Supporting Information for: Solvation Free Energies for Periodic Surfaces: Comparison of Implicit and Explicit Solvation Models

Stephan N. Steinmann,* Philippe Sautet, and Carine Michel

Univ Lyon, Ecole Normale Supérieure de Lyon, CNRS Université Lyon 1, Laboratoire de Chimie UMR 5182, 46 allée d'Italie, F-69364, LYON, France

E-mail: stephan.steinmann@ens-lyon.fr

To be published in *Physical Chemistry Chemical Physics*

This supporting information contains 5 pages.

The interaction between the metal surface and the water molecules is underestimated: water adsorbs strongly on Ru(0001) (0.7 eV), but the UFF non-bonded parameters give only a weak physisorption (0.03 eV). Therefore, we have changed the non-bonded interaction parameters of Ru, in order to improve the agreement between DFT and UFF.

When computing the adsorption energy of a single water molecule on Ru(0001) by a force field as a function of the distance, the first non-trivial decision to take is the choice of the atomic charges: in the DFT computations, the charges change quite substantially between the chemisorbed state and the gas-phase. However, in a "standard" (i.e., non-polarizable) force field, we need to use one set of atomic charges for the entire binding energy curve in order to guarantee a physically meaningful reference energy. However, since the dissociation limit needs to have neutral fragments and the computation of atomic charges in the chemisorbed state will not guarantee neutral fragments, we have taken the charges from the largest distance
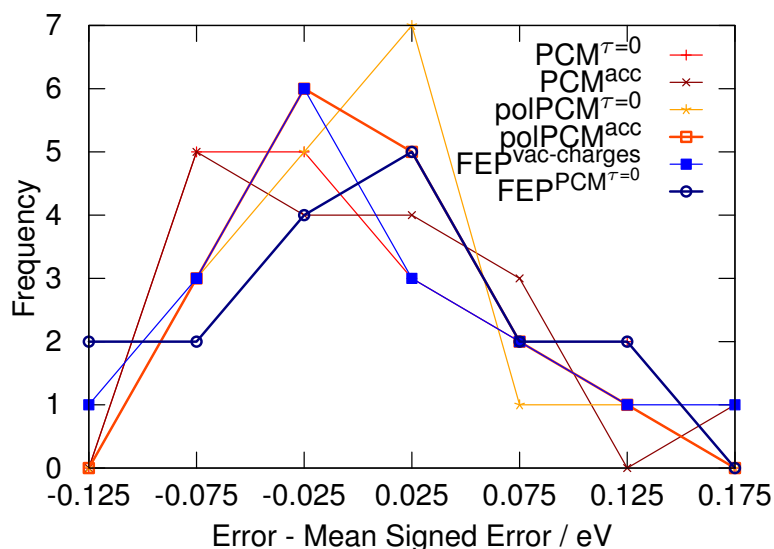
Figure 1: Distributions around the average error of computed solvation free energies $\Delta_s G$ of small molecules compared to experimental data in form of a histogram (the lines are shown as a guide to the eye). Two settings are tested for the PCM: $PCM^{\tau=0}$ refers to the use of standard parameters, except that the cavity surface tension τ is set to zero to improve numerical stability and PCM^{acc} uses the default parameters for the PCM, but with increased numerical precision (600 eV plane-wave basis set and more accurate FFT grids). polPCM includes the polarization contribution to the solvation energy, i.e., $\Delta_s E_{pol,PCM}$. FEP computations are either based on vacuum charges ($FEP^{vac\text{-}charges}$) or on an electronic structure surrounded by an implicit solvent ($PCM^{\tau=0}$).
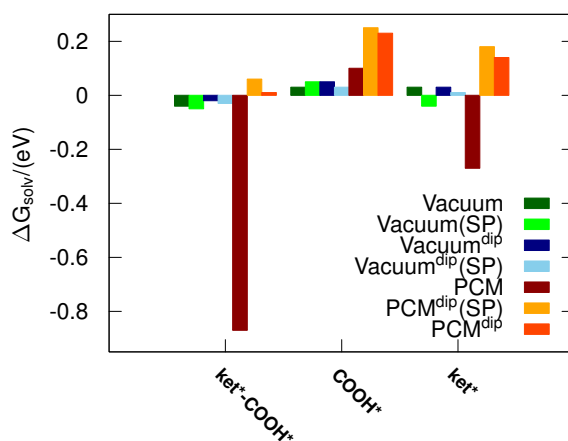

Figure 2: Computed solvation free energy contributions to the adsorption of levulinic acid in three distinct adsorption modes according FEP, based on geometries and atomic charges following different protocols. The appended "(SP)" indicates the use of vacuum geometries for evaluating atomic charges in the PCM and vice versa. The use of the dipole correction is indicated by the superscript "dip".

Table 1: Solvation free energies of molecules in kcal/mol.

Name	Exp	PCM$^{\tau=0}$	FEP	PCM^{acc}	polPCM
12ethandiol	-9.30	-12.80	-7.10	-11.42	-8.09
acetaldehyde	-3.50	-7.55	-4.82	-6.25	-5.22
acetic acid	-6.70	-11.59	-4.75	-10.33	-7.40
acetone	-3.85	-8.13	-5.69	-6.55	-5.57
butanal	-3.18	-7.31	-3.39	-4.58	-4.95
butanoic acid	-6.36	-11.41	-3.45	-9.55	-7.15
butanol	-4.72	-7.37	-4.29	-5.49	-4.58
diethylether	-1.76	-3.80	-3.98	-1.79	-2.17
EtOH	-5.01	-7.11	-4.48	-5.78	-4.48
H2O	-6.31	-10.10	-5.39	-9.52	-6.64
H2O2	-8.58	-12.97	-5.08	-12.16	-8.35
methylamine	-4.56	-5.13	-4.25	-3.95	-3.22
methylformate	-2.78	-7.24	-3.46	-5.84	-4.80
morpholine	-7.17	-6.85	-7.20	-5.01	-4.29
NH3	-4.29	-6.16	-4.65	-5.33	-3.96
phenol	-6.62	-10.33	-5.89	-8.53	-6.56
pyridine	-4.70	-6.31	-7.47	-4.58	-4.19
MAD		3.14	1.35	1.94	0.98

for the entire energy profile. The standard UFF parameters lead to an interaction energy of only 0.03 eV at a distance of 2.8 Åbetween the oxygen atom and the surface, which compares very poorly to the DFT values of 0.7 eV at 2.2 Å. The modified parameters lead to a slight improvement (0.13 eV at 2.4 Å). This modest improvement is obtained for an "almost" physical set of parameters, i.e. the Ru radius is reduced from 1.4815 to 1.075 Åand the well depth increased from 2.4 meV to 173.5 meV (4 kcal/mol).

From this we conclude that the Lennard-Jones potential with physically meaningful parameters is, unfortunately, not suitable to reproduce the strong chemisorption, which includes a charge-transfer (or covalent) contribution. Furthermore, the effect of the modified Ru non-bonded parameters on the solvation energy is disappointing: solvating the naked surface or the adsorbate becomes almost equivalent, i.e., the solvent does no longer discriminate strongly between different adsorption modes.
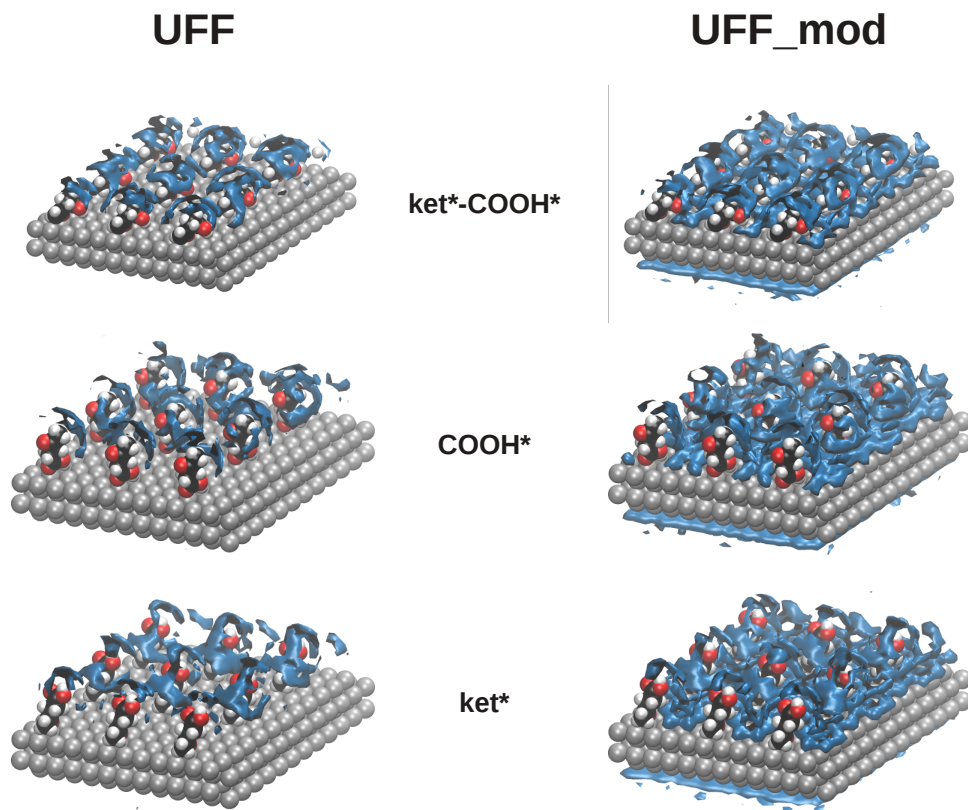
3

UFF **UFF_mod**

ket*-COOH*

COOH*

ket*

Figure 3: Iso-probability maps to find a water molecule with standard UFF non-bonded parameters and with the modified ones, which visibly give a stronger interaction between the surface and the solvent.

Table 2: Adsorption energies (in eV) and their dependence on the geometry both in vacuum and in PCM$^{\tau=0}$. The dipole correction is applied in all the cases. The superscript SP refers to the use of the PCM geometry for vacuum energy evaluation and vice versa.

	Vacuum$^{\text{dip}}$	Vacuum$^{\text{dip,SP}}$	PCM$^{\tau=0\text{dip}}$	PCM$^{\tau=0\text{dip,SP}}$	FEP	FEP$^{\text{mod}}$
ket*-COOH*	-1.68	-1.64	-1.36	-1.35	-1.59	-1.07
COOH*	-1.11	-1.10	-0.83	-0.82	-0.90	-0.65
ket*	-1.04	-1.02	-0.93	-0.92	-0.84	-0.47
ket*-iso	-0.92	-0.89	-0.90	-0.89	-0.81	-0.44

Table 3: Dipole moment (μ in eÅ) of ket*-COOH* as a function of the metal slab thickness (4 to 7 layers) and the length of the unit cell perpendicular to the surface.

	$\mu(\text{PCM}^{\tau=0})/e/\text{Å}$	$\mu(\text{PCM}^{\tau=0\text{dip}})/e\text{Å}$
4L, z=20 Å	5.24	0.93
4L, z=27 Å	5.02	1.17
4L, z=34 Å	4.82	1.38
4L, z=40 Å	4.64	1.55
4L, z=54 Å	4.34	1.84
4L, z=81 Å	3.89	2.18
4L, z=108 Å	3.56	2.34
4L, z=135 Å	3.32	2.41
5L, z=54 Å	5.13	1.69
6L, z=54 Å	5.93	1.60
7L, z=54 Å	6.56	1.42