# Graphene on Ru(0001) Moiré Corrugation Studied by Scanning Tunneling Microscopy on Au/Graphene/Ru(0001) Heterostructures

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S *Supporting Information*

ABSTRACT: Two-dimensional Au islands of different thicknesses grown on graphene/Ru(0001) were used to study the corrugation of the moiré structure of graphene/Ru(0001) and discriminate between its mainly structural or electronic character. A comparison of the apparent corrugation measured by scanning tunneling microscopy (STM) for different Au thicknesses with results of elasticity theory equations applied to a gold film over a corrugated substrate shows that the corrugation observed for the graphene/Ru(0001) moiré is of structural nature rather than electronic. STM showed a large value for the corrugation of the first Au monolayer on graphene/Ru(0001), 1.7 Å; using density functional theory calculations, we explain this large corrugation of the Au monolayer as the result of a strong (weak) binding of the Au layer at the valley (hill) regions of the graphene/Ru(0001) moiré structure and infer an actual corrugation of the graphene/Ru(0001) moiré structure of ~1.2 Å from the measured corrugation of the Au monolayer.
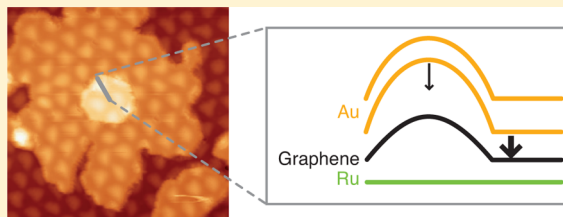
■ INTRODUCTION

Graphene has attracted enormous attention in recent years due to its exceptional properties and its prospective applications in electronics, photonics, energy generation and storage, and sensing, among others.[1] The development of most of these applications requires synthesis processes able to produce large-area single-crystalline graphene domains. Epitaxial growth on transition metals has become a promising method for large-scale graphene synthesis.[2−5] In this context, the epitaxial growth of graphene on Ru allows the formation of truly macroscopic single-crystalline domains.[2] The lattice mismatch between graphene and Ru gives rise to the formation of a long-range ordered moiré pattern, which periodically modifies the graphene properties (e.g., the chemical reactivity) and is observed as a periodic corrugation in scanning tunneling microscopy (STM) images.[6] Moiré-induced modifications can be beneficial as they allow, for example, using graphene as a template for the adsorption of metal nanoclusters[7−9] and organic molecules,[10,11] but a deeper understanding of the moiré structure is still needed.

Despite the large volume of published work dealing with the graphene/Ru(0001) moiré structure, the origin of the periodic moiré observed by STM remains controversial. It is well-known that STM images reflect both the surface topography and the near-surface electronic structure, and the two contributions can be difficult to separate in practice. In STM measurements on graphene/Ru(0001), the apparent corrugation of the moiré structure is highly dependent on the tunneling bias voltage,[12] changing from ~1 to ~−0.7 Å (i.e., inverted contrast) in the −3 to +3 V sample bias range. This, together with helium atom

scattering (HAS) experiments,[12] which showed a small surface corrugation in the range 0.15−0.4 Å, led to the conclusion that the corrugation observed by STM is mainly of electronic origin and that the actual topography of the graphene/Ru(0001) surface is nearly flat. In contrast, a much larger geometrical corrugation, 1.5 Å, was obtained by quantitative low-energy electron diffraction (LEED)-I(V) analysis.[13] Surface X-ray diffraction (SXRD) measurements gave two different values,[14,15] 1.5 and 0.82 Å . Finally, density functional theory (DFT) calculations not including the effect of van der Waals (vdW) interactions[16−19] gave a corrugation in the range 1.5−1.7 Å, while later DFT calculations with vdW corrections[20,21] showed that these corrections reduce the computed corrugation to 1.2−1.3 Å . These calculations suggest that vdW interactions play an important role at the moiré maxima, where the distance between graphene and the Ru surface is close to the interlayer distance in graphite, whereas they are less important at the moiré valleys due to the rather strong covalent interaction between graphene and Ru at those regions.[22]

Au evaporated onto monolayer graphene/Ru(0001) wets the surface of the graphene layer and forms well-defined two-dimensional (2D) islands,[7,19,23,24] which we find to have a range of thicknesses from one to several atomic layers. STM images of the surface of these 2D Au islands show a corrugated periodic structure similar to that of the bare graphene/Ru(0001) moiré, notably consisting of a hill-and-valley

morphology with the same in-plane periodicity as the graphene moiré. The observation of a corrugation at the surface of thin 2D Au islands suggests that the graphene/Ru(0001) moiré structure corrugation is an actual morphological feature and not merely an electronic effect. In this case, it is reasonable to expect that a thin, wetting Au film would conform to the corrugation of the substrate and that the resulting height variations at the surface of a few monolayer thick Au island should be attenuated with increasing Au thickness according to the elastic properties of Au. Therefore, we used in this work Au islands of different thicknesses grown on monolayer graphene/Ru(0001) to study the corrugation of the graphene/Ru(0001) moiré structure and to discriminate between its mainly structural or mainly electronic origin; specifically, we compared the apparent surface corrugation measured by STM and its change with increasing Au thickness with calculations of the expected corrugation and its change considering a sinusoidally corrugated substrate covered by a thin film with the elastic properties of Au. Our results support the notion that the corrugation of the graphene/Ru(0001) moiré is primarily a structural feature. In addition, we observed an enhanced corrugation for the first Au monolayer that is explained using density functional theory calculations. Combining the measured corrugation for a single Au layer with the calculations, we infer the actual corrugation of the graphene/Ru(0001) moiré structure.

METHODS

Graphene was epitaxially grown on Ru(0001) in ultrahigh vacuum (UHV) by C surface segregation as described in detail elsewhere.[2] Briefly, a clean Ru(0001) single crystal was enriched with interstitial C by ethylene exposure at a temperature higher than 1000 °C. Subsequent slow lowering of the sample temperature caused C surface segregation driving the graphene growth. Au was deposited on the graphene/Ru(0001) surface at room temperature by thermal evaporation from a Au drop suspended by a W filament. Samples were studied *in situ* by STM using a Createc low-temperature STM operated at 77 K. In order to decide whether the corrugation observed in the Au films deposited on graphene/Ru(0001) is a mainly electronic effect or an actual morphological feature, we analyzed the measured corrugation at the surface of 2D Au islands with different thicknesses and compared the results with elastic continuum calculations for a Au film conforming to a sinusoidally corrugated substrate. In the calculations, we solved the equilibrium elastic equations for thin Au films with imposed sinusoidal out-of-plane displacements on the bottom surface and with zero normal stress on the upper surface. These equations were cast in terms of the components of the displacement field, and we solved them using a Papkovitch—Neuber solution form in which the displacement components were expressed as combinations of harmonic functions, which were subsequently determined from the boundary conditions. If the corrugation is a true morphological feature of the Au film deposited on epitaxial graphene, then the computed out-of-plane displacement on the upper surface of the Au film and its change with film thickness should, at least qualitatively, match our STM measurements.

In order to assess the nature of the bonding of Au to the graphene/Ru(0001) system, we also performed density functional theory (DFT) calculations in the local (spin) density approximation (LDA).[25,26] In these calculations, we used projector-augmented wave pseudopotentials[27] and the Ceper-ley—Alder exchange-correlation functional.[28] The cutoff for the plane wave energy was 700 eV, the Brillouin zone was sampled using a $5 \times 5 \times 1$ Monkhorst—Pack grid, the vacuum spacing between the periodic slabs was 15 Å, and the geometry relaxations were stopped when residual forces decreased below 0.01 eV/Å. The DFT calculations for model Au/graphene/Ru(0001) systems show a significant change in the binding of Au when placed on graphene/Ru(0001) in comparison to Au on free-standing graphene. We used the results from these model calculations to explain the observed enhanced corrugation of the Au monolayer on graphene/Ru(0001). Finally, we performed large-scale molecular statics calculations to check that the presence of the first Au monolayer does not modify the corrugation of the underlying graphene/Ru(0001). These calculations were performed using the LAMMPS simulation package.[29] The interactions of Au atoms were described by embedded-atom potentials[30] and those of C atoms by Tersoff potentials.[31]

RESULTS

Samples prepared in the described way present a dense distribution of stepped Au islands with different areas and thicknesses, as shown in the overview STM image of Figure 1a. The smallest thickness observed is ~3.4 Å, in contrast with the 5.5 Å thick Au islands that have been reported previously.[19,23] The periodic corrugation characteristic of the moiré structure of
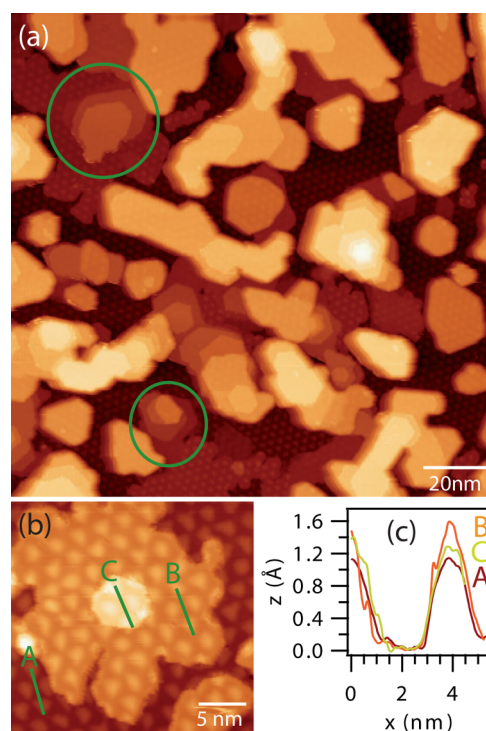

Figure 1. Morphology of room temperature deposited Au on monolayer graphene/Ru(0001), observed by UHV STM at 77 K. (a) Overview STM image showing Au islands of different heights ($V_{sample} = -0.27$ V, $I = 0.46$ nA). Circles mark islands whose terraces are partially or completely flat. (b) Close-up view of one of the islands with two different Au terrace heights ($V_{sample} = -0.45$ V, $I = 0.43$ nA). A moiré-like structure is visible in both of them as well as in the surrounding graphene surface not covered by Au. (c) Height profiles along the lines marked in (b), corresponding to a bare graphene terrace (A), a 1 ML Au terrace (B), and a 2 ML Au terrace (C).

monolayer graphene/Ru(0001) is visible not only in the lowest terrace, which consists of graphene not covered by Au, but also on the surface of most of the islands, formed by one or more Au monolayers (ML). This is clearly observed in the close-up view of a two-level island in Figure 1b. In order to study the change in the corrugation with Au thickness, height profiles along Au terraces at different heights from the graphene were taken in the STM images. A comparison of three of these profiles corresponding to the bare graphene terrace (A), the 1 ML thick Au film (B), and the small two 2 ML thick area (C) in Figure 1b is shown in Figure 1c. The corrugation corresponding to profile B (1 ML Au) is larger than the one corresponding to profile C (2 ML Au). However, perhaps surprisingly, the corrugation of profile B is also larger than the one of profile A, corresponding to bare graphene.

A careful inspection of Figure 1a reveals that, although most of the Au islands have corrugated terraces, in some islands, such as the ones encircled in Figure 1a, the lowest terrace above the graphene presents flat areas or it is even completely flat (see also Supporting Information, Figure S1). The terraces above these flat ones are also flat. The almost complete disappearance of the corrugation of graphene/Ru(0001) intercalated by Au observed by STM[32] suggests that these flat terraces at the lowest apparent height above the bare graphene might correspond to Au intercalated graphene. Similar to other species (e.g., oxygen[33]), Au intercalated between graphene and the Ru(0001) surface removes the moiré structure and therefore the corrugation, while the height of the graphene areas intercalated by Au is expected to be similar to the average height of 1 ML Au on top of the graphene, as is indeed observed in Figure 1a. However, intercalation of Au deposited at room temperature between graphene and Ru(0001) has been reported to happen only after sample annealing at 500 K,[32] and therefore the unambiguous identification of these flat areas requires further investigation. In the following analysis only corrugated Au islands were considered to guarantee that the graphene/Ru(0001) below them has a moiré structure.

In order to quantify the change in the corrugation with Au thickness, height profiles crossing several maxima and minima of the moiré-like corrugation at the surface of 2D Au islands were used to obtain the apparent peak-to-valley surface corrugation in different Au terraces. The values obtained in this way are plotted in Figure 2a as a function of the average height of the corresponding Au terrace above the graphene. In our analysis, we assumed that the lowest terrace in the STM images corresponds to bare graphene/Ru(0001); i.e., it is not covered by Au. This was confirmed by the comparison of the apparent corrugation of that terrace measured by STM at different negative sample bias (Figure 2a) with our own measurements on bare graphene/Ru(0001) and with published values of the graphene/Ru(0001) moiré corrugation measured by STM at similar bias.[12] Figure 2a shows the same trend already observed in Figure 1c: the apparent corrugation at the Au surface monotonically decreases with increasing Au thickness, while the surface corrugation of 1 ML Au films is larger than the one measured for bare graphene at the same sample bias.

The measured peak-to-valley corrugation and its decrease with increasing Au thickness beyond the first Au layer (Figure 2a) were compared with the solution of the equilibrium elastic equations for thin Au films of different thicknesses on a structurally corrugated substrate. After solving the elasticity equations for a thin Au film of thickness h with zero normal
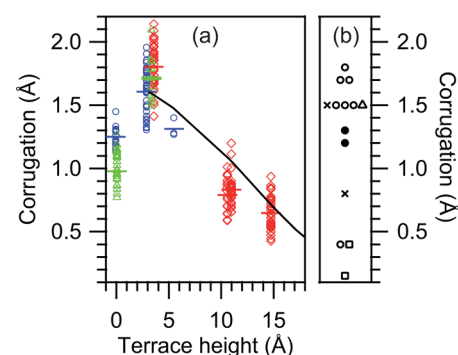

Figure 2. (a) Peak-to-valley corrugation as a function of the average height of the corresponding terrace above the graphene (Au thickness). Markers: values obtained from STM images. Results obtained from terraces in the same STM image are represented by the same marker and color. V_{sample} = −0.45 V (blue circles), V_{sample} = −0.49 V (green triangles), and V_{sample} = −0.27 V (red rhombuses). The average value of the corrugation for each Au thickness is represented by a horizontal line marker. Solid line: expected dependence of the surface corrugation on Au thickness, based on eq 1 (see text). (b) Compilation of several published values of monolayer graphene/Ru(0001) corrugation obtained by HAS[12] (squares), LEED-I(V)[13] (triangle), SXRD[14,15] (crosses), calculations not taking into account the vdW interaction[16−19,21,34] (empty circles), and calculations including vdW forces[20,21] (filled circles).

stress on the upper boundary ($\sigma_z = 0$ at $z = h$), we have found that a sinusoidal displacement of amplitude A_0 imposed on the lower surface of a Au film leads to a sinusoidal profile of the upper surface with the amplitude $A(h)$ given by

$$A(h) = 4A_0(1 - \nu)$$
$$\times \frac{2(1 - \nu)\cosh(h/\lambda) + (h/\lambda)\sinh(h/\lambda)}{2h^2/\lambda^2 + 5 - 4\nu(3 - 2\nu) + (3 - 4\nu)\cosh(2h/\lambda)}$$

$$(1)$$

where $\nu = 0.42$ is the Poisson ratio of Au and $2\pi\lambda = 2.9$ nm is the spatial periodicity of the displacements imposed on the lower surface (see Supporting Information). We then used eq 1 to calculate $A(h)/A_0$ for different values of the Au film thickness h (equivalent to the corresponding terrace height measured from the first Au monolayer), and the result was scaled by varying A_0 to obtain the best fit to the experimental data, shown as a solid line in Figure 2a. The good match with the measured values confirms that the graphene/Ru(0001) moiré corrugation is an actual morphological feature. As the Au film conforms to the corrugation of the substrate, the actual peak-to-valley corrugation of the graphene moiré should correspond to the corrugation at the surface of a 1 ML thick Au island. The mean value of the experimentally determined corrugation for 1 ML Au thickness is 1.7 Å . This value is similar to the highest published ones (based on DFT without or before considering vdW corrections[17,18,21]) but significantly larger than those obtained by HAS,[12] LEED-I(V),[13] and SXRD[14,15] as well as the ones obtained by vdW-corrected DFT.[20,21] A compilation with several published values is shown, for comparison, in Figure 2b.

■ DISCUSSION

While our analysis allows us to conclude that the corrugation of monolayer graphene/Ru(0001) is primarily a morphological feature, the surprisingly large value of the deduced corrugation calls for additional attention and discussion. Particularly

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puzzling are the increase in the corrugation of the first Au monolayer with respect to that of graphene and its large value, which suggest that the interaction of Au with different regions of the moiré pattern of graphene/Ru(0001) acts so as to amplify the corrugation of the Au monolayer.

Graphene interacts weakly with Ru at the hills and strongly at the valley regions,[20] as shown schematically in Figure 3.
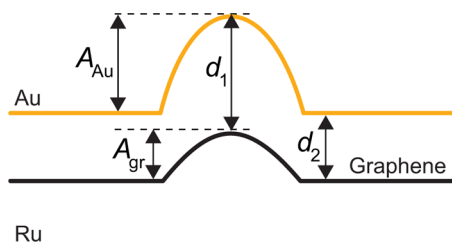

Figure 3. Schematic illustration of a corrugated Au monolayer deposited on graphene/Ru(0001). In the hill regions, the distance between Au and graphene is d_1, while in the flat valley regions the distance is d_2. The spacings d_1 and d_2 relate the corrugation A_{Au} of the Au monolayer to that of the underlying graphene/Ru (A_{gr}) via $A_{Au} = A_{gr} + d_1 - d_2$.

Therefore, at the hill regions, the interactions between graphene and Au layer are not significantly affected by the presence of Ru below graphene; in those regions, the distance between Au and graphene layers may be estimated on the basis of DFT calculations for graphene on a Au substrate, $d_1 \simeq 3.31$ Å, with a weak binding of 80 meV per Au atom at the surface (or 30 meV/C atom).[35] Using DFT calculations for a single Au monolayer and (2×2) graphene cells with the experimental lattice constant of 2.46 Å, we have predicted the interlayer distance to be $d_1 = 3.26$ Å and a binding energy between Au monolayer and graphene of 97 meV/Au atom. We use a similar definition for binding energy as that of ref 35. The binding energy between the Au monolayer and graphene (or graphene/ Ru system) is defined as the difference, per Au atom, between the total energy of a system in which the Au layer is far from graphene (or from graphene/Ru) and the total energy of Au/ graphene (or Au/graphene/Ru) relaxed to attain the equilibrium distance between the layers.

Assuming that the corrugation of graphene is not significantly altered upon the deposition of Au, the corrugation of the Au monolayer, A_{Au}, can be related to that of graphene, A_{gr}, via $A_{Au} = A_{gr} + d_1 - d_2$, where d_2 is the distance between the Au and graphene layers in the valley region (Figure 3). We have calculated the distance d_2 and the interaction between Au and graphene/Ru(0001) in the valleys using DFT calculations performed on a (2×2) Ru(0001) substrate at the experimental lattice constants of Ru ($a = 2.70$ Å, $c/a = 1.584$). The choice for this supercell (shown in Figure 4) is determined by the fact that over significant portions of the valleys in the graphene/ Ru(0001) moiré superstructure pairs of C atoms of the graphene lattice are one on top of the Ru atom and the other in the hollow site at the surface.[20] The locations of the Au atoms are such that the system is minimally strained while still commensurate (by necessity in DFT calculations) with the graphene/Ru(0001) system.[35] The binding energy of the Au monolayer that we calculated is 199 meV/Au atom. The distance between the Au monolayer and the graphene layer is $d_2 = 2.73$ Å; this is the difference between the average height of the Au atoms and that of the C atoms. The values of the
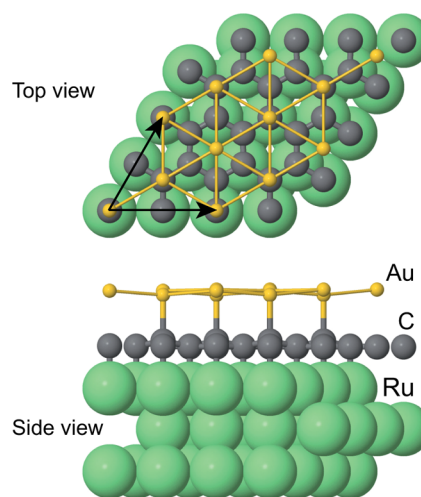

Figure 4. Top and side view of the relaxed Au/graphene/Ru(0001) system. The supercell vectors in the plane of the surface are indicated by the black arrows on the top view. The Au layer is chemically bonded to graphene/Ru(0001), with a binding energy of 199 meV/Au atom and an interlayer spacing of $d_2 = 2.73$ Å. The Au atoms are shown smaller than the C atoms so as to aid the visualization of their locations with respect to graphene and Ru.

binding energy and the Au–graphene interlayer distance are consistent with a chemical bonding between the Au layer and the graphene/Ru(0001) that is significantly stronger than typical vdW interactions. As seen in Figure 4, two of the three Au atoms in the supercell (those located directly above C atoms) are bonded to C. Although one of the Au atoms is not chemically bonded to the graphene/Ru(0001), on average the binding between Au and C remains very strong and effectively clamps down the Au layer at the valley regions of the moiré structure, thus increasing its corrugation. With the values calculated for the spacings d_1 (Au on graphene far away from Ru) and d_2 (Au on graphene/Ru(0001) in the valleys of the moiré structure) the corrugation of the Au monolayer (Figure 3) is $A_{Au} = A_{gr} + d_1 - d_2 = A_{gr} + 0.53$ Å, i.e., ~0.5 Å larger than the one of bare graphene/Ru(0001).

The inability of STM to provide reliable values of the geometrical corrugation for the complex surface structure of graphene/Ru(0001), due to strong electronic effects,[12] has motivated the use of Au layers in our study. The electronic effects are expected to be much less important for a 2D Au layer wetting the graphene/Ru(0001) moiré because, due to effective screening, the electronic properties of Au thin films adsorbed on graphene/Ru(0001) are mainly determined by the electronic structure of the Au adlayers and are essentially independent of the electronic structure of the substrate.[36] Hence, the main contribution to the tunneling current for Au/ graphene/Ru(0001) comes from the electronic density of states of Au and is independent of the one of graphene/Ru(0001). The apparent height of few-layer Au films might be affected by quantum well states confined to Au. However, this would not change the corrugation measured on a specific Au terrace, where the Au thickness is constant due to the 2D growth of Au on graphene/Ru.[7,24] Therefore, STM images of Au thin films on graphene/Ru(0001) can be used to quantitatively study the surface corrugation, in contrast to the STM images on bare graphene/Ru(0001). Using the measured amplified corrugation of the Au monolayer (~1.7 Å) and the results of our DFT

calculations, we can infer the actual corrugation of the bare graphene/Ru(0001) to be $A_{gr} = A_{Au} - 0.53$ Å $= 1.2$ Å.

In the above reasoning for deriving the corrugation of graphene/Ru(0001) from that of a Au layer deposited on it, we made the assumption that the presence of the Au monolayer does not affect the corrugation of the underlying graphene/Ru(0001) system. A posteriori, we tested this assumption using large-scale molecular statics calculations in which a Au layer is brought in the vicinity of an already corrugated graphene sheet, and the interactions between Au atoms and C atoms are modeled by Lennard-Jones potentials parametrized according to our DFT results for binding energies and interlayer distances described above. More specifically, the Lennard-Jones potential is modified to have a finite cutoff radius, and the parameters used for the strongly binding C interaction to Au are $\varepsilon = 0.2$ eV, $\sigma = d_2/2^{1/6} = 2.432$ Å, and $r_{cut} = 4.0$ Å, while those corresponding to the weak C–Au interactions are $\varepsilon = 0.097$ eV, $\sigma = d_1/2^{1/6} = 2.90$ Å, and $r_{cut} = 12.0$ Å. Any model potential that incorporates the weak (strong) interactions between Au and graphene at the hills (valleys) of the moiré superstructure suffices for understanding the overall morphological features of Au on corrugated graphene; in particular, this is a clear and efficient way to tell whether the corrugation of the graphene itself is changed upon the deposition of the Au monolayer. The Au layer relaxes toward the corrugated graphene starting at a distance of 5 Å and complies to graphene in the manner described by Figure 3. The physical reason for this compliance (as opposed to, e.g., flattening the graphene so as to maximize the area of stronger, chemical bonding) is that the epitaxial relationship of graphene with the Ru substrate (e.g., ref 20) simply does not allow the graphene to be flat throughout.

The value of the corrugation of graphene/Ru(0001) inferred here from the measured corrugation of the Au monolayer, ~1.2 Å, lies in between the two published values obtained by SXRD[14,15] and is smaller that most of the values provided by calculations not including vdW corrections[16–19,21] (Figure 2), while it is in agreement with the published values obtained by DFT calculations with vdW corrections.[20,21] This highlights the importance of vdW interactions in defining the corrugated graphene/Ru(0001) moiré structure.

CONCLUSIONS

In conclusion, the comparison of the measured corrugation of 2D Au layers with varying thickness on graphene/Ru(0001) with calculations shows that the moiré structure of graphene on Ru(0001) is strongly geometrically corrugated. The surprisingly large value (~1.7 Å) obtained for the surface corrugation of a single Au monolayer on graphene/Ru(0001) is explained by DFT calculations, which show that a different interaction strength of Au with the hills and valleys of the graphene/Ru(0001) moiré amplifies the corrugation of the Au monolayer. From these calculations and the experimentally measured corrugation of the Au monolayer, a corrugation of the graphene/Ru(0001) moiré of ~1.2 Å is obtained.

ASSOCIATED CONTENT

ⓢ Supporting Information

Close-up views of STM image showing islands whose terraces are partially or completely flat; deduction of eq 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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