Supporting information

A theoretical study on the binding and electrolytic splitting of hydrogen fluoride on Ni(111) and Ni(211)

Stefan Mattsson*, Beate Paulus

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1 Potential energy surface of single HF on Ni(111)

A HF molecule is aligned along the surface normal at one of the high-symmetry adsorption sites at the experimental gas phase bond length 0.917 Å. The F–Ni distance is varied and the potential energy curve is shown in Fig. S1. Dispersion correction schemes D2[1] and D3[2] vary slightly in binding energy (–111 and –89 meV, respectively), while BJ[3] damping decreases the binding by 5 meV (–84 meV for D3(BJ)). All methods show a minimum around 3.0 Å F-Ni distance.

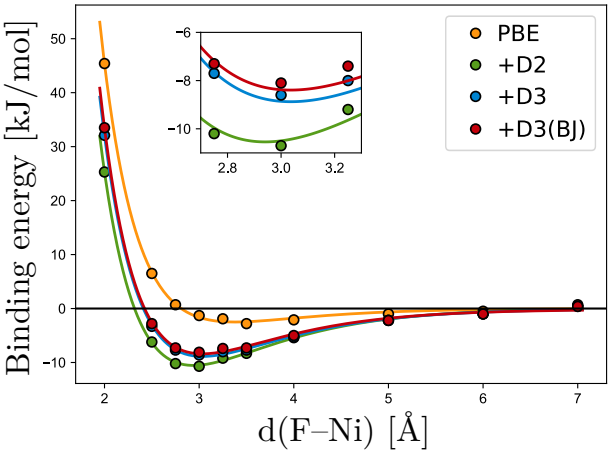

Figure S1: Distance dependency of the binding energy of a single HF molecule, oriented vertically on a Ni(111) surface using a 3×3 supercell. The experimental bond length of HF is used in all calculations and no relaxations are considered. Standard PBE results are presented with and without various dispersion correction schemes.

The potential energy surface is further tested with respect to the HF angle ($0° < \theta < 180°$). Calculations are done by a step-wise rotation of the molecule around its center of mass 3 Å from the surface. No relaxations are considered during the rotation. The results are presented in Fig. S2. The binding is –37 meV stronger with hydrogen pointing towards the surface (H down). Of the total binding energy –135 meV, dispersive binding makes up for –59 meV for the H down conformation, leaving –76 meV as non-dispersive binding. We denote the ΔE_{ads} and its dispersive part as –135 (–59) meV and use this notation throughout.

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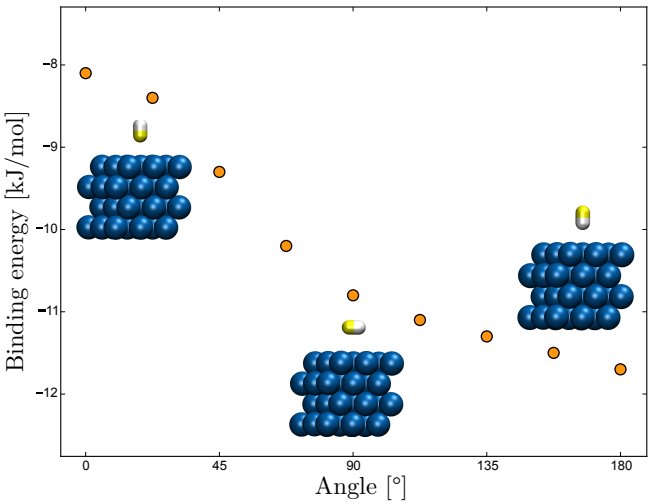

Figure S2: Binding angle dependency of the binding energy of a single HF molecule, oriented vertically on the fcc site of a Ni(111) surface using a 3×3 supercell. The bond length and center of mass of HF are fixed throughout the calculations and no relaxations are considered.

2 Density of states plots

Fig. S4 shows the density of states (DOS) plot for a single HF molecule adsorbed onto pristine Ni(111) (fcc position, F down and H down) as well as Ni(111) with a single atom vacancy (F down and H down) and a single adatom. In all cases the HF states are well below the Fermi energy. The highest-energy HF peak corresponds to the lone pairs $2p_x$ and $2p_y$ in a molecular orbital picture, and is situated at –5 and –3.5 eV for the pristine surface, depending on the orientation of the molecule. The second highest-energy peak corresponds to the σ orbital and is situated at –8.5 and –7.5 eV. Fig. S3 shows the DOS plot for a monolayer (ML) of HF on Ni(111). In it, the orbitals levels are spread out over larger energy ranges due to the higher amount of HF molecules (9 per 3×3 supercell). The lone pairs occur between –6.6 and –5.2 eV and, due to the interactions between HF molecules, the σ orbitals are smeared out between –11.5 and –7.8 eV.

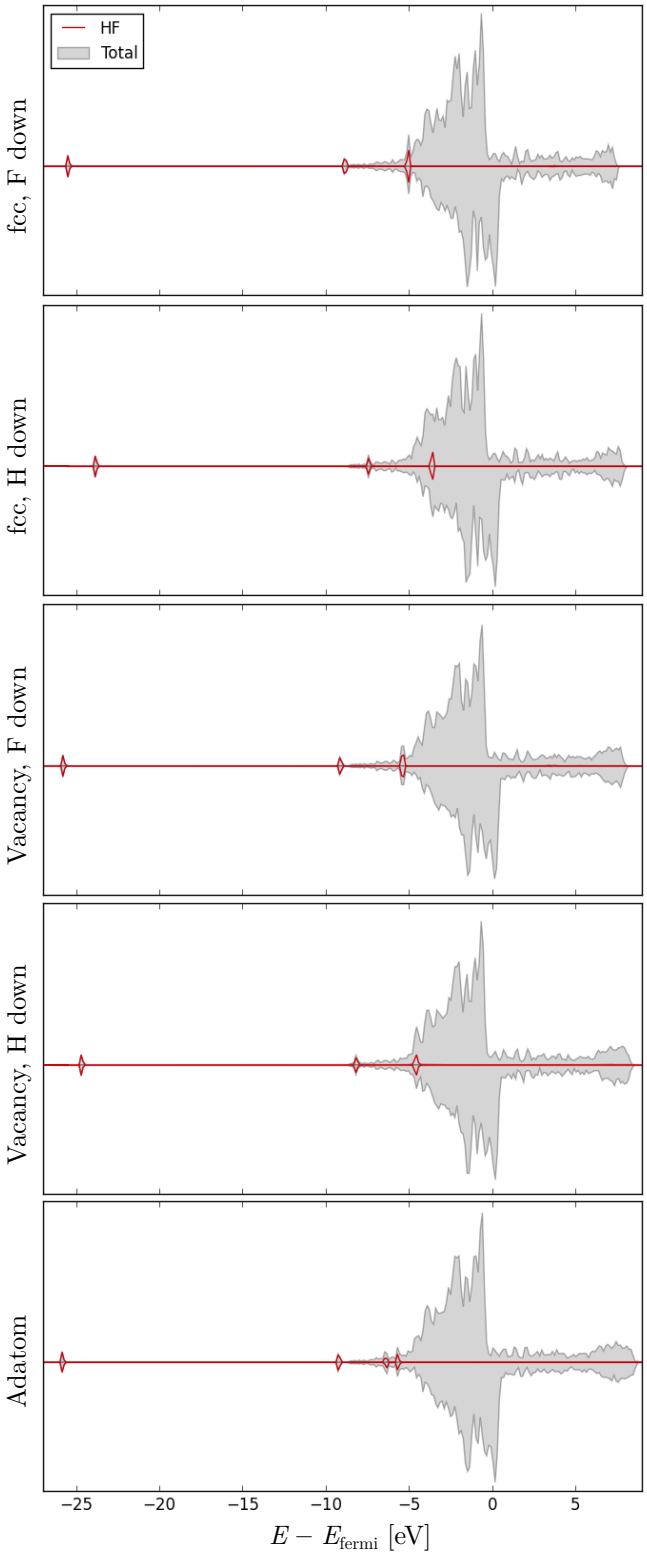

Figure S3: Density of states plot for a single HF molecule adsorbed onto pristine Ni(111) as well as with point defects.

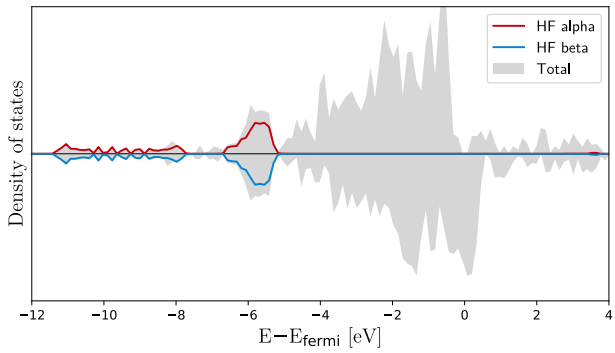

Figure S4: Density of states plot for the HF layer on Ni(111).

3 Structures for the electrified HF/Ni interfaces

We here list the structures used for initial and final states (IS and FS) of the anode and cathode reactions as described in the paper. The structures are given in the POSCAR format of VASP 5.4.1,[4,5] and may be viewed by *e.g.* VESTA 3.4.4.[6]

POSCAR (Anode reaction, IS)

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     7.4538817406000000     0.0000000000000000     0.0000000000000000
    -3.7269408703000000     6.4552509441000003     0.0000000000000000
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   Ni    H     F
    36     9     10
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POSCAR (Anode reaction, FS)

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    -3.7269408703000000     6.4552509441000003     0.0000000000000000
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   Ni    H     F
    36     9     10
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   Ni    H     F
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   Ni    H     F
    36     9     10
Direct
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