

## ABSTRACT

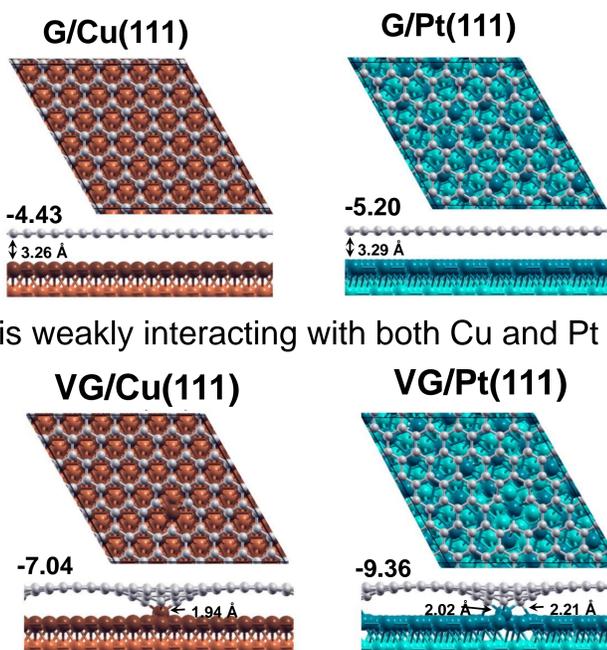
Graphene is usually grown or supported on metal substrates. The presence of defects in the graphenic layers deposited on metal surfaces modifies the nature of the interaction. Unsaturated carbon atoms, due to vacancies in the lattice, form strong organometallic bonds with surface metal atoms that highly enhance the binding energy between the two materials.

We investigate by means of a wide set of dispersion-corrected DFT calculations how such strong chemical bonds affect both the electronic properties of these hybrid interfaces and the chemical reactivity with water, which is commonly present in the working conditions. We compare different metal substrates (Cu vs Pt) that present a different type of interaction with graphene (G) and with defective graphene (VG).

## COMPUTATIONAL DETAILS

- Quantum ESPRESSO package
- vdW-DF2<sup>C09x</sup> functional
- 6×6 supercell for VG, 1.38% carbon monovacancy concentration
- 4-layer (6×6) cell for Cu, 4-layer (2√7×2√7) R19° cell for Pt

## ADSORPTION



- G is weakly interacting with both Cu and Pt
- VG adsorption is much stronger due to the formation of organometallic bonds with the metals
- For VG/Cu we have the formation of three C-Cu bonds, instead for VG/Pt the carbon atoms around the vacancy form two C-Pt bonds each, leading to a much stronger interaction.

## ACKNOWLEDGMENTS

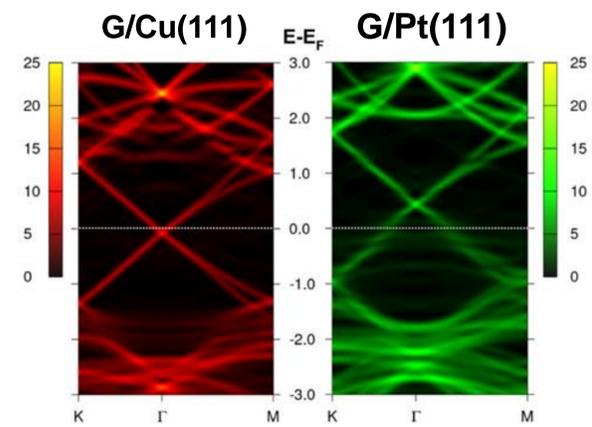
QM-FORMa: Designing New Materials with Quantum Mechanics



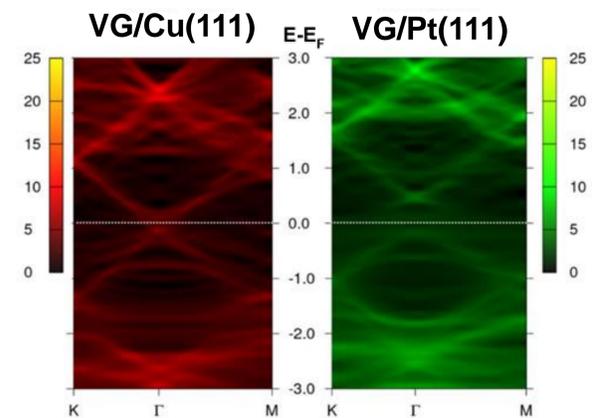
QM-FORMa is a network of world leading material scientists who perform accurate Quantum Mechanics calculations to help in designing new materials from a bottom-up perspective.

<https://eitrawmaterials.eu/project/qmforma/>

## C-PROJECTED BAND STRUCTURE

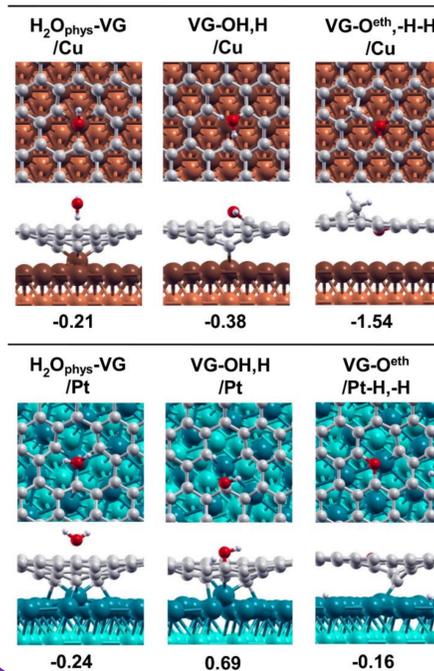


- Cu is donating electrons to G (n-type doping)
- Pt is accepting electrons from G (p-type doping)
- Small hybridization between the states of G and metals



- VG on Cu is an n-type doped system, as G on Cu
- VG on Pt is less p-type doped system than G on Pt
- The mixing between VG and Pt around the Fermi energy is much stronger than VG/Cu mixing

## WATER REACTIVITY



In the case of the VG/Cu interface, the large energy gain associated with the water dissociation at the vacancy site is a sufficient driving force for the breaking of the C-Cu bond: water is found to fully dissociate by forming one ether (-C-O-C-) and one CH<sub>2</sub> group. This is not observed in the case of the Pt substrate because of the much stronger C-Pt bonds.

## CONCLUSION

Water is capable of breaking the C-Cu bond by dissociating at the undercoordinated carbon atom of the vacancy, restoring the weak van der Waals type of interaction between the two materials that allows for an easy detachment of graphene from the metal, but the same is not true in the case of Pt, where C-Pt bonds are much stronger. These conclusions can be used to rationalize water reactivity at other defective graphene/metal interfaces.