HCl on Au(111) PART II

Exp.	PBE	RPBE	rev-PBE-vdW	SRP-32	RPBE-vdW
4.0783	4.1554	4.196	4.2435	4.2236	4.258

Table 1: Experimental and calculated bulk lattice constants [Å] of gold. (The calculations are based on a k-point sampling of 11x11x11 and a 2x2x2 Cell.)

The thermal expansion coefficient at the targeted surface temperature of T_S = 170 K is ξ=1.00142542703 for the gold bulk. Evaluating the remaining kinetic energy in the surface atom motion after surface equilibration, that is after the last NVT step, using the SRP-32 functional and 20 slab configurations yields a final surface temperature of T_S = 157 ± 6 K. Taking also into account the potential energy, we then obtain T_S = 177 ± 3 K (assuming the validity of the virial theorem, that is, $T_S = \langle E_{total} \rangle / (3N_{Au}k_B)$).

E_i [eV] / exp. beam cond.	Type	Functional	reactivity	Nr. traj.	Barriers [eV]
2.56	rigid	MD-PBE	0.4842	50,000	756
2.56	rigid	SRP-32-vdW	0.44±0.05	100	749 (prel.)
2.56	170 K	SRP-32-vdW	0.3775±0.024 (0.37)	400 (200)	
2.56	170K + EHP	SRP-32-vdW	0.35±0.034	200	
2.56	rigid	rev-PBE-vdW	0.37±0.05	100	929 (prel.)
2.56	0 K	rev-PBE-vdW	0.36±0.05	100	

Table 2: Reaction probability of HCl scattering from Au(111) at normal incidence. Results were obtained from AIMD and (former) MD simulations using different DFT functionals and different surface conditions (rigid, T_S=0K and T_S=170K). The quasi-classical initial conditions for the HCl molecule match the experimental beam conditions ($T_{rot} \neq T_{vib}$). For the simulations a 2x2 supercell was used and a four layer slab model. The colored entries indicate simulations that adopt the same initial conditions of the HCl molecule (the positions in skewed coordinates and the initial velocities were the same to allow for an accurate comparability). Energy values of the reaction barriers represent preliminary results, see also below.

Current work load:

-RPBE-vdW slab
- few AIMD(EF) simulations

Ready for AIMD simulations are:

- SRP-32 (2x2) slab at T_S = 170 K
- SRP-32 (3x3) slab at Ts = 170 K (POSCARS comming soon)
- Rev-PBE (2x2) slab at TS = 170 K (POSCARS comming soon)

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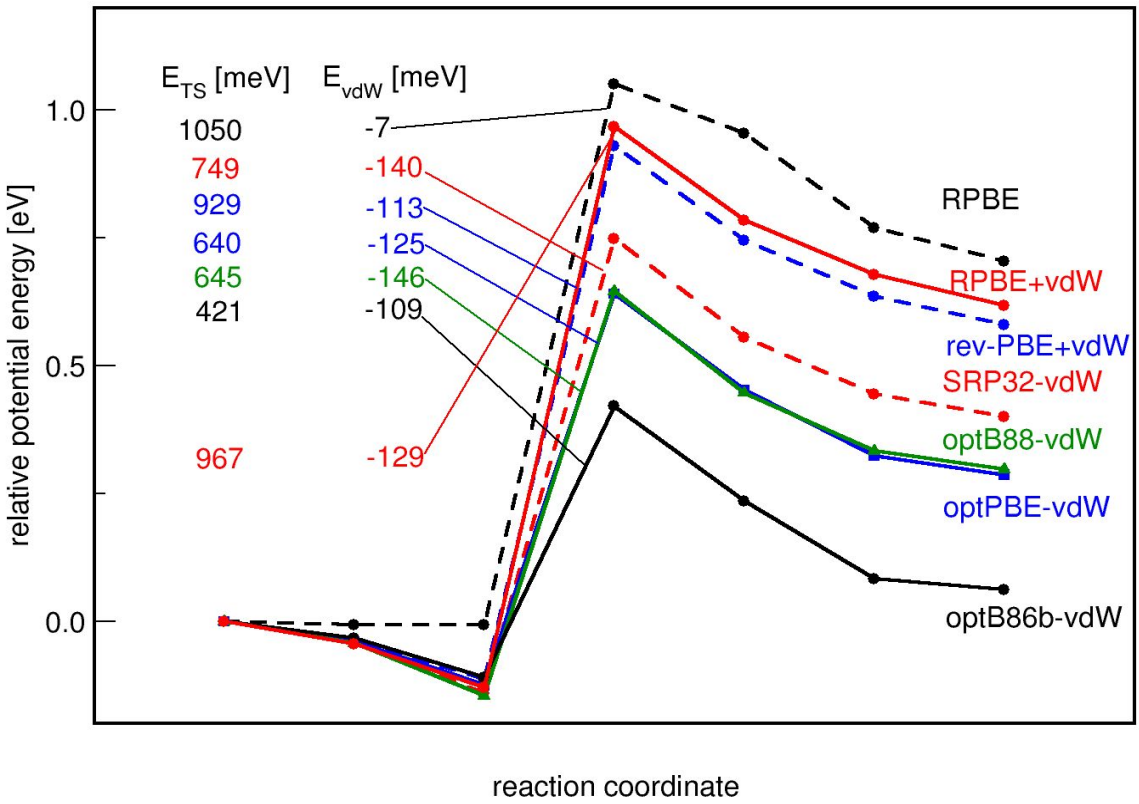

Figure 1: Preliminary results for physisorption wells and reaction barrier heights of the HCl+Au(111) system obtained from different DFT functional calculations. The RPBE-results (without dispersion correction) were previously computed with the help of the NEB/DIMER method. The geometries of the optimized RPBE-NEB images were then used to perform subsequent single point calculations employing the other DFT functionals listed in the figure (geometry optimizations are not yet carried out).

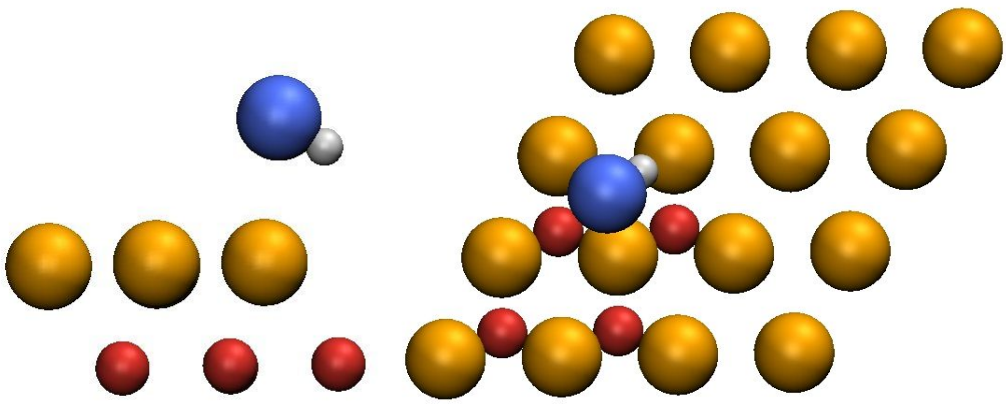

Figure 2: Minimum geometry of HCl on Au(111) in the physisorption well calculated with SRP32-DF including dispersion correction. A site view along the (u+v) line is shown to the left, and a top view to the right. The corresponding coordinates are r = 1.2922 Å, Z = 3.4386 Å, θ = 123.37° with the COM located near the bridge site. The

geometry is stabilized by 216 meV relative to the (classical) gas phase minimum energy value. (Remark, the slab was not yet optimized with SRP32-DF, instead the slab optimized with the RPBE functional was used.)