Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Understanding the effect of mechanical strains on the catalytic activity of transition metals
Supporting Information

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1. Calculation of free energies

The free energies (G) for the three steps of the oxygen reduction reaction (ORR) along the dissociative mechanism can be expressed as

$$G_0 = G_{\mathrm{O^*+H_2}} - G_{\mathrm{H_2O+^*}} \tag{1}$$

$$G_1 = G_{\mathrm{HO^*+\frac{1}{2}H_2}} - G_{\mathrm{O^*+H_2}} \tag{2}$$

$$G_2 = G_{\mathrm{H_2O+^*}} - G_{\mathrm{HO^*+\frac{1}{2}H_2}} \tag{3}$$

which lead to

$$G_0 = [E_{O^*} + E_{H_2} + E_{ZPE_{(O^*+H_2)}} - T\Delta S_{(O^*+H_2)}] - [E_{H_2O} + E_{*} + E_{ZPE_{(H_2O+*)}} - T\Delta S_{(H_2O+*)}] \tag{4}$$

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$$G_1 = [E_{HO^*} + \frac{1}{2}E_{H_2} + E_{ZPE_{(HO^*+\frac{1}{2}H_2)}} - T\Delta S_{(HO^*+\frac{1}{2}H_2)}] - [E_{O^*} + E_{H_2} + E_{ZPE_{(O^*+H_2)}} - T\Delta S_{(O^*+H_2)}] \tag{5}$$

$$G_2 = [E_{H_2O} + E_* + E_{ZPE_{(H_2O+*)}} - T\Delta S_{(H_2O+*)}] - [E_{HO^*} + \frac{1}{2}E_{H_2} + E_{ZPE_{(HO^*+\frac{1}{2}H_2)}} - T\Delta S_{(HO^*+\frac{1}{2}H_2)}] \tag{6}$$

where E_{ZPE} and ΔS stand for the zero point energy for each species and the change in entropy for each reaction and can be found in Table 3 of [1]. At $T = 300$K, the final expressions can be reduced to

$$G_0 = E_{\text{ads0}'} + 0.01\ eV \tag{7}$$

$$G_1 = E_{\text{ads0H}} - E_{\text{ads0}'} - 0.26\ eV \tag{8}$$

$$G_2 = -E_{\text{ads0H}} + 0.25\ eV \tag{9}$$

2. Calculation of the zero-point energies

The difference in zero-point energies (ΔE_{ZPE}) for the Hydrogen Evolution Reaction (HER) is calculated as

$$\Delta E_{\text{ZPE}} = E_{\text{ZPE}_{\text{H}^*}} - \frac{1}{2}E_{\text{ZPE}_{\text{H}_2}} - E_{\text{ZPE}_*} \tag{10}$$

where $E_{\text{ZPE}_{\text{H}^*}}$, $E_{\text{ZPE}_{\text{H}_2}}$, and E_{ZPE_*} stand for the zero-point energies of the hydrogen atom and the metallic slab, the hydrogen molecule, and the metallic slab, respectively. They were computed with the Phonopy3 program [2] together with the Quantum Espresso package [3–5] and $\Delta E_{\text{ZPE}} = 0.04$ for Cu, in agreement with the data in the literature [6]. Very similar results were also obtained for Pt and it was decided to use the same value for the transition metals analyzed in this investigation.

3. Mechanisms of catalysis for the HER and the ORR

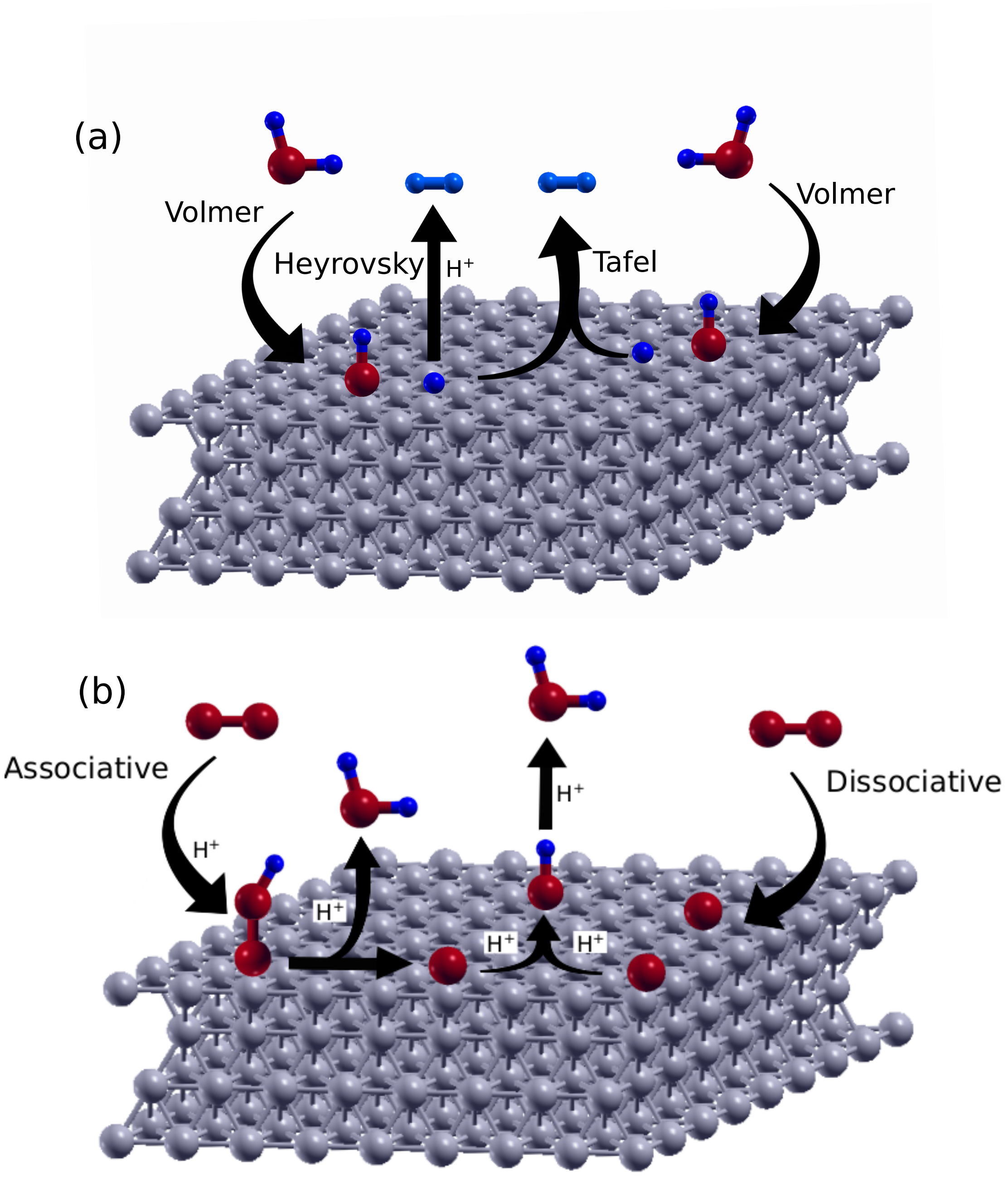

Figure 1: Schematic of the mechanisms for the (a) HER and (b) ORR in a Pt fcc(111) surface and acidic media. Red, blue, and grey atoms represent oxygen, hydrogen, and platinum, respectively.

4. Comparison between theoretical and experimental data

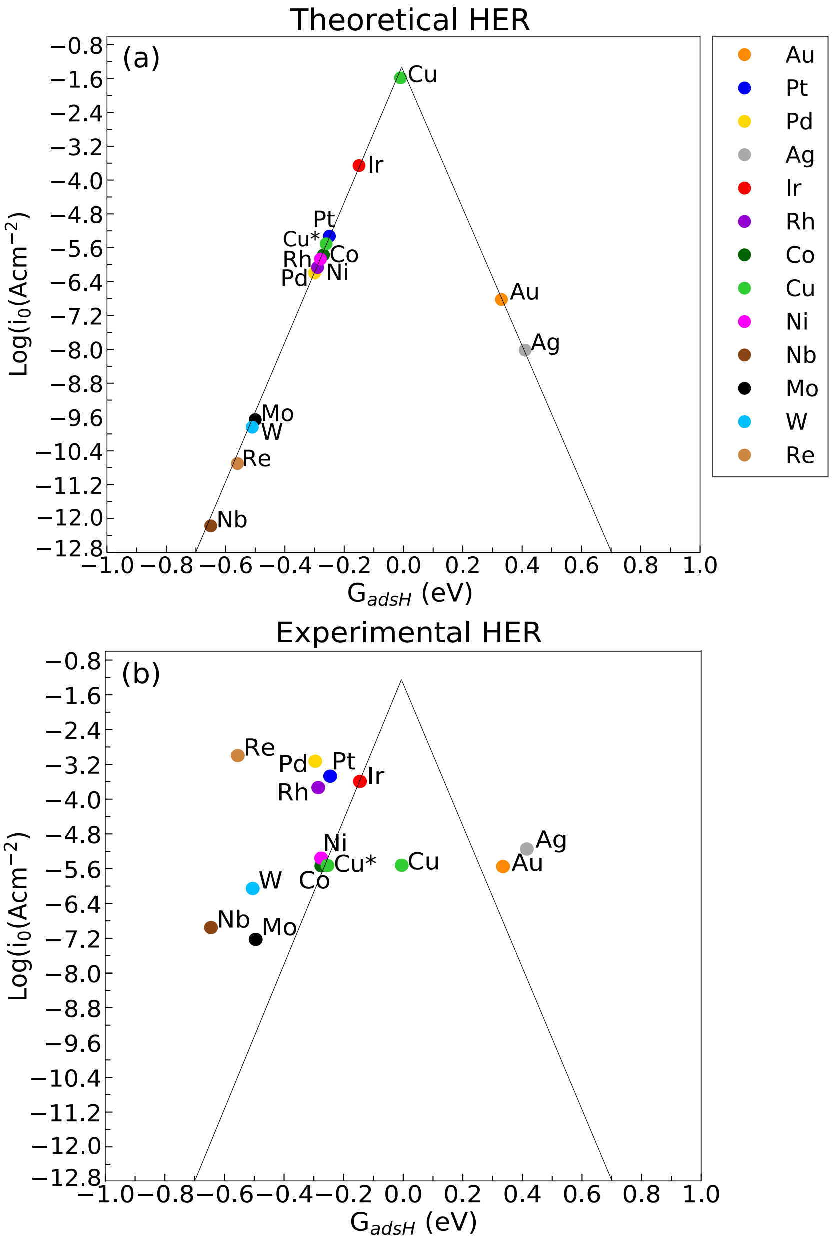

Figure 2: (a) Theoretical and (b) experimental volcano plots at mechanical equilibrium for the HER as a function of G_{adsH}. The experimental values of exchange current density are taken from [6]. Cu* corresponds to free adsorption energy of H obtained from the adsorption energy calculated with the DFT functional SCAN [7].

5. Comparison between DFT functionals for Platinum

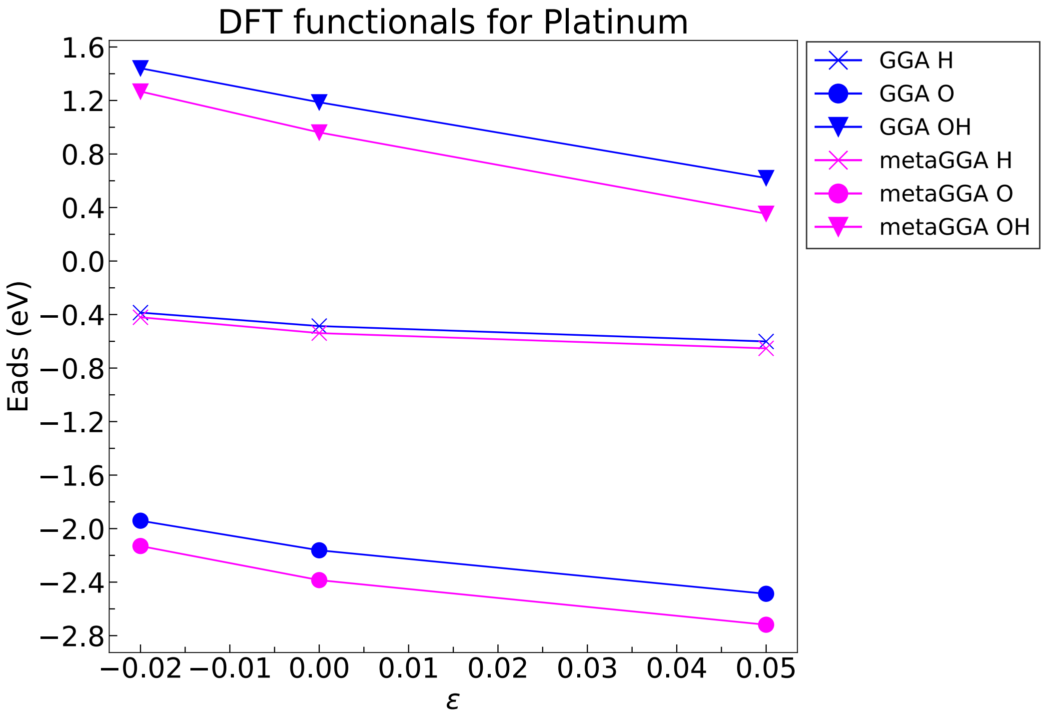

Figure 3: Adsorption energy of H, O, and OH in a Pt(111) slab as a function of biaxial strain. Blue curves represent the calculations performed with a GGA functional (PBE [8]) and magenta curves represent the calculations performed with a metaGGA functional (SCAN [7]).

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