Electrolytes adsorption at the (0001) $\alpha$-quartz/water interface via DFT-MD simulations.

Hydroxylated and singly deprotonated surfaces

12/11/2014
Journée Simulations Orsay - CPPS

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**Why solid/liquid interfaces?**

- New properties / bulk media: adsorption, a/b, redox
- Very varied
- To be understood to do what you want

### Industry

- **Corrosion or biocorrosion** (how sea salts are implied in bacteria aggregation on ship hulls)
- **Heterogeneous catalysis** ($H_2O_2$ on TiO$_2$/SiO$_2$ for propene epoxydation or Re$_2$O$_7$/Al$_2$O$_3$ in olefin metathesis)
- **Biomimetic materials** ("shark skin" for hydrodynamism)

### Biology/medicine

- **Medical implants** (for teeth: Ti/TiO$_2$ surface in contact with water and proteins)
- **Biosensors**

Silica (amorphous) or quartz (crystalline) / water interface:

- Very common in geochemistry
- Soil formation
- Transport of nutrients or contaminants
- Dissolution mechanism for nuclear waste storage

**How is the microscopic structure like?**
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**Surface-specific probe and its (mis?)understanding**

**Outline**

- Computational setup
- Ions alone at pH≈2
- Ion pairs and pH effects
- Conclusion

**Questions from SFG spectra**

- Origin of the "ice-like" and "liquid-like" bands?
- Where can the ions locate?
- Why does the intensity shrink when ions are added?
- Why does the intensity increases with pH (yet, until pH∈ [8, 10])?

**Strategy for AIMD - CP2K**

- Simple cristalline slab of (0001) α-quartz + water
- Adsorption of singly-charged ions - K⁺, Na⁺, Cl⁻, I⁻
- Mimick local pH effects via surface deprotonation
- Study changes in the very first water layers (here)
Electrolytes adsorption at the (0001) α-quartz/water interface via DFT-MD simulations.

Contents

1. Computational setup
   - Technical details
   - Global views of the systems

2. Ions alone at pH≈2

3. Ion pairs and pH effects

4. Conclusion
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**Technical details**

**System**

- (0001) $\alpha$-quartz/water interface
- Tetragonal supercell $9.82 \times 8.504 \times 32.165$ Å$^3$
- 64 $\text{H}_2\text{O}$ (neat interface) - 63 $\text{H}_2\text{O}$ (interface with ions)
- 6 O-Si-O layers
- Fully hydroxylated surface: 8 SiOH - Low pH ($\approx 2$)
- Deprotonated surface: 1 SiO$^-$ and 7 SiOH - Basic pH ($> 8$)

**Computational details**

- Functional BLYP + D2 Grimme dispersion correction
- Density cutoff 280 Ry
- GTH-BLYP pseudopotentials
- TZV2P gaussian basis set - DZVP-MOLOPT-SR for K$^+$ and I$^-$ only
- Microcanonical ensemble (NVE)
- $T \approx 330$ K
- Equilibration ($\approx 9$ ps), dynamics ($\approx 12$ ps)
Global views of the systems

Electrolytes adsorption at the (0001) α-quartz/water interface via DFT-MD simulations.
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Contents

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   - Characteristics of adsorption
   - Focus on the very first layers - water + SiOH
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**Initial conditions**

- Put one ion close to the interface by replacing a water molecule H-bonded to a silanol group
  - same results for HB donor or HB acceptor (checked *a posteriori*)
- No counterion
- Same starting positions for all 4 ions, Na$^{+}$, K$^{+}$, Cl$^{-}$, I$^{-}$
- Random choice of velocities among a Boltzmann distribution centered at $T$
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**Location and coordination**

- Inner-sphere adsorption
- Silanols inside the solvation shells
  - Coordination: 6 O (4 Ow + 2 OSi) for Na\(^+\), 8 O (5 Ow + 3 OSi) for K\(^+\)
- Intermediate inner/outer-sphere adsorption
  - 1 or 2 bridging water molecules
  - Coordination: 5 Hw for Cl\(^-\) and I\(^-\)
H-bond strengths between water and silanols

**Cations**

- **Donation Hw -- OSi**
  - Neat, Na+ shell, Na+ out, K+ shell, K+ out

- **Acceptation Ow -- HSi**
  - Neat, Na+ shell, Na+ out, K+ shell, K+ out

**Anions**

- **Donation Hw -- OSi**
  - Neat, Cl- shell, Cl- out, I- shell, I- out

- **Acceptation Ow -- HSi**
  - Neat, Cl- shell, Cl- out, I- shell, I- out

- H-bonds between silanols and water donors (blue) are the most affected by ions
- Systematic decrease of the strength of these H-bonds, their distances become larger with the following tendency: neat < Na⁺ < K⁺
- On the contrary, slight increase on the whole with anions
- About H-bonds involving water acceptors from out-of-plane silanols, very few differences
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**Initial conditions - pH≈2**

**Test case with NaCl**

- Built from the final positions of the Na\(^+\)-containing supercell
- Starting point: **tight ion pair geometry** close to the surface (Guardia, Chem. Phys. 1991)
- End of trajectory: stable ion pair separated by one solvent molecule

**Starting point**

- Built from the final positions of the NaCl test case
- Starting point: **ion pair separated by one solvent molecule**
- Same positions for NaI, NaCl and KCl
- Velocities following Boltzmann distribution
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**Ion pairs geometries**

<table>
<thead>
<tr>
<th>System</th>
<th>K⁺ KCl</th>
<th>Na⁺ NaCl</th>
<th>Na⁺ NaI</th>
<th>Cl⁻ KCl</th>
<th>Cl⁻ NaCl</th>
<th>I⁻ NaI</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₂ (Å)</td>
<td>2.7±0.4</td>
<td>1.6±0.2</td>
<td>1.7±0.2</td>
<td>5.2±0.8</td>
<td>6.1±0.7</td>
<td>5.8±0.5</td>
</tr>
<tr>
<td>Nc</td>
<td>8</td>
<td>6</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table: Individual geometrical characteristics for each ion in the three different ion pairs, KCl, NaCl and NaI. R₂: Averaged distance from the surface along the vertical direction. Nc: Whole coordination number (silanols and water molecules included).
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**Water orientation wrt z axis**

- Neat interface in basic conditions
- Orientation of water donors unchanged with pH (see $\cos \theta \approx -0.75$)
- However, disappearance of the sharp feature for $\cos \theta > 0.8$
- Explained by a strong HB network ($9.2\text{ps}$) that forces different angular distributions
- Strong organization probably responsible for $I_{SFG}$ enhancement with pH

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- Computational setup
- Ions alone at pH $\approx 2$
- Ion pairs and pH effects
- Initial conditions
- Focus on the very first layers - water + SiOH

**Conclusions**
- Systematic disordering by ions

**Key Diagrams**
- Angular distribution of water molecules wrt z axis
- Comparison of adsorbed layers
- Neat interface in basic conditions
- Orientation of water donors unchanged with pH (see $\cos \theta \approx -0.75$)
- However, disappearance of the sharp feature for $\cos \theta > 0.8$
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Band assignment from VDOS analysis

Previously evidenced by Gaigeot, Sprik and Sulpizi in J. Phys.: Condens. Matter, 24, 124106, 2012:

- Water **HB donors** to the surface → **liquid-like**
- Water **HB acceptors** from SiOH → **ice-like**

![Diagram](image-url)

**Acidic pH**
- Both
- Liquid-like
- Ice-like
- Both ice- and liquid-like

**Basic pH**
- Both but more liquid-like
- Mostly ice-like
- Mostly ice-like
- Neat: mostly liquid-like
- KCl: low freq. ice-like

Outline

Computational setup

Ions alone at pH ≈ 2

Ion pairs and pH effects

Initial conditions

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Conclusion
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Conclusion: What we have learnt

Structure - Ions location

- Direct adsorption of cations on protonated silanols: 2 O in their solvation shells, mostly 2 IP SiOH. No SiO$^-$ remaining in the shell
- High surface coverage: anions do not stay close to the surface when we use ion pairs
- Solvation shells not strongly modified from bulk to interface and interface with ion pairs

Spectroscopy

- Origins of bands in SFG: many possible contributions according to ionic force and pH, but water acceptors mostly "ice-like" while water donors to SiOH's are more "liquid-like"
- $I_{SFG}$ $\downarrow$ with ions because of increasing disorder: loss of orientation of water molecules, larger fluctuations of H-bonds between water and silanols, more intra-surface movements
- $I_{SFG}$ $\uparrow$ with pH since a deprotonated site stabilizes intra-surface dynamics and, accordingly, enables stable H-bonds with water (in particular, donations from water). Possible HB network to maintain more tightly the interfacial structure
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Outline

Computational setup

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Thank you for your attention