

## Electronic Supplementary Information

# Interfacial Coupling in Rotational Monolayer and Bilayer Graphene on Ru(0001) from First Principles

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### Methods to choose the rotational bilayer graphene on Ru(0001).

In the calculations, we only consider bilayer graphene with lattice constant equal to or smaller than the one of monolayer moiré. In addition, the second layer has to be commensurate with the metal substrate due to the periodic structure adopted in the calculations. Moreover, the size of the commensurate structure is restricted by the moiré of underlying layer. Thus, we can simplify the question of selection of bilayer graphene on Ru(0001) by searching for commensurate structures of single-layer graphene on Ru(0001) with a fixed boundary condition (see below). It should be noted that the mandatory condition is due to the supercell approach adopted in the calculations and may not be required in reality.

We use a numerical method to search for the possible rotational structures in which the induced strain in graphene is minimized. To do so, we build a system shown in Fig. S1 by superposing a graphene layer on a Ru surface. The [210] direction of graphene and Ru are aligned with the X axis.

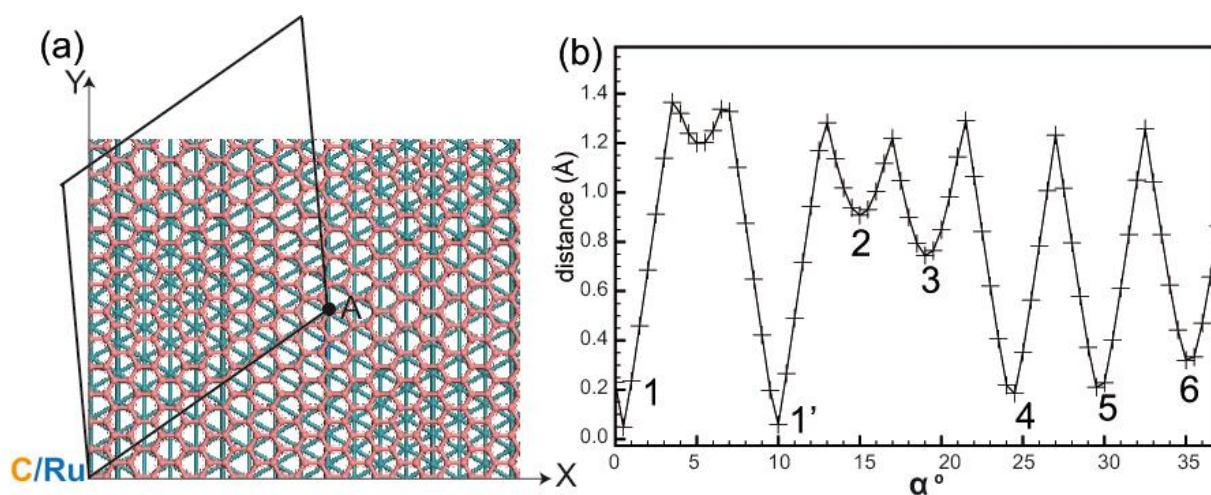


Fig. S1 (a) model used to choose the possible rotational structures. The moiré cell is indicated by the black rhombus. At the origin (0, 0), a C atom is exactly on top of a Ru atom. Another Ru atom (named A) at the boundary of the periodic cell is highlighted by a black dot. (b) The smallest lateral distance between C atoms in graphene and atom A as a function of the rotation.

In the model, the positions of each Ru and C atom can be defined by  $R(x, y)$  and  $C(x, y)$ , respectively. At the origin  $(0, 0)$ , there is one C on top of Ru. In the commensurate structures, due to the restricted boundary condition, there must be another C (in the same sublattice as the one at the origin) on top of the Ru atom (atom A in Fig. S1) at the boundary of the moiré cell.

By rotating the graphene structure with respect to the Ru one with a step of  $0.5^\circ$ , one can create rotational structures with new positions of C,  $C(x', y')$ . In each step, we numerically calculate the lateral distances between C atoms (except the one at the origin) in the graphene lattice and atom A in Ru lattice to search for the smallest mismatch. Only C atoms in the same sublattice as the one at the origin are considered in the distance calculation.

Once the C atom with the smallest distance to atom A is found, a 'nearly commensurate' structure has been reached. This C atom and the one at the origin are used to define a graphene superstructure to be commensurate with the metal substrate. In Fig. S1, the smallest lateral distance between C atoms and atom A is plotted as a function of angles, the relative rotation of  $[210]$  direction of graphene with respect to X axis. We find six minimum (1-6). Structure 1 and 1' correspond to the same structure due to the symmetry. In fact, this one is exactly the monolayer graphene structure ( $0.5^\circ$  rotation) used in the calculations. It also corresponds to the second layer in AB- and AA- stacked bilayer. Structure 2 and 3 have a larger mismatch, so those two structures are not included in the calculations. Structure 4, 5, 6 correspond to the second layer graphene with a rotational angle of 14, 20, 25 degree, respectively. In our calculations, structure 4 and 6 have been taken into account to study the dependence of the electronic structure of the second graphene layer on the rotational angle.