

Theoretical studies on reactions of gas phase ions with water covered α -quartz surfaces

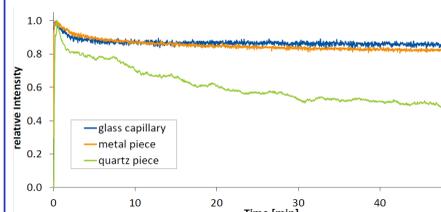


¹Physical & Theoretical Chemistry
Wuppertal, Germany
(Institute for Pure and Applied Mass Spectrometry)

Alexander Haack¹; Walter Wissdorf¹; Hendrik Kersten¹; Thorsten Benter¹

Introduction

Experiments^[1] on the transmission efficiency of different capillaries – as used as first pressure reduction stage in many common MS – showed temporal changes in the ion signal. Increasing the ion flux, a rapid increase of the ion signal was followed by an exponential decay over the time scale of minutes.



Temporal evolution of ion signal for different capillary materials.

Because this effect was observed for unipolar ion fluxes only and was especially pronounced for non-conductive materials such as quartz capillaries, it was argued that surface charging might be the reason for the observed effects. Charge uptake onto the surface would lead to a repelling potential and thus lower the transmission efficiency until an equilibrium between the surface and the gas phase is reached. Materials with high conductivity, however, would be able to transport the charge to a grounded part of the apparatus and thus, no potential could be build up.

It was also found, that the amount of water in the gas phase is an important parameter. Flushing the capillaries with humid air prior to ion measurements led to a delayed response of the ion signal. Higher uptake capacities of a thick water layer or an enhanced surface conductivity could be possible reasons for this observation.

A theoretical investigation of the involved molecular processes should gain more insight into the ion-surface interactions and its dependence on the amount of water present at the surface. As a general and well studied model, the (0001) α -quartz surface site was chosen. Interactions with neutral water and with the ionic species H^+ and $MeOH_2^+$ (as a model for small organic $[M+H]^+$ analytes) were conducted with DFT, molecular mechanics and molecular dynamics simulations. The results are used to check, whether charge is adsorbed onto the surface and if a $[M+H]^+$ can loose its charge through proton transfer to the surface.

Computational Details

Software package:

Gaussian09, Revision C.01 ^[2] for calculations
GaussView 4.1 ^[3] for visualization
Python scripts for plotting

Machine:

Linux-based computer cluster, 4x16-Core CPUs (6282SE AMD Opteron; Advanced Micro Devices GmbH, Dornach, Germany) and 32x16 GB memory

PBC-DFT

Computational Method:

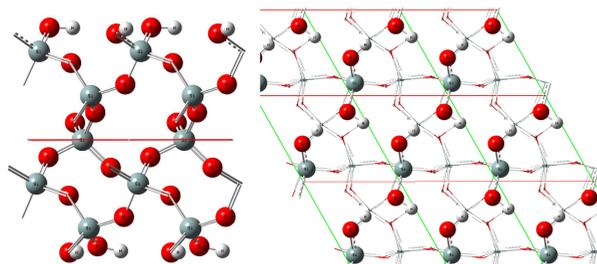
- Density Functional Theory (DFT) with Periodic Boundary Conditions (PBC)^[4]
- PW91 exchange-correlation functional^[5], Pople 6-31G(d,p) basis^[6]
- ultrafine integration grid and density fitting
- Gives the best results with reasonable computation time (15 combinations of different functionals and basis sets tested)

Model System:

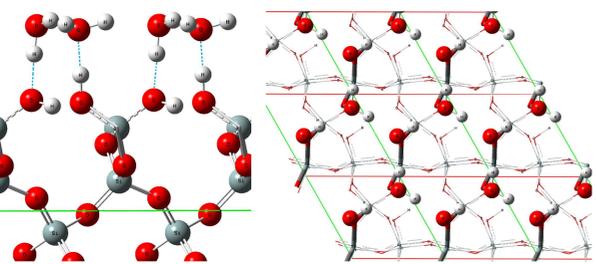
- (0001) α -quartz surface site modeled by a 5 Si-atom thick slab (2D periodic along the surface directions), geminal OH-groups at the surface

Results:

- For the **clean surface**, a flat hydrogen bond system (zigzag form) is found. Every O atom is an H-bond acceptor and donor, forming six-membered rings. One of the H-bonds is longer (thus weaker) than the other one. OH stretching bands ($\sim 3700\text{ cm}^{-1}$) are slightly red-shifted.



- A dense **monolayer of water** ($\sim 2.6\text{ \AA}$ above) is formed, when the surface is covered with two H_2O per elementary cell. One binds as H-bond donor to the surface, one as acceptor. Redshifted OH stretching bands (3100 cm^{-1}) indicate strong H-bonds. The H_2O molecules as well form flat zigzag H-bonds and six-membered rings (similar to ice). Hence, every O atom is surrounded by four H's.



- Going from the dense mono- to a bilayer (4 H_2O per cell), the **adsorption energy** per water molecule is reduced by $\sim 100\text{ meV}$. The area per H_2O molecule is half, hence, the energy change per area is almost double.

system	A/n_{H_2O} [\AA^2]	ΔE_{ads} [meV]	ΔE_{area} [meV \AA^{-2}]
monolayer	10.563	-1018	-96.4
bilayer	5.293	-927	-175

$$\Delta E_{\text{ads}} = \frac{E(\text{covered}) - (E(\text{clean}) + n_{H_2O} \cdot E(H_2O))}{n_{H_2O}} \quad \Delta E_{\text{area}} = \frac{n_{H_2O} \cdot \Delta E_{\text{ads}}}{A}$$

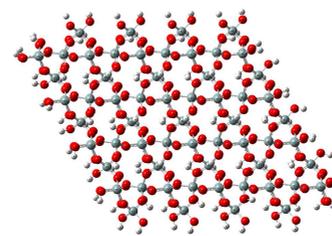
QM/MM superslab

Computational Method:

- The **ONIOM**^[7] model is a hybrid model, where one part (High Layer) is calculated with quantum mechanical (QM) and its surrounding (Low Layer) with molecular mechanical (MM) methods
- QM part: PW91/6-31G(d,p) MM part: AMBER^[8], with own defined parameters
$$E_{\text{ONIOM}} = E_{\text{MM}}^{\text{HL+LL}} + E_{\text{QM}}^{\text{HL}} - E_{\text{MM}}^{\text{HL}}$$
- During the HL calculations, the dangling bonds are saturated with Link Atoms

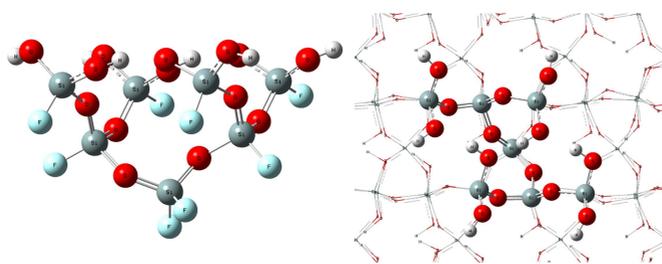
Model System:

- Because PBC are not available for MM based calculations in *Gaussian09*, a superslab was defined
- (5x5) elementary cells, 5 Si-atom thick, all dangling bonds were saturated by OH groups



Results:

- Definition of the **Force Field Parameters** by comparing the pure MM optimized geometry with the PBC-DFT one. Atoms were divided into 7 classes (e.g. $O_{\text{surface}}/O_{\text{bulk}}/O_{\text{water}}$). 48 geometric parameters in the middle of the model system were chosen for comparison. Mean absolute deviation of 1.4%, max. absolute deviation 6.4%.
- The **High Layer** was chosen to be right in the middle of the superslab to reduce errors from the non-periodic boundaries. Not only surface atoms but also some below were chosen, hence, the HL consists of one covalently bonded fragment. Fluorine atoms were chosen as Link-Atoms because of their similarity to oxygen atoms. With this assignment, three hydrogen bonds are calculated on the QM level.



- For the water covered surfaces, all water molecules were incorporated in the High Layer additionally to the shown fragment at the surface.
- The ONIOM models were then optimized regarding the ONIOM energy and compared with the PBC-DFT results. To minimize errors induced by the non-periodic boundaries, the outer most oxygen atoms were fixed during optimization.

- Covalent bonds inside the bulk are reproduced nicely by bond distances, angles and dihedrals (High and Low Layer)
- Inside the High Layer, the H-bond system is reproduced by means of structure but the H-bond distances are shortened (e.g. $3.05\text{ \AA} \rightarrow 2.86\text{ \AA}$)
- H-bonds between High and Low Layer are not accurately described and sometimes even cleaved (probably difficult to model weak H-bonds with MM)
- Water adsorption is reproduced qualitatively: The structure of the dense monolayer (six-membered rings, in-plane zigzag H-bonds, binding to the surface as H-bond acceptor and donor) is also visible in the ONIOM results. Geometrical parameters of the different H-bonds differ by a few percent

AIMD

Computational Method:

- Atom Centered Density Matrix Propagation Molecular Dynamics (**ADMP**)^[9] is a MD code, where the electron density is propagated instead of calculated through an SCF procedure at each time step of the trajectory calculation (similar to Car-Parrinello approach^[10])
- Combinable with the ONIOM model^[11]
- MD simulations conducted with $\Delta t = 0.2\text{ fs}$ and at $T = 298.15\text{ K}$

Model System:

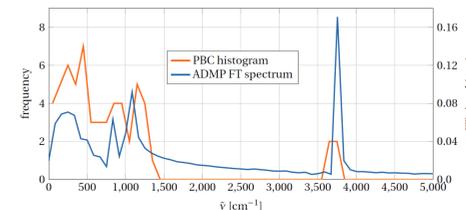
- Converged ONIOM results (clean and water-monolayer covered surface) without fixed boundary atoms
- H^+ and $MeOH_2^+$ adsorption and charge stabilization investigated

Results:

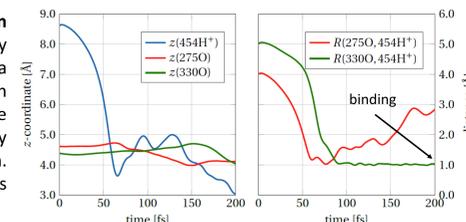
- FT of the *Velocity Auto Correlation Function* C_v gives **vibrational spectra** similar to the one from the PBC solution (e.g. OH stretching band $\sim 3760\text{ cm}^{-1}$)

$$C_v = \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i^{(t_0)} \cdot \mathbf{v}_i^{(t)}$$

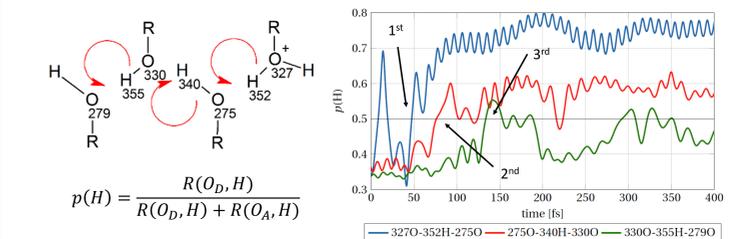
FT



- Interactions with a proton** were investigated by placing a H^+ 4 \AA above a surface O atom. The proton is attracted to the surface and after $\sim 90\text{ fs}$ covalently bonded to an oxygen atom. This clearly represents charge adsorption.



- Proton movement lateral to the surface** was observed as well, when an additional H^+ was introduced to the surface. Along the H-bond zigzag chain, the charge was transported by moving a proton along the H-bond to its acceptor oxygen.



- Proton movement was even **more pronounced with water** adsorbed at the surface. The charge was stabilized as flat H_3O^+ inside the water layer, H-bonded from all three sides (only possible because of additional H-bond inside the water layer). The great stability of the H_3O^+ molecules can also be seen from the fact, that even spontaneous deprotonation from the surface OH-groups towards the water layer was observed. During all proton transfer reactions, the O-O distances were reduced by $\sim 0.4\text{ \AA}$.
- Interactions with $MeOH_2^+$** were also investigated by placing the ion close to the surface. In both cases (clean and water covered surface) it is only adsorbed through H-bonds. No proton transfer to the surface was observed. The ion showed a somewhat freely lateral movement and never penetrated the surface or water layer. However, the charge was stabilized through an H-bond. With more thermal energy or a less basic M, proton transfer might be feasible since the charge is well stabilized at the surface and especially inside the water layer.

Conclusions

- The fully hydroxylated (0001) α -quartz surface was investigated with PBC-DFT methods. Geometry optimization showed a zigzag-chain of H-bonds along the surface. Water adsorbs readily through H-bonds from and to the surface and especially 2 and 4 H_2O molecules per cell are stable (-1018 meV and -927 meV). Calculated vibrational spectra compare well with experimental ones.
- The model was implemented into the ONIOM scheme as a 5x5 superslab. MM parameters for the AMBER force field were developed by comparison with the PBC-DFT results.
- With the ONIOM model, AIMD simulations were conducted. They show, that charge is well adsorbed and stabilized at the surface, especially in presence of water. A protonated organic molecule, such as $MeOH_2^+$, however, only binds to the surface and doesn't undergo proton transfer. Nevertheless, PT seems to be feasible with weaker bases/higher temperatures/more impact energy.

Outlook

- Investigate other analyte molecules (weaker bases, negative ions) for a more general statement
- Different temperatures could be assigned during the MD simulations
- Different surface sites could also be investigated

Literature

- [1] Müller, D., Diermann, V., Benter, T. (2013): #MP278, 61st ASMS Conference on Mass Spectrometry and Allied Topics. Minneapolis, MN, USA.
- [2] Gaussian 09, Revision C.01, Frisch, M.J. et al.: Gaussian Inc., Wallingford CT (2009)
- [3] Dennington, R.; Keith, T.; Millam, J.: GaussView, Semichem Inc., Shawnee Mission (2007)
- [4] Kudin, K. N., Scuseria, G. E. (2000): *Phys. Rev. B*, 61(24), 16440–16453.
- [5] Perdew, J. P. (1991): *Electronic Structure of Solids '91*, 17, 11–20.
- [6] Ditchfield, R., et al. (1971): *J. Chem. Phys.*, 54(2), 724–728.
- [7] Dapprich, S., et al. (1999): *J. Molec. Struct. THEOCHEM*, 461–462, 1–21.
- [8] Cornell, W. D., et al. (1995): *J. Am. Chem. Soc.*, 117(19), 5179–5197.
- [9] Schlegel, H. B., et al. (2001): *J. Chem. Phys.*, 114(22), 9758–9763.
- [10] Car, R., Parrinello, M. (1985): *Phys. Rev. Lett.*, 55(22), 2471–2474.
- [11] Rega, N., et al. (2004): *J. Phys. Chem. B*, 108(13), 4210–4220.

Acknowledgement

Financial support by iGenTraX UG (Haan, Germany) is gratefully acknowledged.