Water Infrared Spectrum at the interface with silicon and hydrogen-terminated silicon surfaces using molecular dynamics approach

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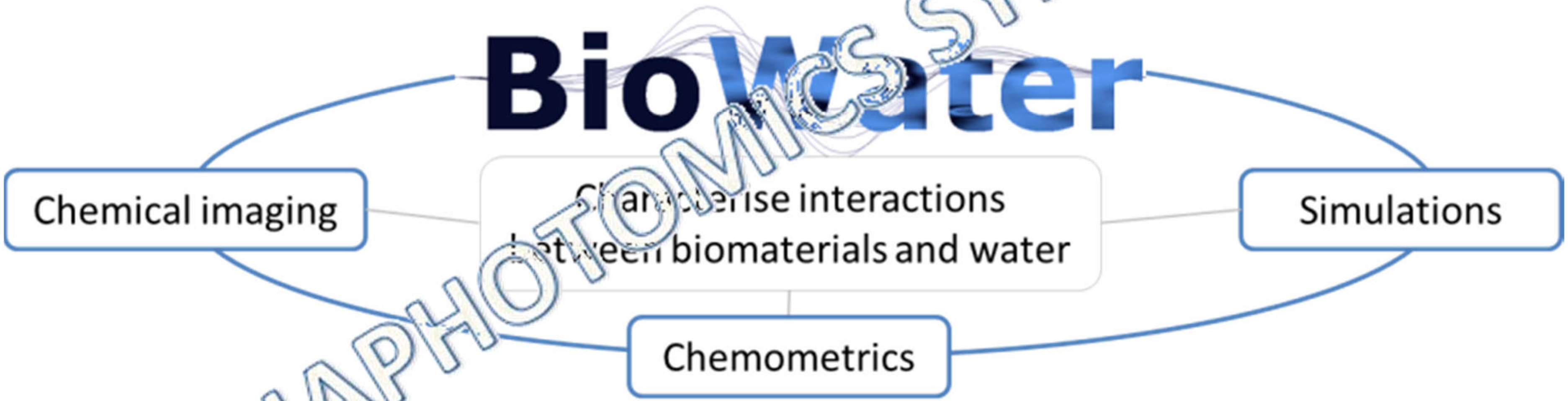
AQUAPHOTOMICS: UNDERSTANDING WATER in BIOLOGY
2nd INTERNATIONAL SYMPOSIUM

Biowater Project

European Research Council



http://cms.ucd.ie/biowater/
Twitter: #BioWaterERC

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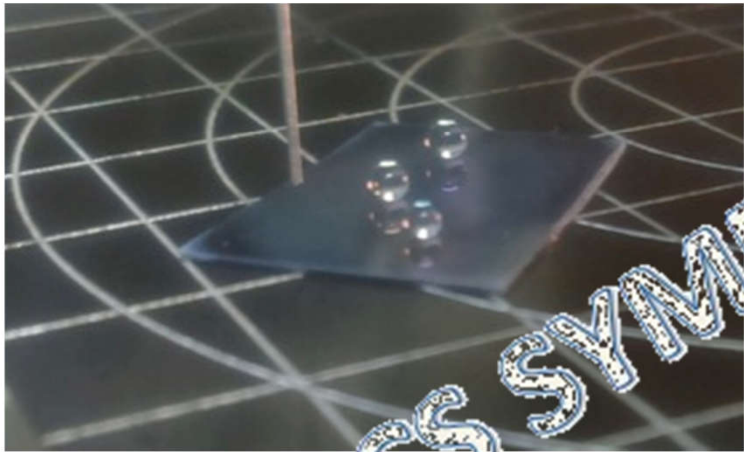
Overview



Water

Biomaterial

Biomaterial-water interface *not very well understood*[1]

How does the water structure change depending of the material?

Is it possible explain the hydrophobic effect from these changes in the structure?

1. Bunkin, N., Ignatiev, P., Kozlov, V., Shkirin, A., Zakharov, S., Zinchenko, A. (2013) 'Study of the Phase States of Water Close to Nafion Interface', *Water*, 4(Mauritz 2004), 129–154

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Biowater Project

Sindhuraj Mukherjee

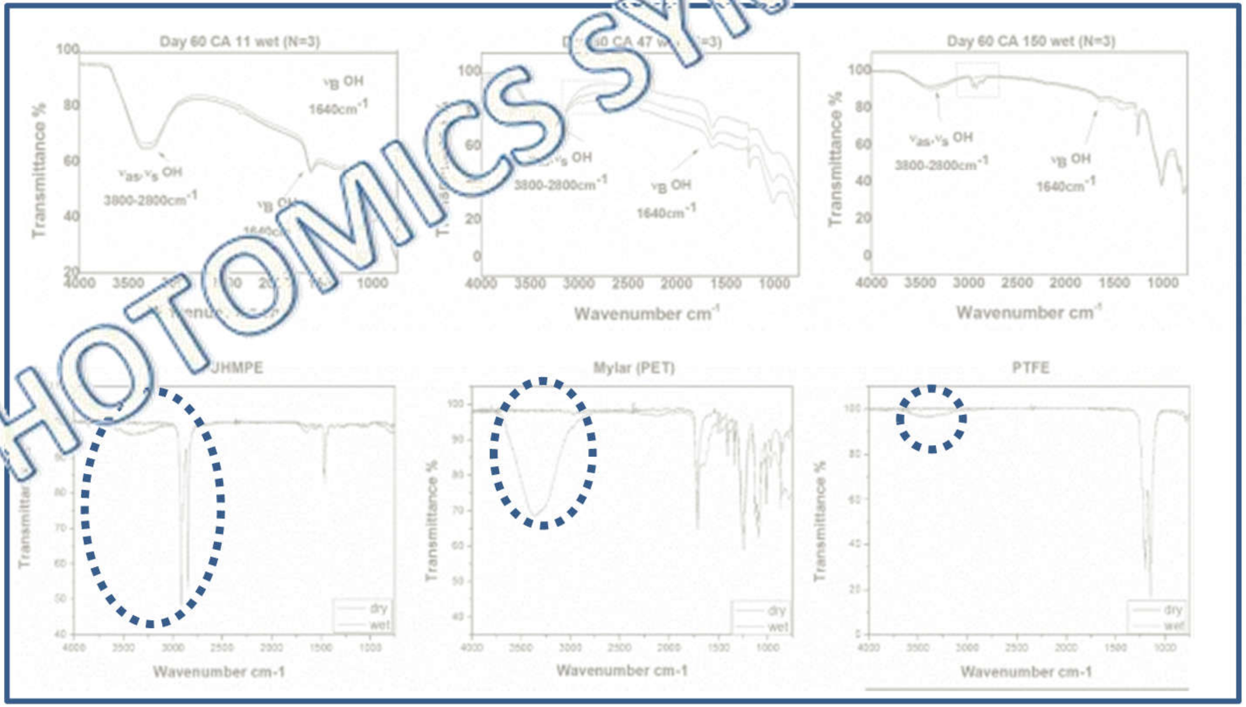
Interactions: polymer biomaterials & water

Polymers

UHMPE
PET
PTFE
PLLA
P3HB
Silicones
HMDSO coatings

Measurements

ATR-FTIR
Contact angle



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Simulation of water in heterogeneous environments

Simulation liquid, supercooled and ice water

Theoretical Background

Molecular Dynamics Simulation

$$F_i = m_i a_i$$

$$-\frac{dU}{dr_i} = m_i \frac{d^2 r_i}{dt^2}$$

calculate the time evolution of the position (Trajectory)

$$r_{i+1} = r_i + \frac{\partial r_i}{\partial t}\delta t + \frac{1}{2!}\frac{\partial^2 r_i}{\partial t^2}\delta t^2 + \frac{1}{3!}\frac{\partial^3 r_i}{\partial t^3}\delta t^3 + \ldots$$

$$v = \frac{dr_i}{dt}$$

$$a_i = \frac{d^2 r_i}{dt^2} = -\frac{1}{m}\frac{dV}{dr_i}$$

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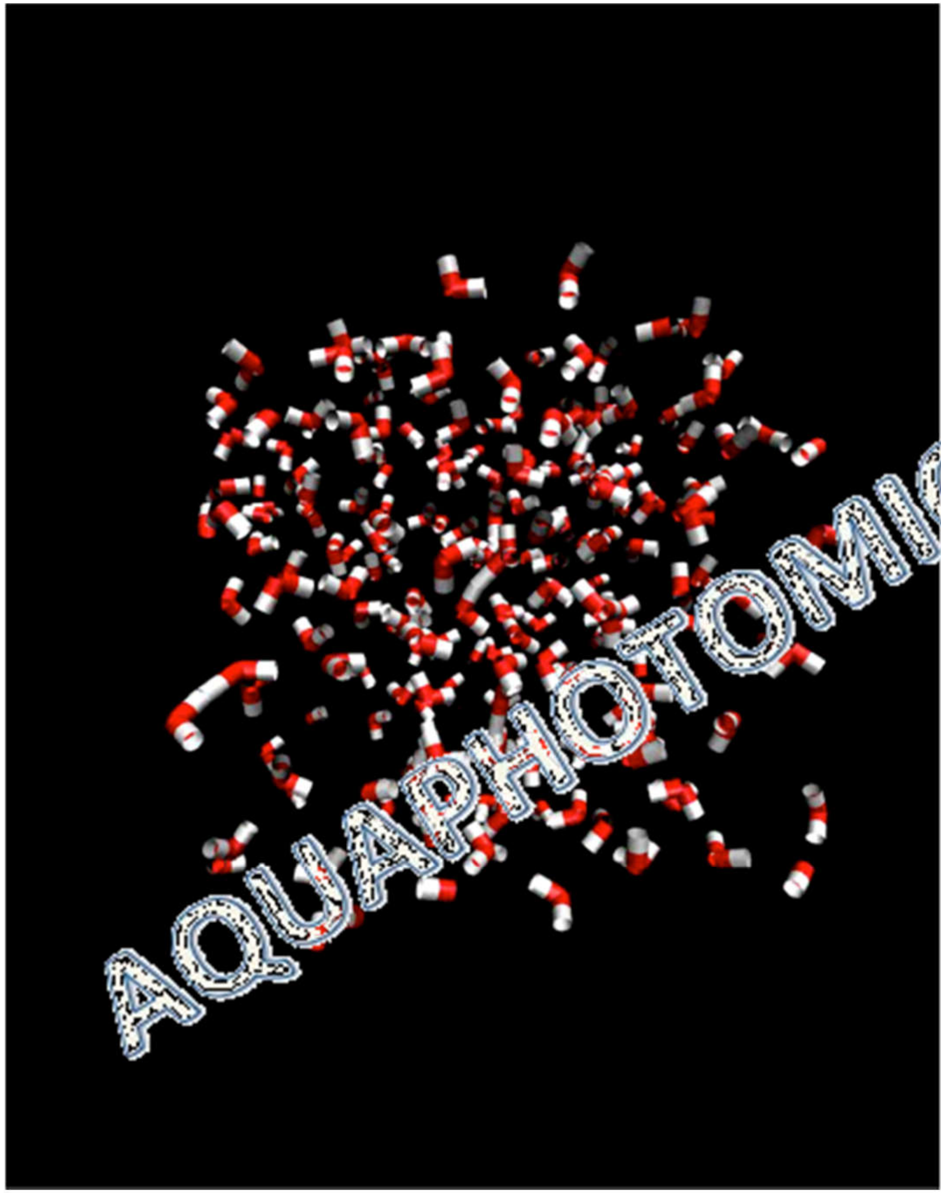
Water Model Parameters



Water Models

$$V^{\text{intra}} = \frac{k_b}{2}\left[(r_{\text{OH}_1} - r^0_{\text{OH}})^2 + (r_{\text{OH}_2} - r^0_{\text{OH}})^2\right] + \frac{k_a}{2}(\theta_{\angle\text{HOH}} - \theta^0_{\angle\text{HOH}})^2,$$

$$V^{\text{inter}} = \sum_{i,j}^{\text{pairs}} \left\{4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{r_{ij}}\right\},$$

	SPC/Fw[1]
r(OH), Å	1.012
HOH, deg	113.24
Ka·10^{-3}, kcal·rad^{-2}·mol^{-1}	75.90
Kb, kcal·Å^{-2}·mol^{-1}	1059.162
q(O)	-0.82
q(H)	0.41
σ(OO), Å	3.165492
ε(OO), kcal·mol^{-1}	0.1554253

1. Y. Wu, H. L. Tepper and G. A. Voth, Flexible simple point-charge water model with improved liquid state properties, J. Chem. Phys. **124** (2006) 024503

AQUAPHOTOMICS SYMPOSIUM

Theoretical Background

Velocity Autocorrelation Function

$$C_{vv}(t) = \frac{1}{N}\sum_{i=1}^{N}\langle v_i(t) \cdot v_0(t)\rangle$$

→ VDOS (power spectra)

Dipole Autocorrelation Function

$$\langle M(t) \cdot M(0)\rangle = \left\langle \sum_{j=1}^{n} e_j r_j(t) \cdot \sum_{j=1}^{n} e_j r_j(0) \right\rangle$$

→ Infrared Spectra

$$I(\omega) \propto \int_0^{\infty} \langle M(t) \cdot M(0)\rangle \cos(\omega t)\, dt$$

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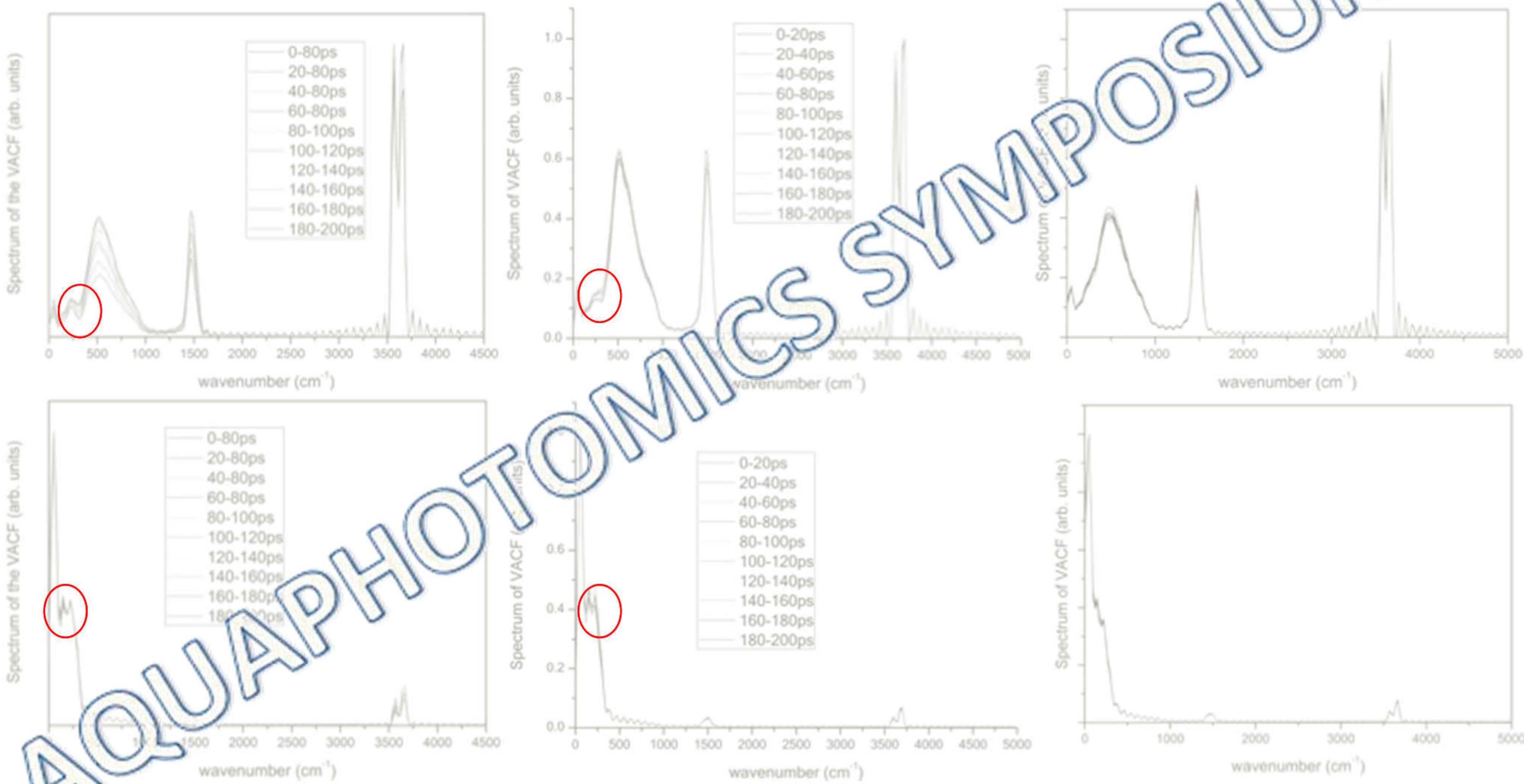
Water-Ice VACF

ICE (220K) | H_2O (220K) | H_2O (3[illegible]K)

H

O



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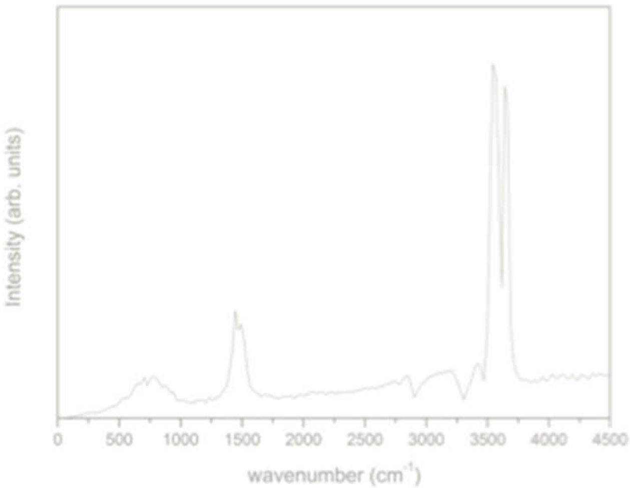
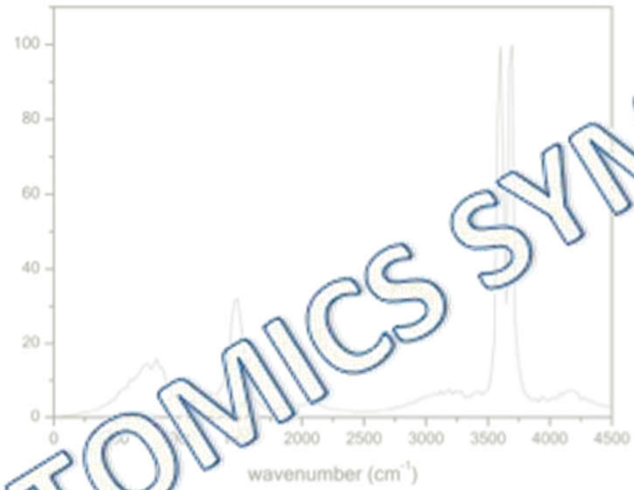
Water-Ice IR

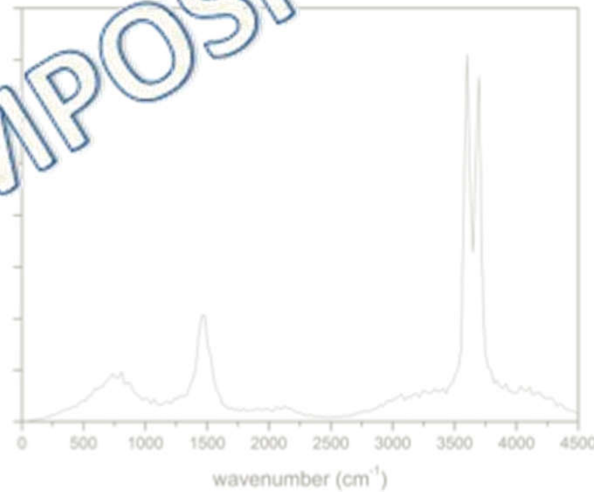
ICE (220K)



H_2O (220K)



H_2O (300K)



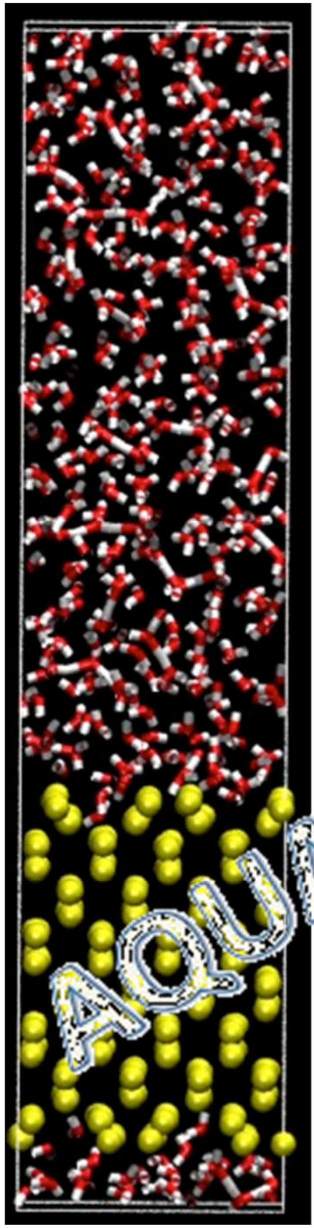
	Ice (220K)	H_2O (220K)	H_2O (300K)
ν_s ([illegible] n-sym)	3639-3544	3696-3600	3696-3600
ν[illegible]	1443-1490	1481	1481

AQUAPHOTOMICS SYMPOSIUM

Simulation of water in heterogeneous environments

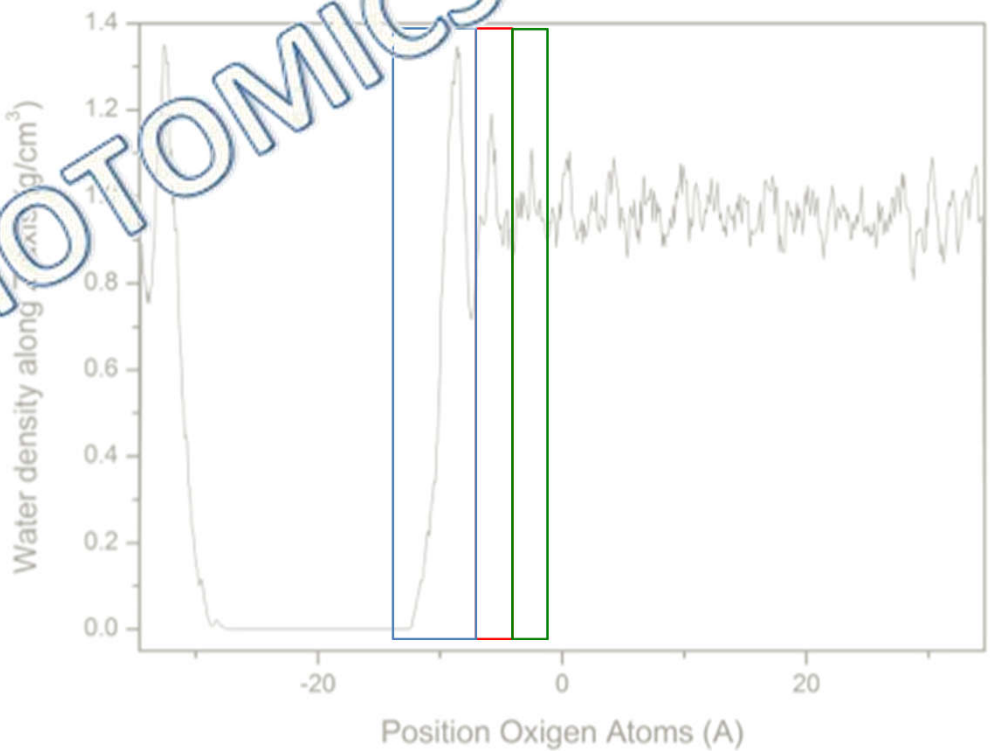
Simulation water silicon interface

Water Silicon Interface



Box size: 15.566 Å x 15.566 Å x 69.0 Å
378 H_2O molecules
256 Si atoms

Simulation parameters :
ensemble nvt evans, velocity verlet
200 ps, t_{step} 0.1fs, $t_{sampling}$ 2 fs, 300K



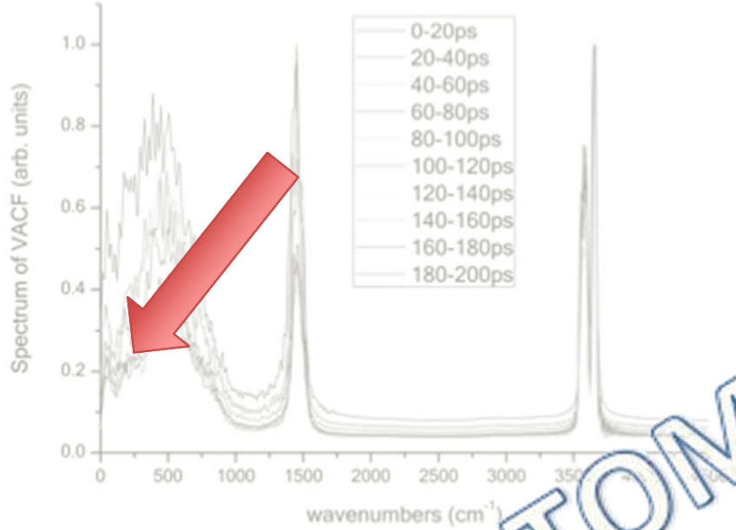
AQUAPHOTOMICS SYMPOSIUM

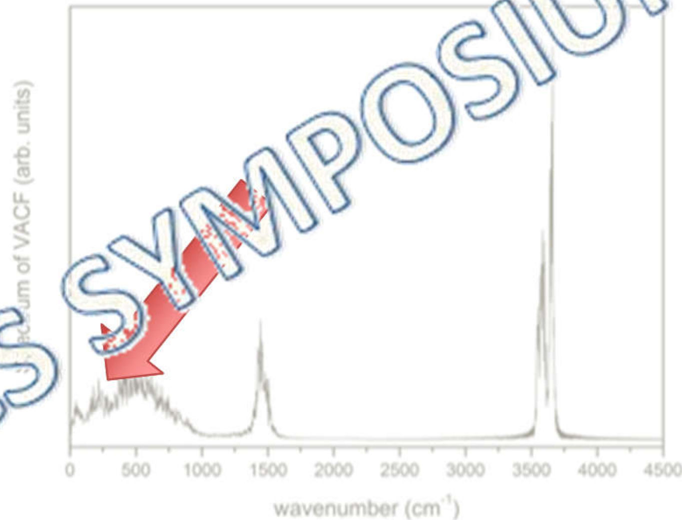
Water Silicon Interface VACF

After 200ps

After 2 ns

H





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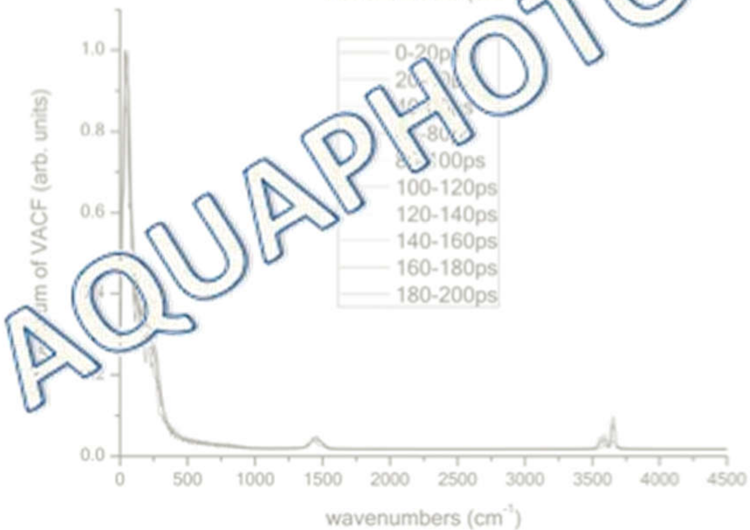

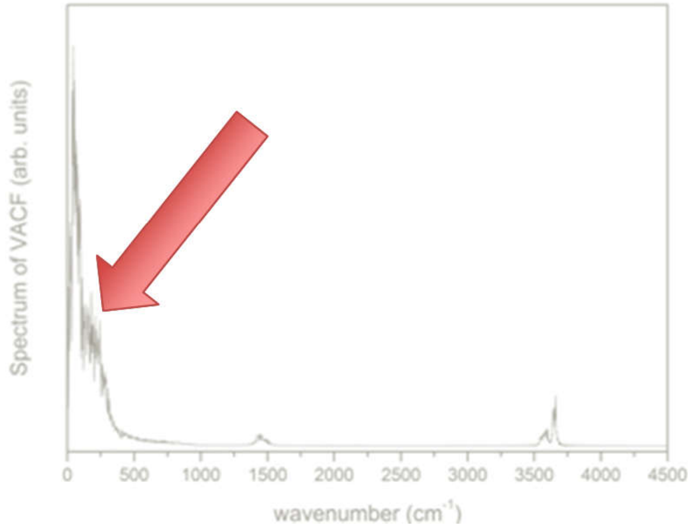

AQUAPHOTOMICS SYMPOSIUM

Theoretical Background

Dipole Autocorrelation Function

$$\langle M(t)\cdot M(0)\rangle = \left\langle \sum_{j=1}^{n} e_j r_j(t)\cdot \sum_{j=1}^{n} e_j r_j(0) \right\rangle$$

Electrical Flux-Flux Autocorrelation Function

$$\left\langle \frac{dM(t)}{dt}\cdot\frac{dM(0)}{dt} \right\rangle = \left\langle \sum_{j=1}^{n} e_j \frac{dr_j(t)}{dt}\cdot \sum_{j=1}^{n} e_j \frac{dr_j(0)}{dt} \right\rangle = \left\langle \sum_{j=1}^{n} e_j v_j(t)\cdot \sum_{j=1}^{n} e_j v_j(0) \right\rangle$$

$$I(\omega) \propto \int_0^{\infty} \left\langle \frac{dM(t)}{dt}\cdot\frac{dM(0)}{dt} \right\rangle \cos(\omega t)\,dt =$$

$$= \int_0^{\infty} \left\langle \sum_{j=1}^{n} e_j v_j(t)\cdot \sum_{j=1}^{n} e_j v_j(0) \right\rangle \cos(\omega t)\,dt$$

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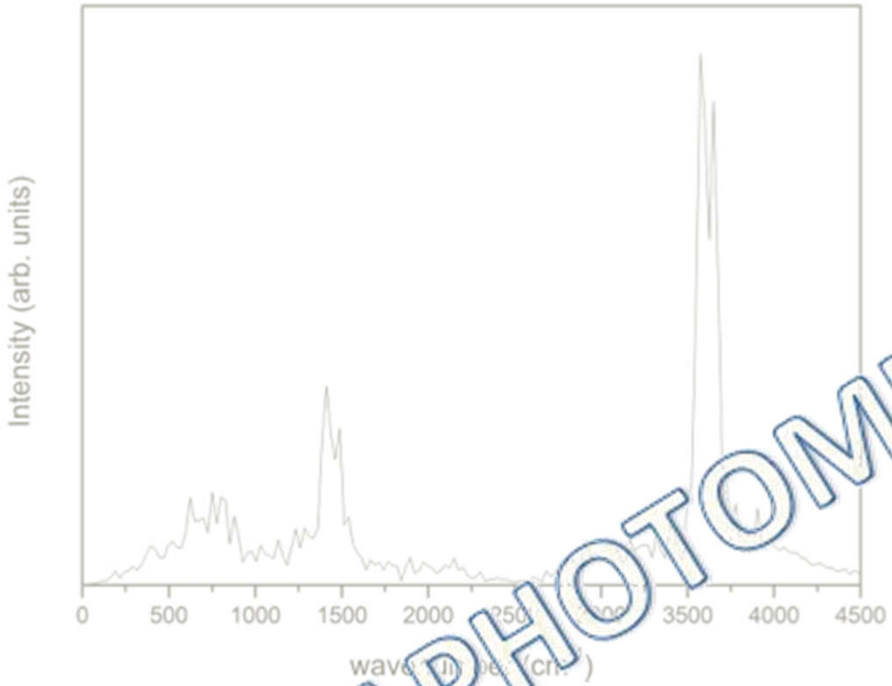
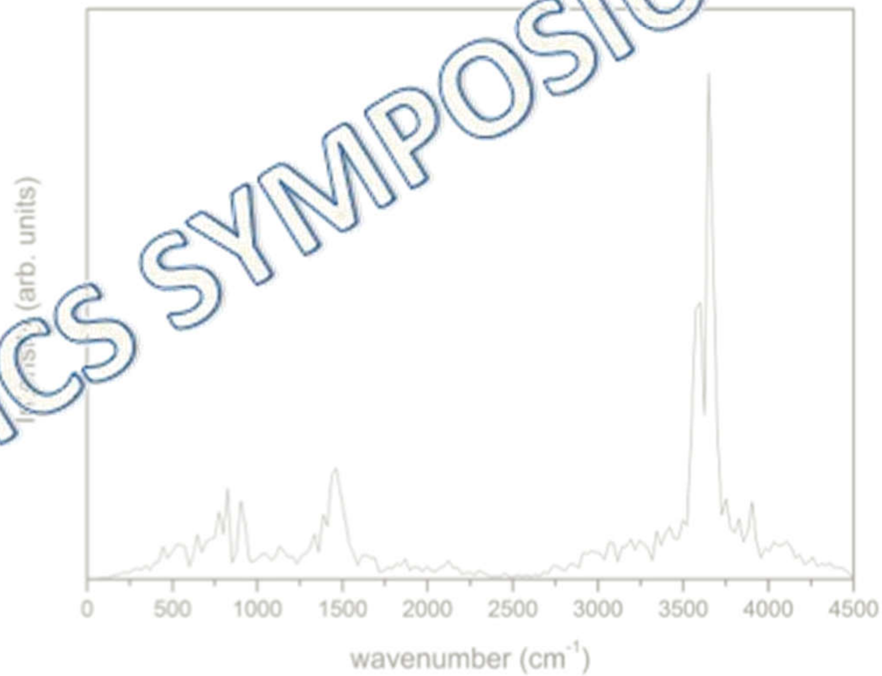
Water Silicon Interface IR

After 200ps



After 2 ns



	After 200ps	After 2ns
ν_s (asym-sym)	3649-3573	3649-3579
ν_b	1437-1480	1462

	Ice (220K)	H_2O (220K)	H_2O (300K)
ν_s (asym-sym)	3639-3544	3696-3600	3696-3600
ν_b	1443-1490	1481	1481

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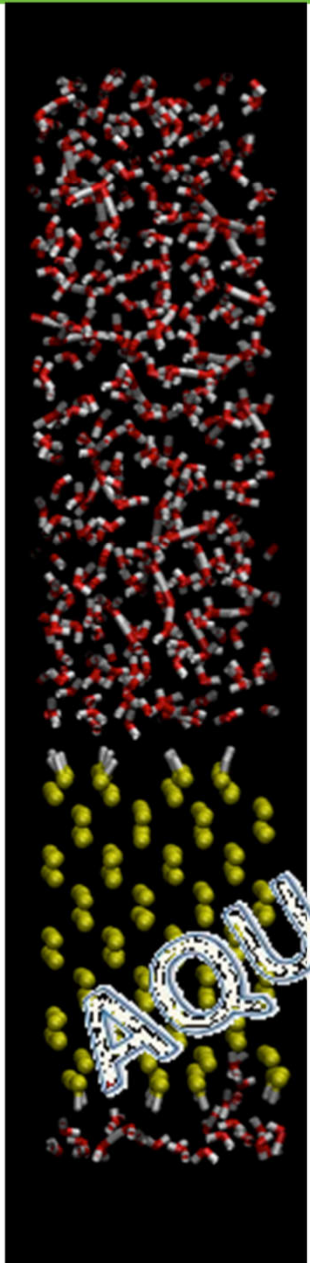
Simulation of water in heterogeneous environments

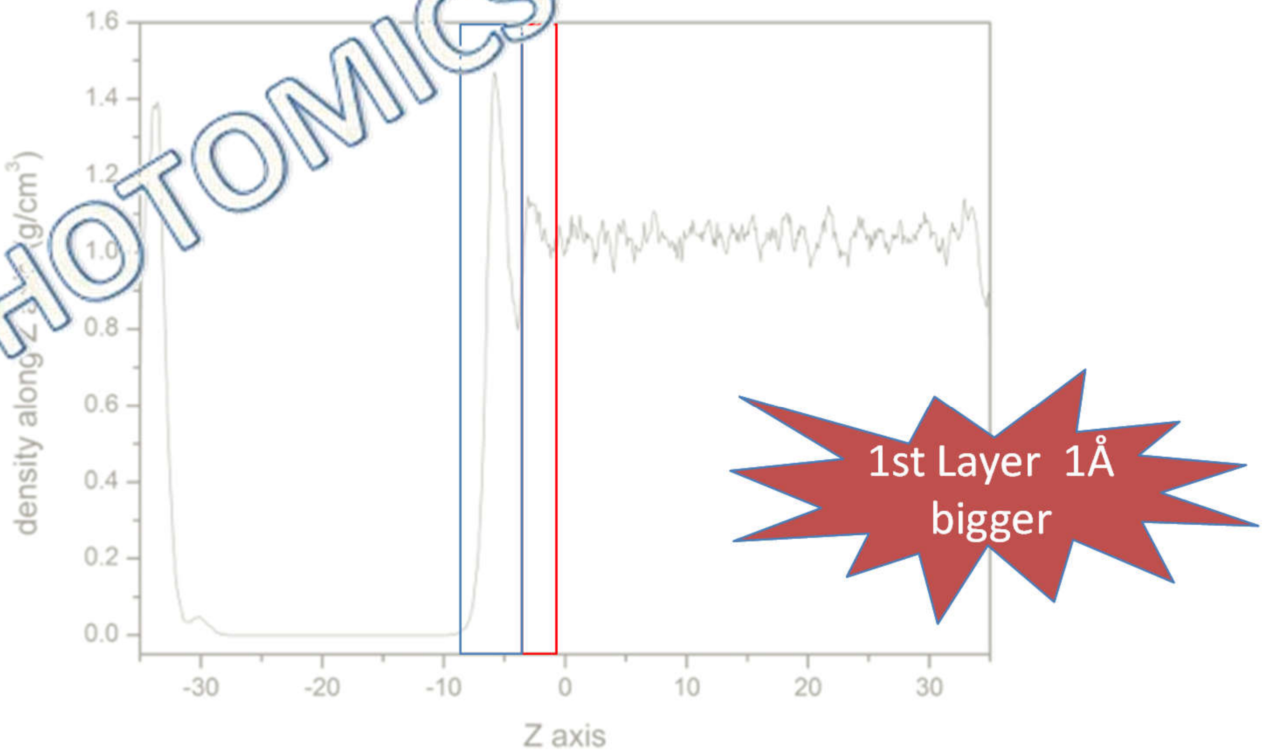
Simulation hydrogen-terminated silicon water interface

Water Silicon-Hydrogen Interface



Box size: 15.566 Å x 15.566 Å x 69.0 Å
378 H_2O molecules
256 Si atoms + 32 H atoms

Simulation parameters :
ensemble nvt evans, velocity verlet
200 ps, t_{step} 0.1fs, $t_{sampling}$ 2 fs, 300K



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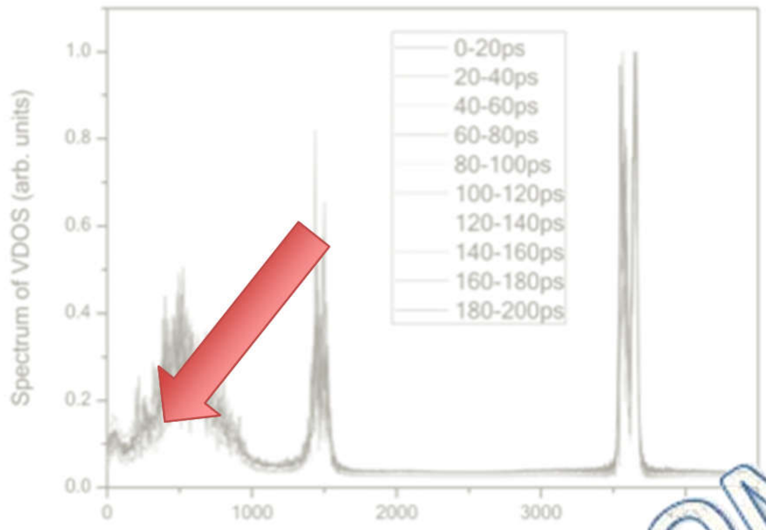
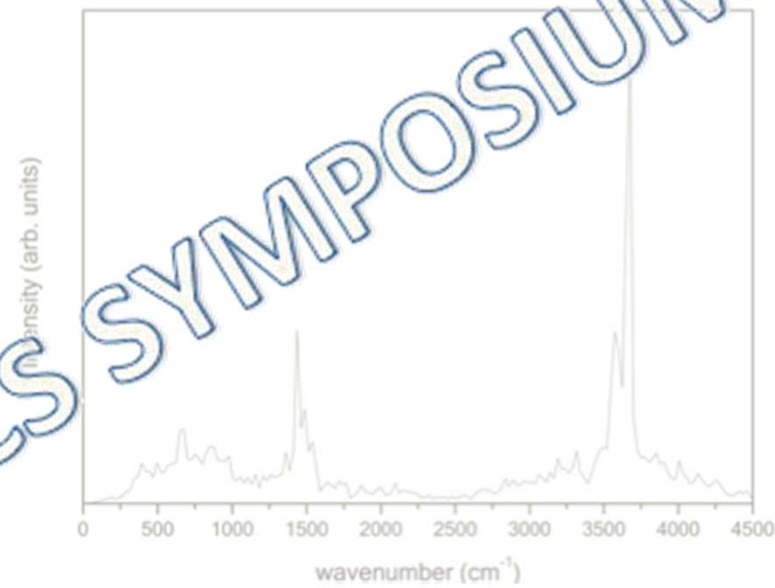
Water Silicon-Hydrogen Interface

VACF

mid-IR

H





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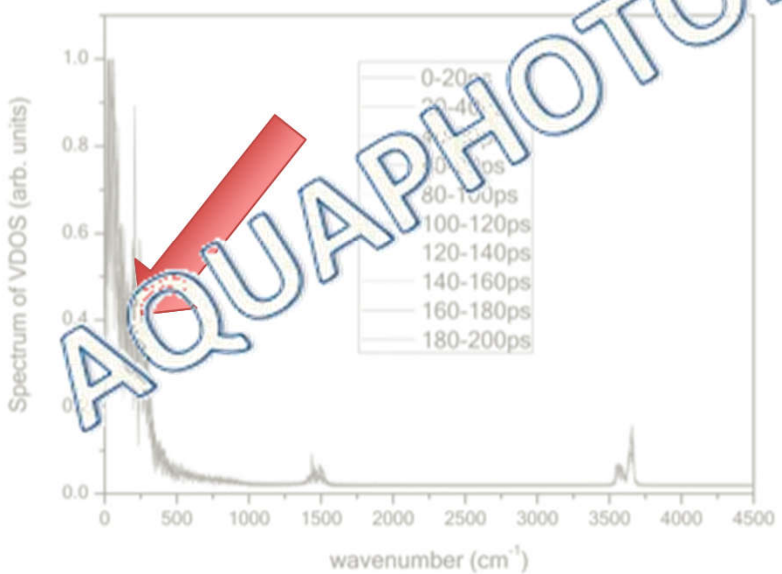

	Si-H+H_2O	Si + H_2O
v_s (asym-sym)	3673-3573	3649-3573
v_b	1437-1487	1437-1480

	Ice (220K)	H_2O (220K)	H_2O (300K)
v_s (asym-sym)	3639-3544	3696-3600	3696-3600
v_b	1443-1490	1481	1481

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Final Remarks

Liquid, Supercooled and Ice Water Simulations:

- Differences in librational bands for VACF and IR
- Movements to lower wavenumbers when water acquires structure.

Silicon with Water System:

- Density water variation along Z axis gives the different solvation layers.
- 1st solvation layer is bigger for Hydrogen terminal surface. Hydrophobic effect.

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Final Remarks

Silicon with Water System:

- 1st solvation layer power spectra after 200ps show some water organisation similar to ice water.

- 1st solvation IR spectra , achieved through the electrical flux-flux approach, confirms the organisation of water in a halfway between liquid and ice water.

Future plans:

- Simulation of Hydroxyl-terminated Silicon surface.

- Protein water interface

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