Fraunhofer KIT Karlsruhe Institute of Technology

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The electrostatic origin of polar hydrophobicity:

Why perfluorinated carbons can be polar and hydrophobic

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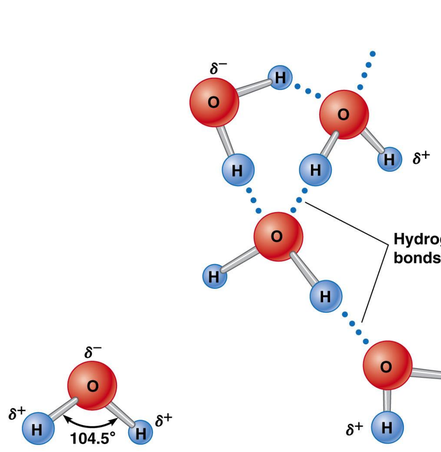
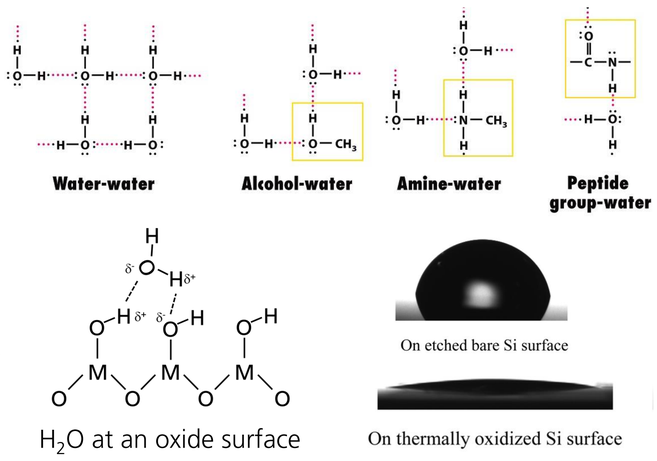
Polar = hydrophilic?

Water is a polar molecule and in general forms hydrogen bonds to other polar molecules and polar surfaces

- Good solvation of polar molecules in water
- Good wetting of polar surfaces





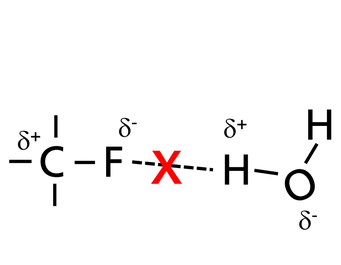
H_2O at an oxide surface

On thermally oxidized Si surface

An Exception: Fluorinated Carbon Materials

- Perfluorinated carbon materials are in general hydrophobic
- **But**: C-F bond is highly polar
- C-F bond is most stable bond in organic chemistry

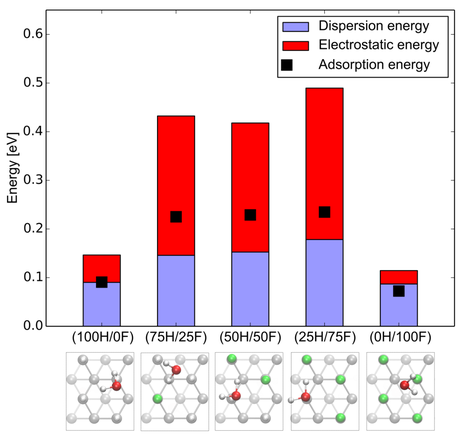
Perfluorinated carbon compounds are of importance as water repellent surfaces (»Teflon«, »Gore Tex«), in biology, pharmacy etc.



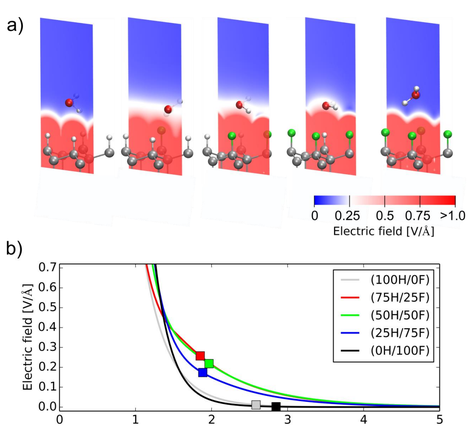
Ab initio DFT results

Adsorption energy calculations of single water molecules on the C(111) surfaces using the PBE functional + Grimme's D2 dispersion energy correction

- Enhancement of adsorption strength for mixed H/F coverage of C(111)
- Strongly suppressed electrostatic interaction at highly polar 100% F surface

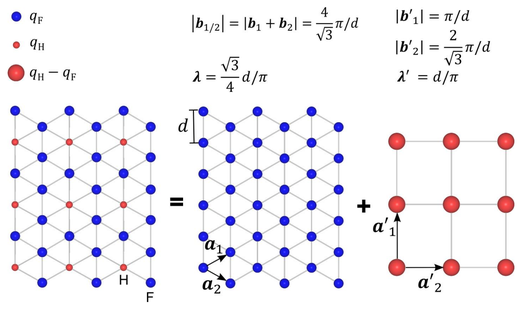


Adsorption energies of single H_2O molecules



Near surface electric field strength for the different surfaces

A simple Point Charge Model (2D dipole lattice[2])



$$\mathbf{E} = \frac{\sigma}{2\varepsilon_0} \sum_{l,m\neq 0} \frac{e^{-|\mathbf{G}_{l,m}||z-z_{up}|} - e^{-|\mathbf{G}_{l,m}||z-z_{low}|}}{|\mathbf{G}_{l,m}|} \begin{pmatrix} -\sin(\mathbf{G}_{l,m}\mathbf{r})G_{l,mx} \\ -\sin(\mathbf{G}_{l,m}\mathbf{r})G_{l,my} \\ +\cos(\mathbf{G}_{l,m}\mathbf{r})|G_{l,m}| \end{pmatrix}$$

Example:

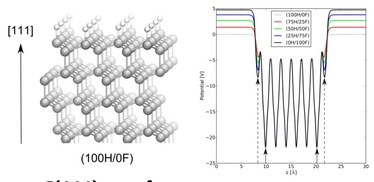
Dipole lattice of mixed 75%F/25% H surface =
Dipole lattices of 100% F terminated surface +
Dipole lattice of inhomogeneities

Electric field strengths of 2D dipole lattices decay exponentially

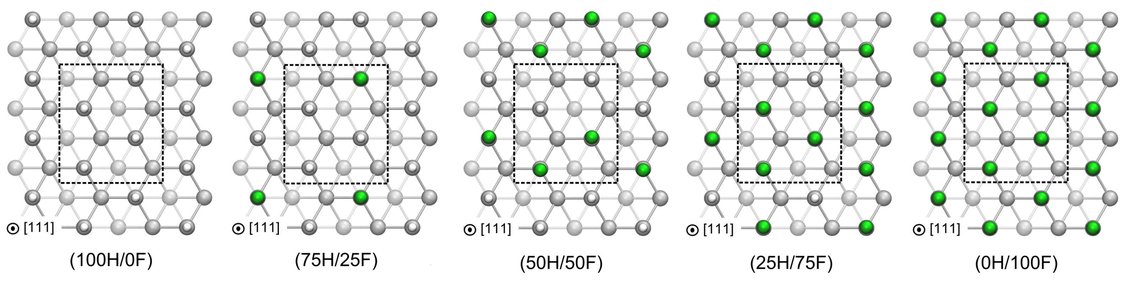
- Decay length proportional to next neighbor distance
- Dense dipole lattices lead to ultrafast decay of surface electric fields

Our Model System: Fluorinated Diamond (111) Surfaces

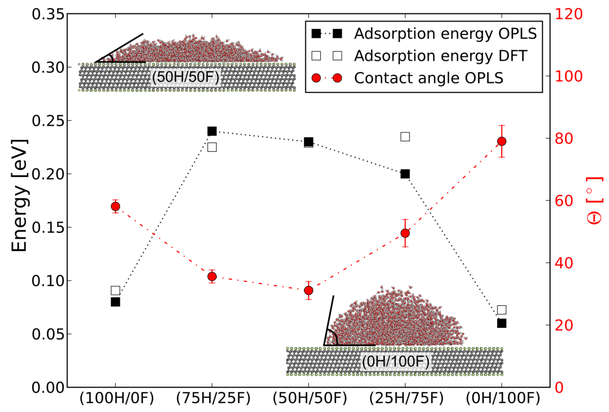
- Increase F coverage from 0% to 100%
- Decrease H coverage from 100% to 0%
- Transition from unpolar to highly polar surface
- Effect on water-surface interaction?



C(111) - surface



From DFT to Wetting: Classical Force Fields



- Classical point charges reproduce electrostatics from ab initio calculations
- Parametrization of OPLS force fields in connection with TIP3P force field for water
- Strong correlation between single molecule adsorption energy and wetting behavior (contact angle)

Polar hydrophobicity results from short-ranged electric fields due to high dipole density and low charge density spill out of C-F bonds → also holds true for perfluorinated molecules[1]

[1] Mayrhofer, L.; Moras, G.; Mulakaluri, N.; Rajogapalan, S.; Stevens, P. A.; Moseler, M.; J. Am. Chem. Soc. 138, 4018–4028 (2016).

[2] Lennard-Jones, J. E.; Dent, B. M. Trans. Faraday Soc. 24, 92 (1928).