Supplementary materials to "Predicting paint resistance to pull-off by first principles calculations: the case of acrylic acid on (oxidised) metals"

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S1. DFT geometrical structure of acrylic acid

We placed the isolated acrylic acid molecule in a 20 Å × 20 Å × 20 Å supercell and optimising its structure. We found a planar geometry for the molecule, whose bond lengths and angles, reported in Tab. S1, are in agreement with literature [1].

Table S1: Relevant bond lengths (in Å) and angles (in °) of acrylic acid molecule calculated after its structural optimization (see Fig. 1 of the manuscript). Literature values were taken from Ref. [1].

Id.	Bond length		Id.	Bond angle	
	Calculated	Literature		Calculated	Literature
$H_1 - O_1$	0.980	0.968	$H_1 - O_1 - C_1$	106.0	106.8
$C_1 - O_1$	1.371	1.362	$O_1 - C_1 - O_2$	122.6	122.0
$C_1 - O_2$	1.220	1.212	$O_2 - C_1 - C_2$	126.5	126.6
$C_1 - C_2$	1.481	1.469	$C_1 - C_2 - C_3$	120.9	120.2
$C_2 - C_3$	1.336	1.346	$H_2 - C_2 - C_3$	122.3	122.8

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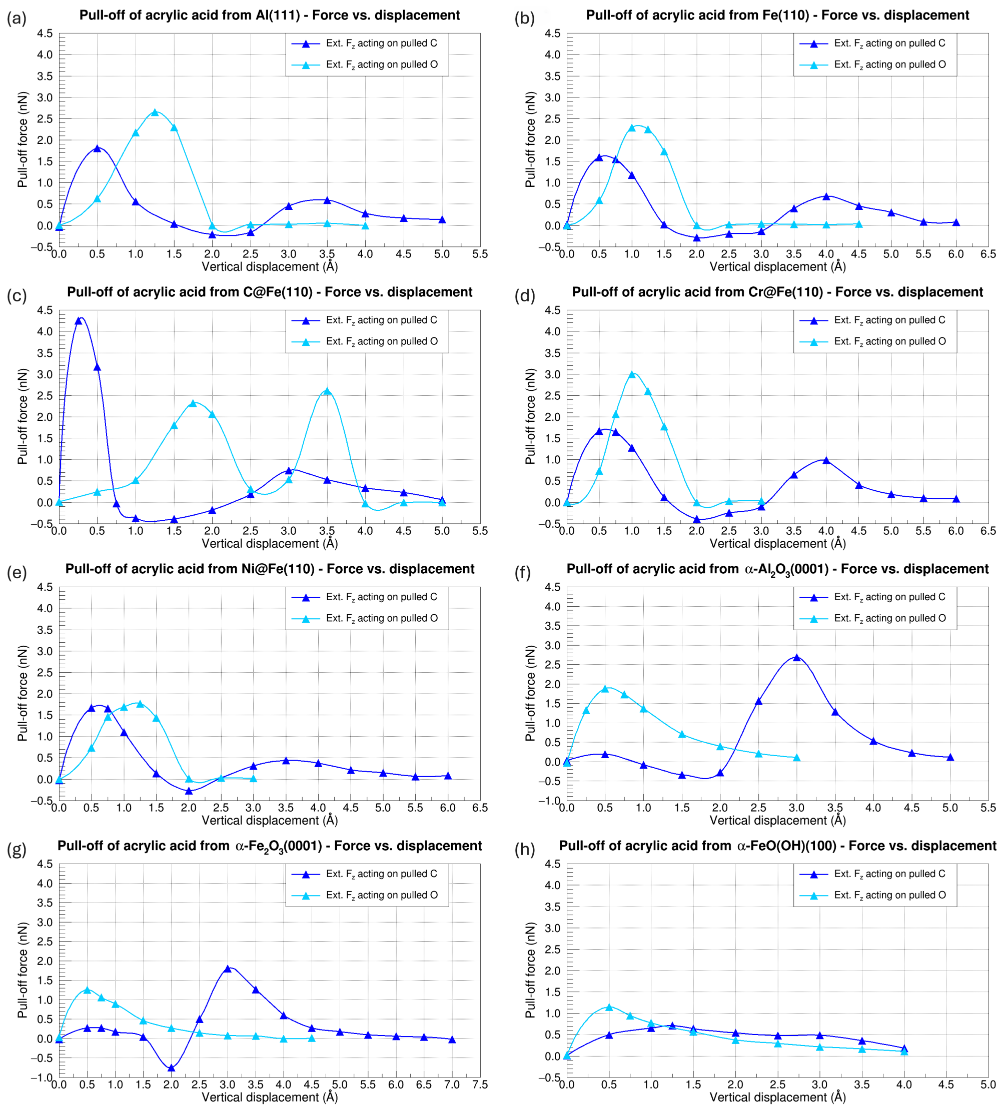

Figure S1: Pull-off force graphs for Al(111) (a), Fe(110) (b), C@Fe(110) (c), Cr@Fe(110) (d), Ni@Fe(110) (e), Al_2O_3(0001) (f), Fe_2O_3(0001) (g), and FeO(OH)(100) (h) systems.

S2. Theoretical Pull-off force and energy graphs

In Fig. S1 we report the theoretical pull-off force graphs for all the considered systems. In order, the plots are for the Al(111), Fe(110), C@Fe(110), Cr@Fe(110), Ni@Fe(110), Al_2O_3(0001), Fe_2O_3(0001) and FeO(OH)(100) substrates. The blue line reports the pull-off force when the apical C atom of the CH_2 group was pulled, the cyan line indicates the force over the protonated O atom bound to the carbon chain.

S3. Charge transfer on C−C bond

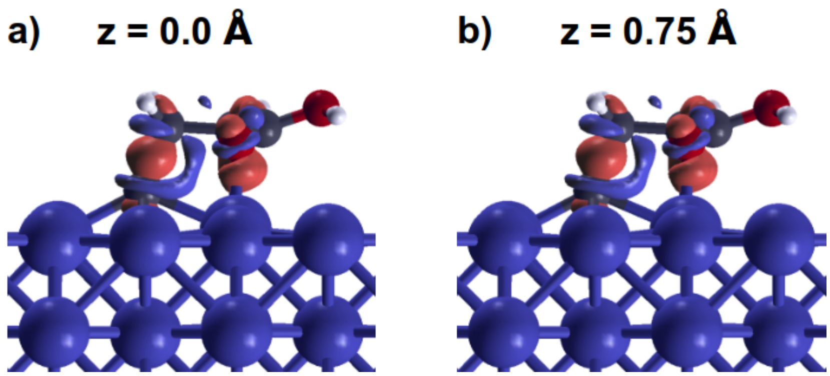

Figure S2: Charge transfer on C−C bond for the acrylic acid adsorbed on C@Fe(110) in the optimal configuration (panel a) and with a vertical displacement of 0.75 Å (panel b). Red (blue) indicates an accumulation (depletion) of the charge density and the value for the isosurface is set to 0.01 $e^-/Å^3$.

To understand the nature of the C−C present in the acrylic acid molecule adsorbed over the C@Fe(110) substrate, we computed the charge transfer during the molecule displacement ρ_{tr}. This quantity has been computed using the following formula:

$$\rho_{tr} = \rho_{tot} - \rho_{slab} - \rho_{mol} \tag{1}$$

where ρ_{tot} is the charge density of the overall system with the molecule adsorbed over the substrate, and ρ_{slab} (ρ_{mol}) is the charge density for the isolated system containing the slab (molecule). In this way, we can evaluate how the charge is distributed during the bond-breaking process.

It is evident that in the optimal adsorption configuration (Fig. S2a), the charge was redistributed to have a large accumulation within the C−C bond and a depletion around the C atoms. When the molecule was displaced 0.75 Å from the optimal configuration (Fig. S2b), the charge transfer immediately dropped to zero, suggesting complete bond breaking. This evidence clearly indicates the covalent nature of the C−C bond.

S4. Qualitative evaluation of the experimental paint detachment

The type of fractures that occurred during dollies detachment was evaluated following the visual assessment method described in standard UNI EN ISO 4624 [2], according to which the following types of fracture could be found for our systems:

- Type *A* fracture: cohesive failure of substrate;
- Type *A/B* fracture: adhesive failure between substrate and paint;
- Type *B* fracture: cohesive failure of paint.

Table S2: Visual assessment of the type of fracture occurred during detachment of acrylic paint from oxidised aluminium, S235JRG2 steel, AISI 304 stainless steel, oxidised S235JRG2 steel samples.

Substrate	Type of fracture
Oxidised aluminium	90% A/B, 10% B
Steel	30% A/B, 70% B
Stainless steel	50% A/B, 50% B
Oxidised steel	60% A/B, 30% A, 10% B

Specifically, a type *A* fracture indicates that part of the sample substrate fails and detaches, remaining adhered to the paint. In a type *A/B* fracture, the paint is attached solely to the glue, with no residue left on the substrate. Finally, type *B* fractures are those in which the paint remains attached to both the sample substrate and the glue. The fracture areas on the sample were qualitatively estimated as percentages to the nearest 10% for each type of fracture, as prescribed by the standard. It was found that adhesive failure between the substrate and paint was prevalent for all oxidised surfaces, whereas significant percentages of cohesive paint failure was found for steel and stainless steel, emphasizing the conclusion that adhesion was stronger on these substrates. Cohesive failure of the substrate was observed only for oxidised steel samples, due to the presence of brittle rust zone, while clean metals were not damaged by the detachments. Adhesion on rusted samples was weaker than clean steel, as expected from literature [3].

References

[1] N. Issaoui, H. Ghalla, F. Bardak, M. Karabacak, N. Aouled Dlala, H. Flakus, B. Oujia, Combined experimental and theoretical studies on the molecular structures, spectroscopy, and inhibitor activity of 3-(2-thienyl)a-crylic acid through AIM, NBO,FT-IR, FT-Raman, UV and HOMO-LUMO analyses, and molecular docking, Journal of Molecular Structure 1130 (2017) 659–668. doi:10.1016/j.molstruc.2016.11.019.
URL https://www.sciencedirect.com/science/article/pii/S0022286016311759

[2] Paints and varnishes - Pull-off test for adhesion, Standard, International Organization for Standardization (2023).
URL https://www.iso.org/standard/83350.html

[3] Y. Li, B. Lei, X. Guo, Influence of phosphoric acid on the adhesion strength between rusted steel and epoxy coating, Coatings 11 (2021) 246. doi:10.3390/coatings11020246.