

Interaction of small molecules with epitaxial graphene

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Abstract

A full understanding of the nature and dynamics of interactions between graphene (GR) and gas molecules is very important for technological applications of GR: in fact, the electronic properties of GR – such as its doping – can be modified even by a very small quantity of adsorbates, including most gasses commonly found in the atmosphere [1], potentially reducing the efficiency of GR-based devices.

This interaction is dominated by van der Waals forces, weaker than chemical bonds, yet characterized by a wider range of interaction: therefore, an accurate determination of the interaction between GR and gas molecules can not neglect the substrate over which GR is supported [2,3]. Since GR often forms moiré structures on metallic surfaces (containing hundreds of atoms per unit cell), numeric computations of such systems are very demanding, usually based on Density Functional Theory (DFT) implementations of van der Waals forces, which however have often provided contradictory results [4,5].

In order to benchmark these calculations and improve their reliability, we have performed an experimental study of an ideal system, consisting of CO molecules adsorbed on GR supported on Ir(111), combined with DFT numerical calculations on the same system. This experimental work combines complementary state-of-the-art experimental techniques such as NEXAFS, LEED and time-resolved high energy resolution core level photoelectron spectroscopy (TR-XPS) to obtain quantitative information on the adsorption geometry and energy of CO on GR and compare them to theoretical predictions. In particular, we have found that CO molecules form commensurate long-range-ordered structures on the GR moiré cell (Fig. 1a), and they lie with their axis almost parallel to the surface. From TR-XPS spectra we were able to obtain accurate desorption curves for a full CO layer as well as for coverages as low as few percent of Monolayer (Fig. 1b), from which we calculated the desorption energy with an accuracy of few meV. These results are in good agreement with theoretical calculations (Fig. 1c).

To understand the role of the substrate on CO adsorption on GR, we modified its electronic structure by intercalating cobalt below GR; moreover, we repeated the theoretical calculations after removing the substrate. Both new systems showed a variation in CO adsorption energy of tens of meV, *i.e.* around 10% of the adsorption energy, showing that this quantity increases for increasing GR-substrate interaction (Fig. 1b).

In this experiment, therefore, we have acquired very high quality experimental data and used them to verify the accuracy of DFT calculations implementing van der Waals forces. Moreover, this experiment shows that the contribution of the substrate on the van der Waals interactions of GR with adsorbates is significant and must be taken into account to obtain accurate results from computations.

References

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Figures

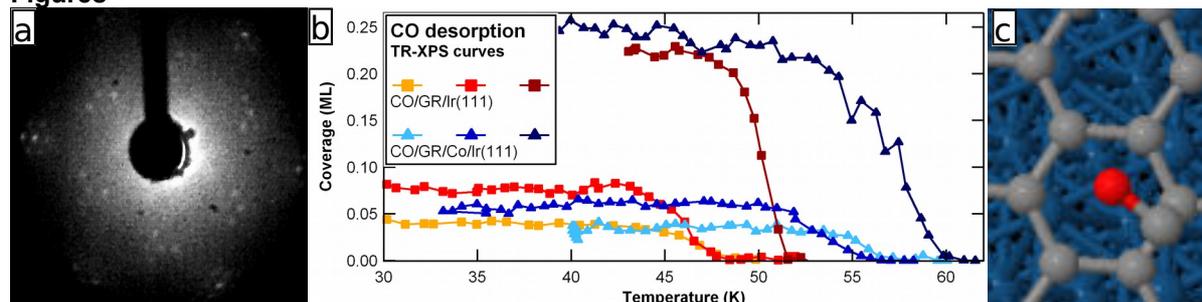


Fig. 1: a) LEED pattern of CO/GR/Ir(111); b) Desorption curves of CO from GR/Ir(111) and GR/Co/Ir(111) for different initial coverages; c) Calculated minimum energy configuration of CO/GR/Ir(111).