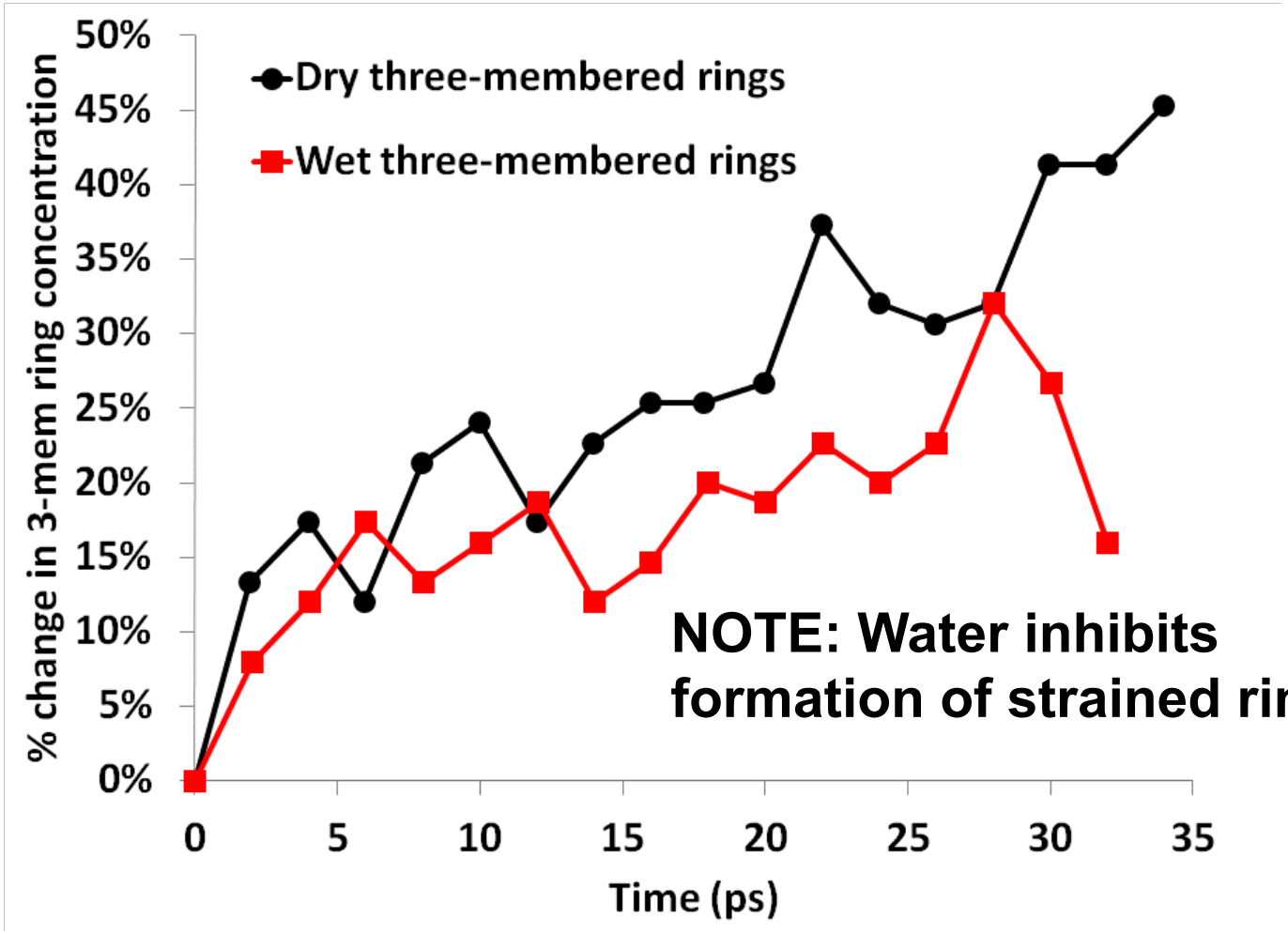
Destruction of 5- and 6-Member Rings

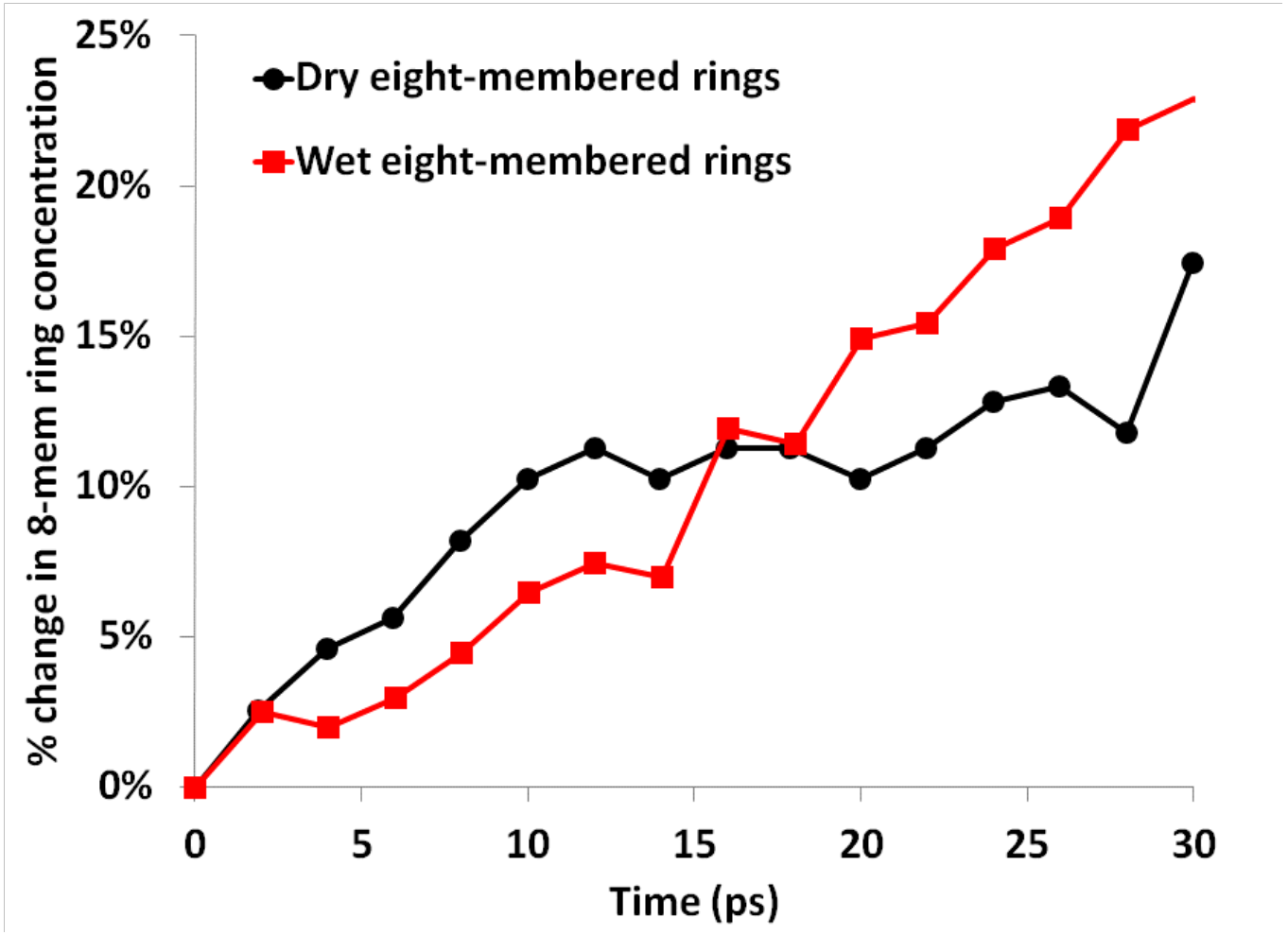


3-mem Rings (Strained)



RUTGERS

8-mem Rings



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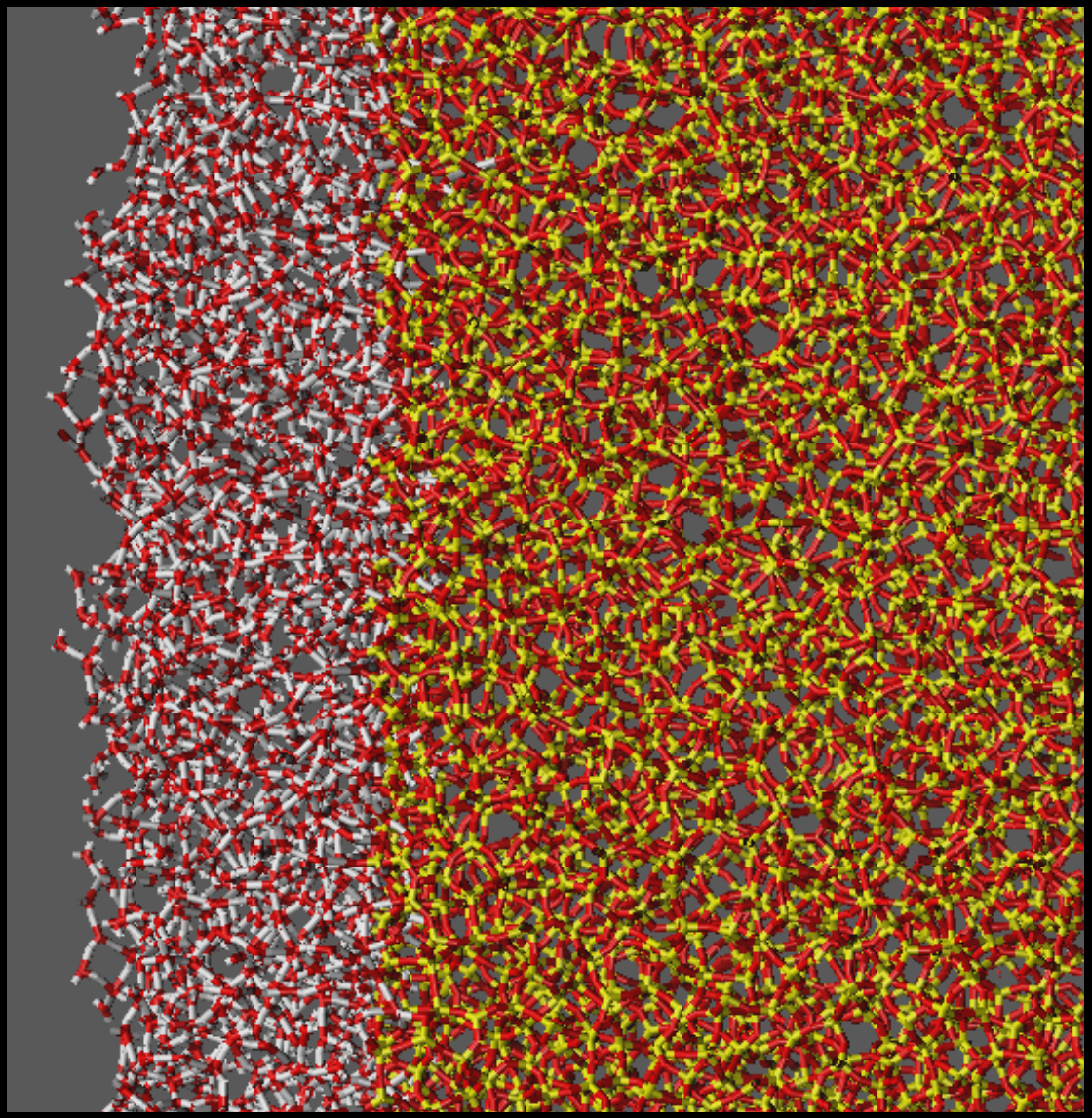
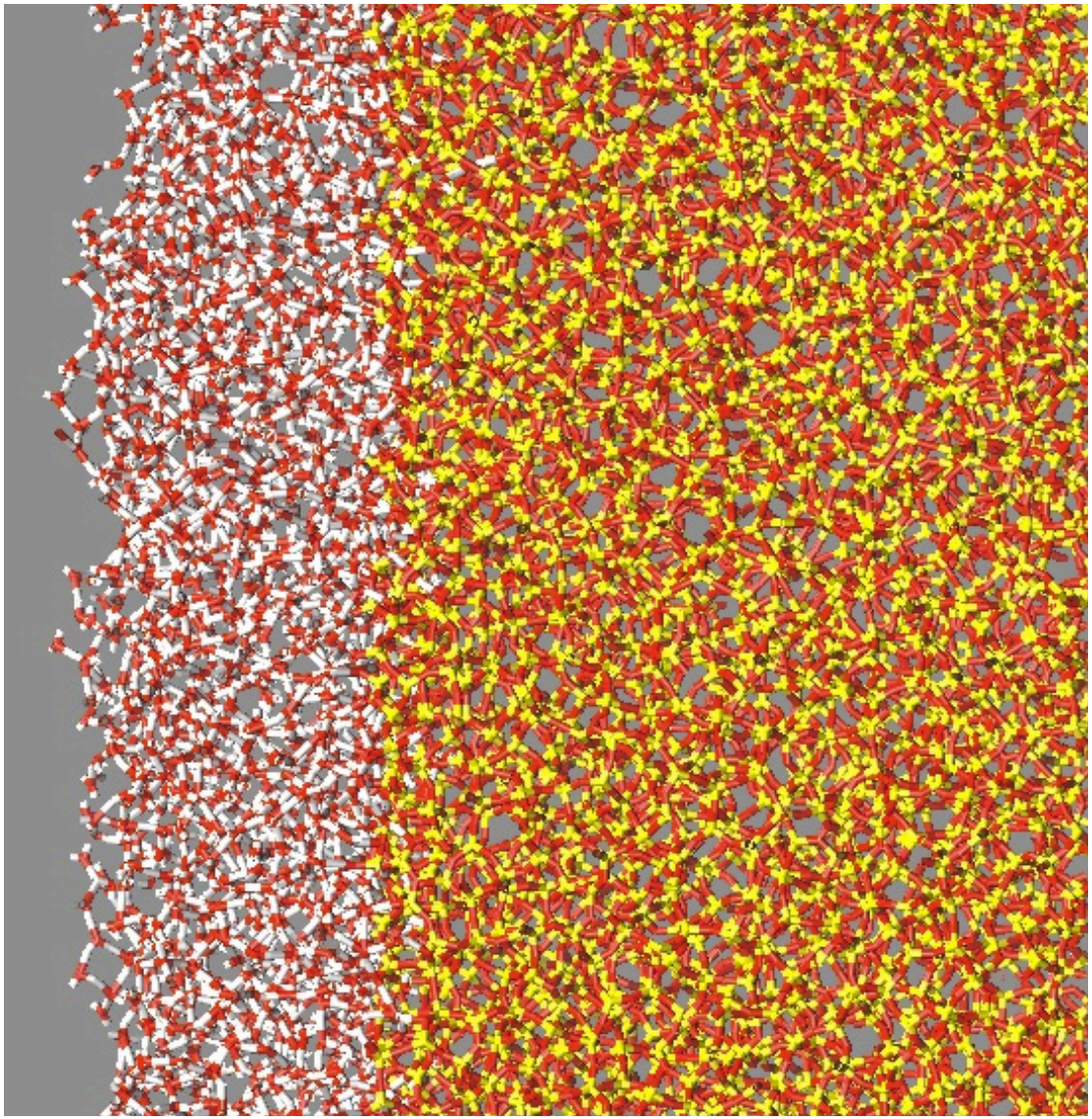
What occurs during irradiation of silica in contact with a film of water?

Does the formation of larger rings allow for ingress of water into the glass?

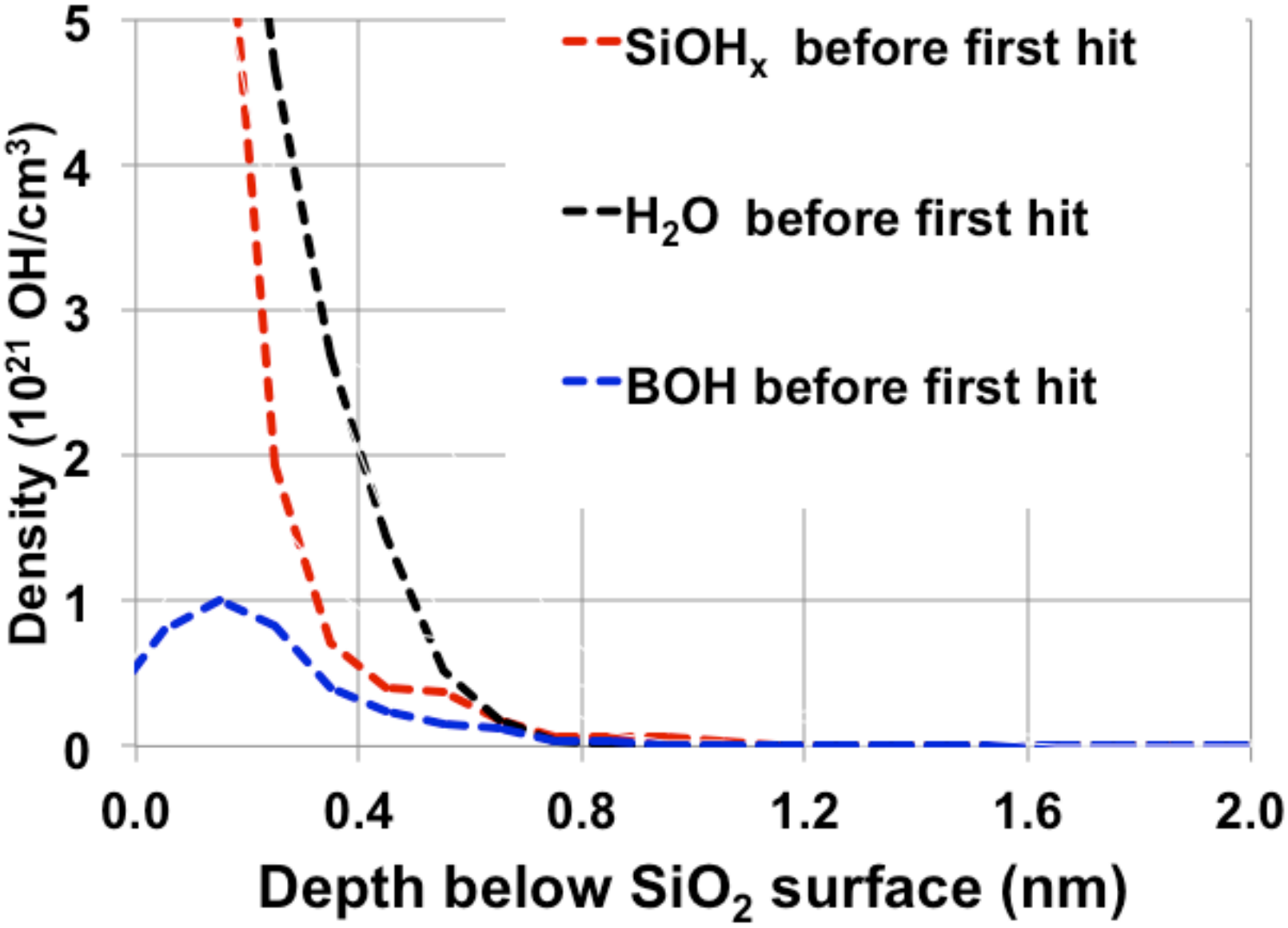
SIDE VIEW – THIN SECTION INTO FIGURE

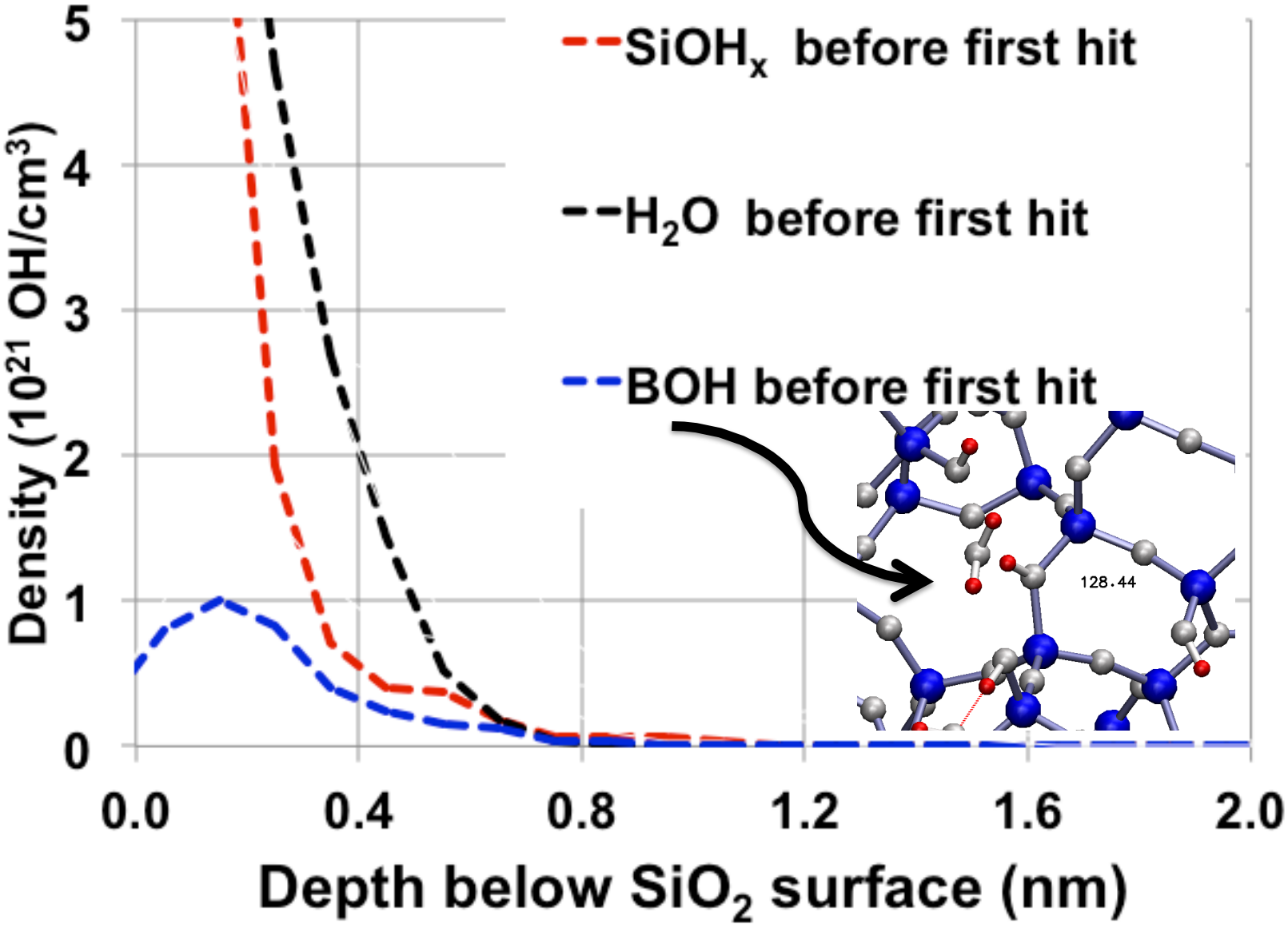


RUTGERS



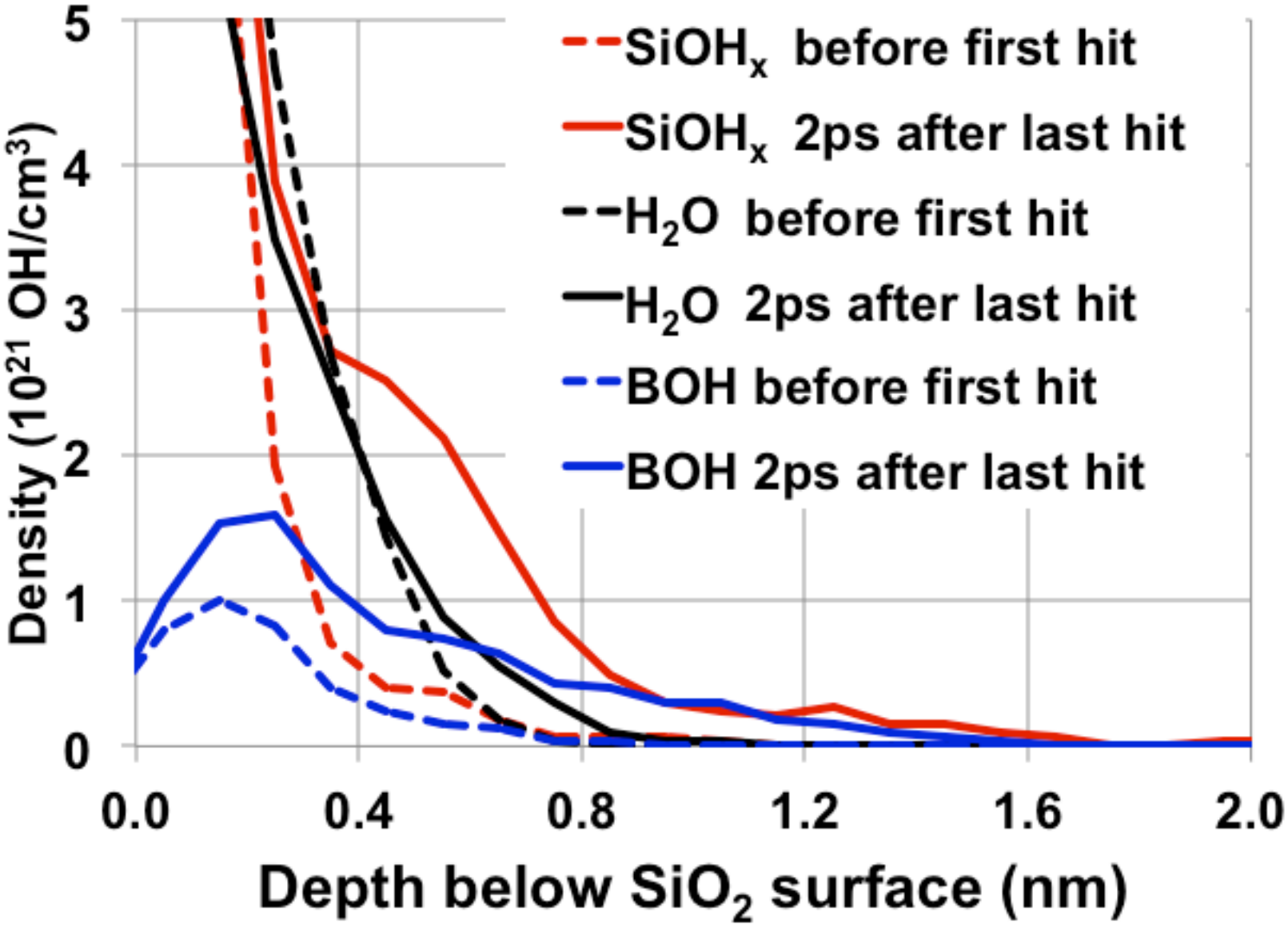
RUTGERS


SiOHx before first hit
H2O before first hit
BOH before first hit
Density (10^21 OH/cm^3)
0
1
2
3
4
5
0.0
0.4
0.8
1.2
1.6
2.0
Depth below SiO2 surface (nm)

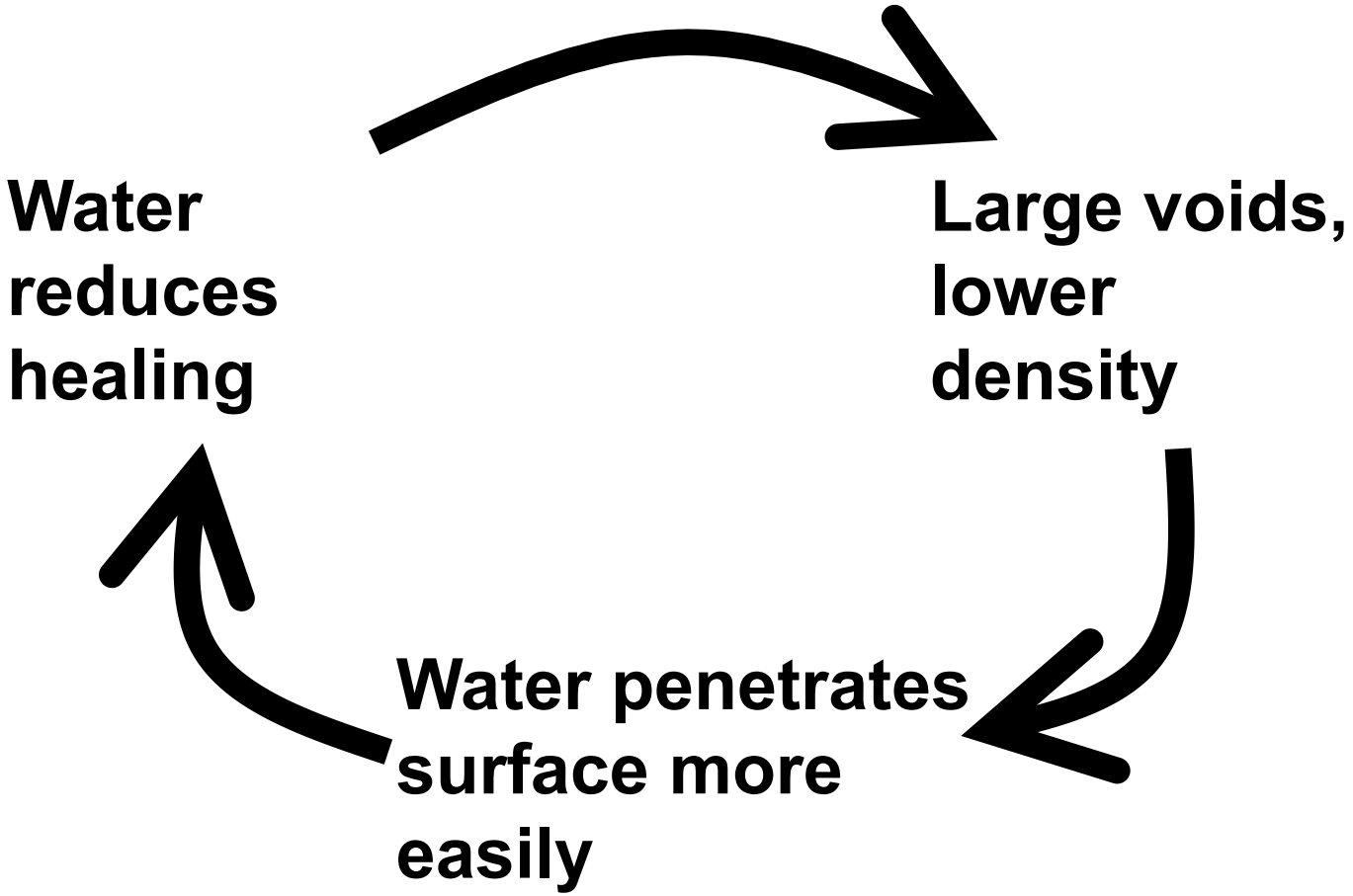


BOH→Lockwood and Garofalini J Chem Phys 131 (2009) 074703

RUTGERS


SiOHx before first hit
SiOHx 2ps after last hit
H2O before first hit
H2O 2ps after last hit
BOH before first hit
BOH 2ps after last hit
Density (10^21 OH/cm^3)
0
1
2
3
4
5
0.0
0.4
0.8
1.2
1.6
2.0
Depth below SiO2 surface (nm)

Effect of Water



CONCLUSIONS

Without changing parameters in the potential

Simulations reproduce BULK and NANOCONFINED water

water REACTIONS on SiO_2 surfaces

PROTON transport and lifetimes in bulk water

and

Provide mechanism of high thermal expansion of nanoconfined water

and

Show that moisture inhibits self-healing in SiO_2 under irradiation, opening network to further ingress of protons and water