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Tunneling Electronic Excitations Spatial Mapping of a Single Graphene Nanoribbon on Ag(111)

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Abstract:

Using low temperature scanning tunneling microscopy (STM), spectroscopy (STS) and precise dI/dV mapping in combination with DFT-parametrized semi-empirical calculations, we report and discuss the origin of different tunneling electronic excitations that occur along a seven carbon atom wide armchair graphene nanoribbon (7-aGNR) physisorbed on Ag(111) as compared to a reference on Au(111) surface. On both surfaces, on-surface synthesized 7-aGNRs of variable lengths are selectively chosen for performing the STM and STS (dI/dV) excitation

mapping along a truly isolated molecule. For exactly the same 7-aGNR molecule length, the difference in work functions between Ag(111) and Au(111) generates different edge states electronic configuration that result in a curved molecular conformation on Ag(111) and a strictly flat one on Au(111). At the interface between the 7-aGNR and Ag(111), this curved conformation produces an additional set of quantum-box-like tunneling resonances that partially mix with the intrinsic 7-aGNR tunneling excitations.

I. INTRODUCTION

The molecular conformation and tunneling electronic excitation spectrum of an on-surface synthesized graphene nanoribbon (GNR)^[1-3] are vulnerable to surface-induced perturbations such as substrate polarization,^[4] charge transfer,^[5] and/or molecular structural deformations.^[6] A free standing GNR predominately interacts with an atomically flat metallic surface through weak van der Waals (vdW) forces.^[7,8] The alignment of the GNR electronic structure with respect to the Fermi level (E_F) of the metallic surface can generate charge screening and re-normalization effects.^[4,5,9] These interactions introduce new electronic excitations, which are sometimes intimately entangled with the intrinsic molecular electronic structure in locally probed signals.^[10] In order to capture the intrinsic electronic properties of GNRs lying on a metallic surface or to avoid the entanglement effects resulting from such interactions with the metal, different configurations have been tested in the past: STM molecular manipulating the GNR onto an insulating NaCl atomic layer spacer,^[11] intercalating one atomic layer of a foreign element,^[12] direct on-surface synthesis of the GNR on an insulating substrate.^[13,14] However, the charging effects occurring, for example, in a GNR/NaCl/Au(111) junction configuration or the positioning of the GNR molecular electronic states relative to the insulating substrate make these composite

systems^[15] more complex to interpret and model, which usually fails to provide a precise characterization and understanding of the tunneling electronic excitation spectrum of an adsorbed GNR on a surface.

Here, we compare highly resolved tunneling electronic excitation spectra of a 7-carbon-atom wide armchair GNR (7-aGNR) obtained by STM on a Ag(111) and on a standard Au(111) surface. Exploring a few eV around E_F , we spatially map the tunneling dI/dV resonances of a 7-aGNR on Ag(111) and on Au(111) with respect to the vacuum level. We reveal that the two different surfaces generate different electronic configuration of the edge states (ESs) of the same length 7-aGNR, owing to the difference in their work function. A striking feature is the curved conformation adopted by the 7-aGNR on Ag(111) whereas it remains strictly flat on Au(111). As a consequence of this conformational difference, new electronic effects at the interface between a 7-aGNR and the Ag(111) surface are observed, and discussed. We also find that the Ag(111) Shockley surface electrons are confined and **quantized laterally** under the curved 7-aGNR. By comparing the dI/dV spectra and maps on the two metallic surfaces, we are able to separate the tunneling electronic excitations specific to the 7-aGNR/Ag(111) interface from the ones intrinsically borne by the 7-aGNR molecule.

II. MATERIALS AND METHODS

A. Materials

All samples were prepared in the preparation chamber of a low-temperature ultrahigh vacuum (LT-UHV) 4-STM instrument.^[16] Ag(111) and Au(111) single crystal surfaces (*Mateck GmbH*) were first cleaned under UHV conditions by repeated cycles of Ar^+ ion sputtering at 1.0 keV and $\sim 10^{-6}$ mbar for about 10 minutes and subsequent annealing at about 740 K for 1 h. These single

crystal surfaces were checked for cleanliness by using one of the STM of our LT-UHV 4-STM operated at sample temperatures of ~ 4.5 K. Monomer precursors ‘10,10’-dibromo-9,9’-bianthryl (DBBA, $>98\%$)’ from *Aldrich* were thermally evaporated at 160 °C onto the clean surfaces of Ag(111) and Au(111) from the quartz crucible of a *Kentax* thermal evaporator (*Knudsen-cell*), while the substrates were kept below 40 °C and ca. 50 mm away from the evaporation source. These precursor molecules were out gassed for more than 24 hours in UHV preparation chamber of our LT-UHV 4-STM to remove the residual contaminants prior to their depositions onto Ag(111) and Au(111) surfaces.

B. On-surface synthesis of 7-aGNRs.

On-surface synthesis of 7-aGNRs was carried out on Ag(111) and, for comparison, on Au(111) by following the standard two-steps on-surface synthesis approach for DBBA monomer precursor molecules, by annealing the samples 10 minutes each at 200 °C and 350 °C in UHV conditions.^[17] This standard approach for DBBA monomers follows the Ullmann coupling reaction between the monomers at the cleaved bromine sites resulting in polyanthryl oligomers at the first annealing step (200 °C) and then the cyclodehydrogenation of the polyanthryl oligomers at the second annealing step (350 °C), producing the 7-aGNRs (Fig. 1(a)). This on-surface chemical reaction procedure results in a broad length distribution of well isolated 7-aGNRs from as small as 1-monomer unit equivalent to as long as several tens of monomer units long on both metallic surfaces. This allows us selectively choosing the well-defined 7-aGNR length (in the units of number of monomer precursor molecules) for further characterization of 7-aGNR length dependent tunneling electronic excitation characteristics (dI/dV spectra and maps).

C. Characterization of 7-aGNRs.

STM imaging and scanning tunneling spectroscopic (STS) characteristics (also referred to as dI/dV spectra and maps) of 7-aGNRs were precisely characterized *in situ* with a *Scienta Omicron* 4-STM instrument. STM and STS were recorded with an electrochemically etched PtIr (Ir: 20%) tips and in constant-current configuration using a lock-in detection technique (frequency ~ 460 Hz, modulation voltage = 20 mV). Prior to the STS characterization of well isolated individual and selected 7-aGNR, STM tip apex was checked for its purity and cleaned whenever necessary by probing the Au(111) surface state (SS) characteristics. A pure STM tip apex is always characterized by the step like dI/dV characteristic at energetic positions of ~ -50 mV for Ag(111) surface and ~ -460 mV for Au(111) surface.

D. Theoretical calculation details.

To compute the conformational differences of a 7-aGNR on Ag(111) and Au(111) surfaces, semi-empirical calculations were performed using the ASED+ code, including van der Waals interactions and a new 3-body term. A semiempirical approach with the extended Hückel molecular orbital theory constitutes the core of the ASED-MO method.^[18,19] The so-called ASED+ code^[20] is a powerful numerical tool to describe reasonably well the structural properties of various types of molecules adsorbed on surfaces or in the gas phase.^[21-24] Standard DFT codes are not appropriate in the present case due expensive computational needs to address the 7-aGNR adsorption. However, ASED+ was parametrized using DFT calculations for small unit cell surfaces. This parametrization is described in Ref. 20 where a new 3-body term was introduced and the standard Wolfsberg–Helmholtz semi-empirical parameters optimized accordingly.

III. RESULTS AND DISCUSSION

A. The electronic tunneling excitation spectra and maps of a 7-aGNR on Ag(111) and Au(111)

Fig. 1(b) and 1(c) presents the large scale STM images of on-surface synthesized 7-aGNRs on Ag(111) and, for comparison, on Au(111) using two-step annealing approach. The STM images present different 7-aGNR coverages on Au(111) and Ag(111) starting from different initial monomer concentrations (0.1 monolayer on Ag(111) and 1.5 monolayer on Au(111)) at room temperature surface deposition conditions. A well isolated 7-aGNR of predefined length (in the number of DBBA monomer molecule units) can be selectively chosen for the precise measurement of tunneling electronic excitations occurring within an individual 7-aGNR molecule. Many electronic tunneling resonances are captured at both positive and negative bias voltages on an Ag(111) surface as the STM tip apex is positioned along the armchair side of a 7-aGNR comprising 5-monomer units (i.e. 10-anthracene long) as shown in Figs. 2(a)-2(c). At positive (resp. negative) bias with respect to E_F , these resonances, labeled as $R+n$ (resp. $R-n$) with an integer $n \geq 1$, are the elastic electronic tunneling excitations when the STM current tunnels through the 7-aGNR (see Supplemental Material, Sec. 1 for more details about negative bias $R-n$ resonances). Each resonance results from the contribution of the electron (resp. hole) transfer through mono-electronic channels of the 7-aGNR at positive (resp. negative) bias voltage with respect to the grounded Ag(111) surface. In the dI/dV spectra, RE1 resonance corresponds to the well-known edge state (ES) resonance intrinsic to a 7-aGNR.^[2] On either side of the E_F , the dI/dV maps recorded at the first delocalized resonances ($R-1$ and $R+1$) and at the end localized resonance (RE1) of the 7-aGNR can be described in first approximation by their corresponding highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital

(LUMO), and spin occupied molecular orbital (SOMO) mono-electronic probability distribution in space.^[21] The resonances noted as IR_n ($n \geq 1$, integer) at +0.275 V and +0.6 V originate from the surface quantum-box-like effect generated only at the 7-aGNR/Ag(111) interface due to the curved molecular conformation, as discussed in section D. Higher bias voltage maps ($R+n$ and $R-n$ with $n \geq 2$) must be described by a superposition of several virtual hole and electron transfer processes through the 7-aGNR. In principle, each resonance involves many molecular orbitals below the HOMO and above the LUMO levels and belongs to the active quantum state space describing the electronic tunneling effect through the 7-aGNR in a complete configuration interaction (CI) approach.^[25] As a consequence, the best dI/dV map contrast for each of the resonance (as assessed by the contrast between the minima and maxima of a given differential conductance map) is not obtained at the corresponding peak position of a dI/dV resonance but at a slightly shifted bias.^[26] Indeed, following the principle above,^[26] all the dI/dV mappings reported in this investigation are recorded at the sideways of the spectral peak positions.

Figs. 2(d)-2(f) presents the STM image and STS characteristics recorded on an Au(111) surface for a 7-aGNR with the exact same length of 5-monomer-units (10-anthracene long). Similarly to other dI/dV characteristics of 7-aGNR on Au(111) reported in the literature (armchair eigenmodes ($R+n$ and $R-n$) and low-bias ESs (RE1)),^[27] several additional resonances ($R \pm n$ and RE2) are clearly observed and spatially resolved/mapped. These measurements were performed far above and below E_F to gather a complete STS reference in the experimentally-allowed bias voltage window before destabilization of the STM tip apex. Here again, it should be noted that the measured tunneling current intensity of a selected dI/dV resonance and map pixel results from the quantum superposition of all contributions involved in an elementary hole (electron) transfer event through the 7-aGNR electronic cloud. The corresponding dI/dV maps

recorded at these resonances bear the combined characteristics of the main spatial contribution of the mono-electronic eigenmodes involved in the respective virtual (electron or hole) tunneling excitations quantum superposition of the CI.^[25] Nonetheless, similarly to the Ag(111) case, these eigenmodes on Au(111) can be considered as a virtual hole (resp. electron) occupation in a HOMO- n (resp. LUMO+ n) molecular orbital. In particular, the bias difference between $R-1 = -0.9$ eV and $R+1 = +1.6$ eV gives a quasi-single-particle electronic gap of ~ 2.5 eV (i.e. the HOMO-LUMO gap), consistent with previously reported values for 7-aGNRs on-surface synthesized on Au(111).^[1,5]

Notably, on Au(111), the electronic eigenmode like behavior observed from the dI/dV maps (for $R-n$ and $R+n$) in Fig. 2(f) reveal that the highest dI/dV intensities mainly located at the armchair side with null amplitude in the interior part of the 7-aGNR. This particular spatial behavior of 7-aGNR dI/dV maps is well documented by Söde et al.,^[28] where the authors illustrated how a specific STM tip height trajectory in a constant-current or a constant-height mode STS measurements affect the respective dI/dV intensity maxima concentrating at the armchair sides or inside of the 7-AGNR, respectively. This is in good agreement with our armchair side localization of $R\pm n$ electronic eigenmodes captured in constant-current configuration. Unlike on the Au(111) surface, our data on the Ag(111) shows non-negligible dI/dV intensities inside of the 7-aGNR with intriguing dI/dV spatial map patterns, which follow a different electronic eigenmode like character as can be seen in Fig. 2(c). Below, we focus on revealing, step-by-step, the origin of this distinct tunneling electronic excitation behavior within the 7-aGNR on the Ag(111) surface as compared to that on Au(111) surface.

In contrast to Au(111), only one electronic resonance is captured from the 7-aGNR on Ag(111) at negative bias voltage ($R-1$ at -1.7 V), i.e. below RE1 (see Supplemental Material,

Sec. 1 for more details). The corresponding dI/dV map (at -1.7 V in Fig. 2(c)) exhibits a uniform bright contrast at the armchair sides resembling the $R-1$ dI/dV map (at -0.9 V in Fig. 2(f)) of the same-length 7-aGNR on Au(111). Remarkably, on Ag(111), the difference between $R-1$ and $R+1$ is found to be ~ 2.5 eV, which matches exactly the quasi-single-particle gap of 7-aGNR observed on Au(111). However, STS measurements carried out on Ag(111) for 7-aGNR with different lengths reveal that the position of the $R-1$ resonance remains fixed at -1.7 V and is independent of the 7-aGNR length (see Supplemental Material, Sec. 1 for more details). It results from the opening of a hole transfer channel coming from a topological length invariant mono-electronic state contribution to the 7-aGNR ground electronic state on Ag(111) located well below E_F .^[29] On Au(111), this low lying virtual excitation channel is not accessible in our present LT-UHV 4-STM set-up. Compared to the 7-aGNR dI/dV spectra/maps on Au(111) presented in Figs. 2(e) and 2(f), more dI/dV resonances/maps were recorded on Ag(111) at positive bias voltage in Figs. 2(b) and 2(c). Moreover, as can be seen from the spatial distribution of positive bias dI/dV maps of 7-aGNR on both surfaces (Figs. 2(c) and 2(f)), the maps of the pure armchair resonances ($R+n$) on Ag(111) can still be identified but they are modulated by other tunneling channel contributions that we attribute to the presence of **interface resonances/states (IRs)** between 7-aGNR and Ag(111) as discussed later in section D.

To understand the tunneling electronic excitations behavior in the 7-aGNRs on Ag(111) surface, we have systematically recorded the dI/dV maps at different tunneling resonances for different 7-aGNR lengths. Corresponding spatially mapped tunneling excitations presented in Fig. 3 clearly allow the visualization of 7-aGNR length *vs* electronic stabilization on Ag(111) surface. **By plotting the energy eigenvalues defining the quasi-particle gaps (V_{bias} of $R\pm 1$) against the 7-aGNR length on both Ag(111) and Au(111) surfaces clearly showcase the gap evolution**

that follows the $\sim 1/L^2$ dependence (except $R-1$ on Ag(111)) with respect to length ' L ' of the 7-aGNR (Figs. 4(a) and 4(b)).^[30] Notice that a single cyclodehydrogenated monomer was only observed on Au(111) surface but not on Ag(111). This leads to the observed deviation in the $R\pm 1$ resonances energies for cyclodehydrogenated single DBBA monomer unit on Au(111) surface (Fig. 4(b)). For 7-aGNRs longer than 2-monomer units, an intrinsic confinement effect gives rise to a decrease of the quasi-particle resonances with increasing length of 7-aGNR. With quasi-particle resonances varying as a function of $1/L^2$, it should be noted that these energetic positions of STS measured electronic resonances certainly includes the substrate induced electronic structure renormalization effects in addition to the GNR size related confinement effects. One such substrate surface related phenomenon can be directly seen by plotting the stabilized 7-aGNR tunneling resonance energetic positions against the work function of Ag(111) and Au(111) surfaces (~ 5.3 eV for Au(111) and ~ 4.7 eV for Ag(111)).³¹ A clear relative positioning offset of ~ 0.9 eV in the HOMO and LUMO electronic resonances of a 7-aGNR with respect to the E_F of two different surfaces can be visualized in Fig. 4(c).

B. Edge states of 7-aGNRs on Ag(111) and Au(111) surfaces

Another impact of the substrate surface work function difference on the 7-aGNR is its ESs electronic configuration, which are localized at the zigzag structure termini.^[2,32,33] On Ag(111), the low-bias ESs (RE1) are located at ~ -450 mV and remains unchanged as a function of 7-aGNR length beyond 2-monomer units (Fig. 5(a) and see Supplemental Material, Sec. 2 for more details). This indicates negligible longitudinal electronic interactions between the two zigzag edges through the 7-aGNR chemical structure. On Au(111), these ESs are located at $\sim +20$ mV, in perfect agreement with the values reported in the literature (Fig. 5(b)).^[2] The detailed dI/dV

spectra and maps presented in Figs. 5(a) and 5(b) compare with a good match the typical low-bias ES characteristics of a 7-aGNR on Ag(111) and Au(111) surfaces.

On Ag(111), the end position of a 7-aGNR also revealed an extra broad dI/dV resonance centered at $\sim +1.25$ V (Fig. 5(c)). The corresponding dI/dV map exhibits a new ES character (RE2) located at both ends of the 7-aGNR (Fig. 5(c), lower panel). Interestingly, its differential conductance maxima coincides with the central carbon (C) atom position at the zigzag termini, unlike the low bias ES (RE1), the maxima of which are located at the outermost C atoms. Moreover, this new high-bias ES map coincides with the regular $R+n$ eigenmode of the 7-aGNR on Ag(111). Similar high-bias dI/dV measurements carried out at both ends of the 7-aGNR on Au(111) also captured the onset of an additional and new ES resonance at $+2.3$ V (Fig. 5(d)). The corresponding dI/dV map consistently shows a large differential conductance coinciding with the central C position at the zigzag termini. Moreover, similar to the low-bias ESs, these new high-bias ESs are also found to be independent of the 7-aGNR length on both Ag(111) and Au(111) (see Supplemental Material, sec. 2 for more details). They are the positive bias equivalent to the $R-1$ topological length invariant mono-electronic contribution of the 7-aGNR STS resonance observed at -1.7 V on Ag(111). Surprisingly, in spite of numerous and extensive studies of 7-aGNR on Au(111), no such high-bias ES characteristic was reported so far on Au(111).

The neutral electronic ground state of an unsupported 7-aGNR can be described in first approximation by a single Slater determinant like electronic configuration where half of its delocalized molecular orbitals are filled up, while each edge-localized SOMO is half-full with an anti-ferromagnetic coupling between the unpaired electrons at both ends.^[11,27,32] When adsorbed on a metallic surface, this neutral electronic ground state configuration of 7-aGNR (including the

SOMOs) is re-aligned in energy with respect to E_F and undergoes an oxidation or reduction mechanism depending on the chemical potential of the metallic surface. As presented in Fig. 5(a), the SOMO-like resonances (RE1) of 7-aGNR on Ag(111) are located well below E_F (−450 mV). As a consequence, a 7-aGNR on Ag(111) is electronically fully reduced at both zigzag termini with its two SOMOs being completely filled up. Therefore, the ground state resonance of this charged 7-aGNR (RE1 at −0.45 V) on Ag(111) is the result of single hole transfer process through each edge of 7-aGNR via the SOMO channels. On Au(111), the same 7-aGNR ESs were found at +20 mV above E_F (Fig. 5(b)). In first approximation, the modified 7-aGNR ground state on Au(111) corresponds to the electronic oxidation at both zigzag termini with its two SOMOs in an almost empty configuration. The RE1 resonance at +20 mV is therefore the result of a single electron transfer process through the 7-aGNR via the new empty configuration of the SOMO channels. Clearly, the observed RE1 of a 7-aGNR on Au(111) is no more the ground state resonance while it is now determined by the first resonance (R−1) captured at negative bias (at −0.90 V in Fig. 2(e)).

The work function difference (~ 5.3 eV for Au(111) and 4.7 eV for Ag(111))^[31] is decisive for stabilizing different 7-aGNR ground states (Fig. 4(c)). **But, the edge-localized SOMO resonances (RE1) are robust irrespective of the substrate materials, as seen in Figs. 5(a) and 5(b).** The RE1 dI/dV maps on both surfaces are nevertheless quantitatively different because the energetic position (+20 mV) on Au(111) is too close to the E_F for the SOMO to be totally quantum empty. On Ag(111), the SOMO at −450 mV is certainly filled up completely and thus leading to a better dI/dV contrast at both 7-aGNR edges as compared to Au(111).

C. Conformation of 7-aGNR on Ag(111) and Au(111)

As discussed above, the lower work function of Ag(111) brings the RE1 resonance well below E_F . As a consequence, the 7-aGNR on Ag(111) is electronically reduced by a filling up of its two SOMO (at both zigzag termini) responsible for the RE1 resonance measured at -0.45 V. The stabilization of this resonance occurs for 7-aGNR length above 2-monomer units. To simulate this SOMO electronic effect by semi-empirical calculations including the molecular mechanics for the curvature, the minimum energy conformation of a 5-monomer-units long 7-aGNR was calculated on Ag(111) and Au(111) by removing or adding one central hydrogen (H) atom at each zigzag termini of the 7-aGNR. The surface conformation of 7-aGNR was optimized in ASED+^[34] by taking into account the underlying bulk metallic surface. For reference, the conformation of an intact 7-aGNR was first optimized on both the Ag(111) and Au(111) surfaces. These reference calculations result in a perfectly planar conformation of 7-aGNR on both surfaces (Fig. 6(a)).^[34]

By removing one H atom at each zigzag termini, the ASED+ optimization leads to a curved conformation of 7-aGNR on Ag(111) (Fig. 6(b)). To simulate the opposite case, i.e. a 7-aGNR oxidation on Au(111), one H atom was added at each edge that creates an sp^3 configuration at the central C position of the zigzag termini. This sp^3 end configuration is equivalent to the removal of one electron per SOMO. In this second case, the optimized 5-monomer-unit long 7-aGNR on Au(111) was found to be strictly flat, according to ASED+ (Fig. 6(c)).

Experimental lateral STM molecular manipulations of 7-aGNR were also attempted to verify the possibility of a native chemical bond formation between the end positions of the 7-aGNR and the metallic surface or, alternatively, the bonding of a metal adatom during the on-

surface synthesis process for example at the site of a missing H atom at one edge,^[35,36] which could possibly stabilize the curved conformation on Ag(111). Our on-surface synthesized 7-aGNRs are easily manipulated from one stable position to the next one on both surfaces with standard STM manipulation conditions (junction resistance: 400 k Ω) therefore confirming the absence of any chemical bond formation.

D. Lateral Quantization of the Ag(111) Shockley surface states at the 7-aGNR/Ag(111) interface

One consequence of the curved 7-aGNR conformation on Ag(111) is that both ends behave as scattering centers^[10] for the two-dimensional (2D) surface electron gas of Ag(111). Indeed, on Ag(111), circular standing waves can be clearly observed, for example at +600 mV around the two 7-aGNR ends, with a maximum scattering strength concentrated at the end positions as presented in Fig. 6(d) (see Supplemental Material, Sec. 3 for more details). In contrast, such scattering effects were not observed on the Au(111) surface (Fig. 6(e)).

Another consequence of the 7-aGNR curvature is the formation of a 2D rectangular quantum box at the interface between the 7-aGNR and the Ag(111) surface, in between the two 7-aGNR ends. In contrast to the Au(111) case, the two supplementary interface resonances (IR1 and IR2) captured at +0.275 V and +0.6 V on Ag(111) (in Fig. 2(b)) and their corresponding dI/dV maps (IR1 and IR2 in Fig. 2(c)) are coming from the eigenmodes of this interfacial quantum box.

To confirm this interpretation, dI/dV spectra were recorded exactly at the central location of the 7-aGNR box, and also for different lengths to change the effective size of this quantum cavity (Figs. 7(a) and 7(b)). As the length of the 7-aGNR increases, all the dI/dV resonances recorded at the central position of 7-aGNR are downshifted in voltage (as indicated by dotted

arrows in Fig. 7(b)). On the other hand, the line profiles extracted from positive bias dI/dV maps of the 5-monomer-units long 7-aGNR (Fig. 2(c)) and plotted in Fig. 7(c) clearly depict the standing wave patterns with its increasing number of nodes as a function of the bias voltage. These characteristic features can be attributed to the lateral quantization of Ag(111) surface electrons at the 2D interface quantum box. By construction, we monitor here the odd eigenmode series (1st, 3rd, 5th, etc.) of the quantized IRs since the dI/dV spectra presented in Fig. 7(b) are recorded at the central position on the 7-aGNR.

To elucidate the mixing between the quantized IRs and the intrinsic 7-aGNR resonances ($R+n$) on Ag(111), the dI/dV spectra recorded at the armchair side (center location) can be compared for different 7-aGNR lengths (Figs. 7(d) and 7(e)). A close inspection of the dI/dV spectra reveals an additional shoulder resonance at +1.5 V for 3-monomer-units long 7-aGNR (indicated with star symbols in Fig. 7(e)) in addition to the intrinsic resonances (indicated with solid arrows). As the length increases, this particular shoulder resonance clearly exhibits a more modest shift toward lower bias voltage than the intrinsic resonances before eventually coinciding with the 1st intrinsic tunneling excitation resonance ($R+1$ at +0.75 V) at 7-monomer-units long 7-aGNR. In Fig. 7(f), the dI/dV maps are recorded at the additional shoulder resonance and at the 1st intrinsic resonance ($R+1$) for 3-, 4- and 5-monomer long 7-aGNRs. These maps clearly show the absence of any hybridization between the armchair and quantized IR resonances, as can be seen from energetically deconvoluted armchair $R+1$ eigenmode from the interface IR3 eigenmode. The isolated nature of armchair and quantized IR modes with the absence of central IR fringes in the former compared to the later can be clearly seen for shorter GNR lengths due to their different energetic positions (Fig. 7(f)). As the length of a GNR increases, the mixing of both eigenmodes at similar bias voltages lead to the complexity in resolving them in STS

mappings. Moreover, these two distinct eigenmodes are spatially separated as well since the origin of armchair modes are intrinsic to a 7-aGNR chemical structure backbone while the interface modes are exclusive to the vacuum cavity formed between the Ag(111) and curved 7-aGNR molecule. Note that similar measurements carried out on Au(111) do not exhibit any interface patterns as can be seen from the dI/dV maps presented in Fig. 2(f), where the central part of $R+n$ eigenmodes along the 7-aGNR length remains featureless.

IV. CONCLUSIONS

In conclusion, the tunneling electronic excitation spectra for a 7-aGNR on Ag(111) surface are complex. Yet, we have successfully deconvoluted the different contributions by systematically correlating, for a 7-aGNR of identical length, the modal landscape on Ag(111) with its equivalent on Au(111) used as a reference surface. In particular, this comparison provides substantial evidence, which is further supported by the theoretical calculations, that the charge transfer between ESs and metallic support surface results in a curved 7-aGNR conformation on the Ag(111) surface but not on the Au(111). The curved conformation creates a 2D quantum-box-like cavity that exhibits laterally quantized Shockley SSs at the interface between the 7-aGNR and the metallic surface. The lower work function of Ag(111) pushes the 7-aGNR ESs below the Fermi level where the intrinsic tunneling electronic excitations significantly entangle with the interfacial Shockley states. As a result, we show that the spatially mapped 7-aGNR tunneling excitations cannot be interpreted solely as its intrinsic electronic character but rather as the complex mixing of intrinsic molecular electronic features with support surface related phenomena. Our work on the 7-aGNR provides a generic methodological approach to disentangle both aspects and finally reach out for the intrinsic molecular electronic resonances.

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Figures:

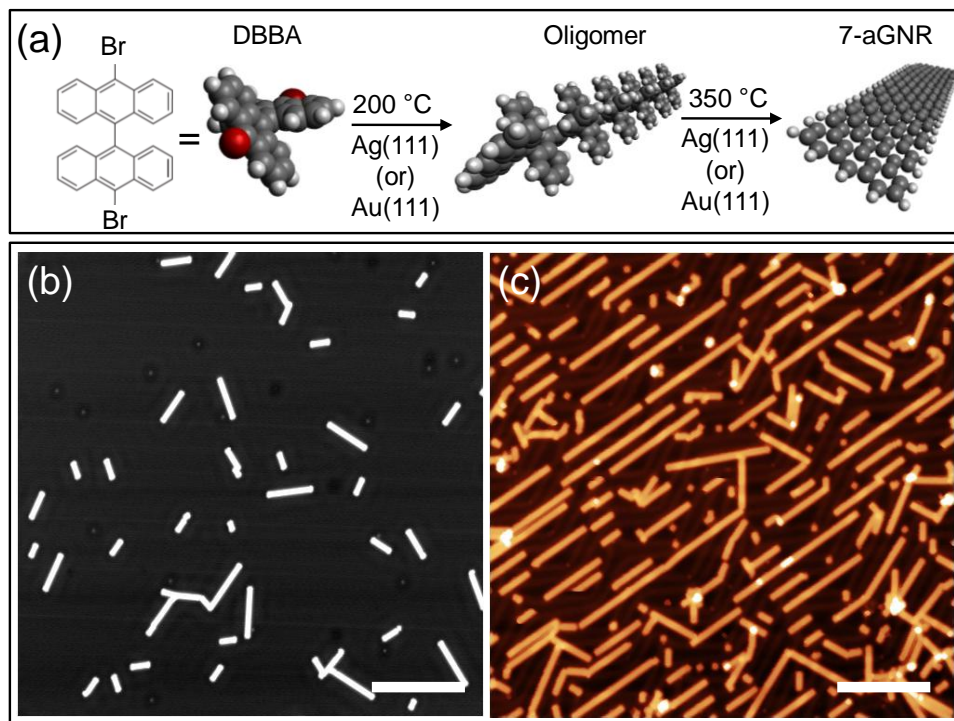


FIG. 1. On-surface synthesis of 7-aGNRs on Ag(111) and Au(111) surfaces. (a) Schematic molecular model illustration of the two-step on-surface synthesis approach of 7-aGNRs using DBBA monomers. Large scale STM images of on-surface synthesized 7-aGNRs, (b) on Ag(111) and (c) on Au(111). Scale bars are 20 nm. Scan-parameters are -2 V/100 pA.

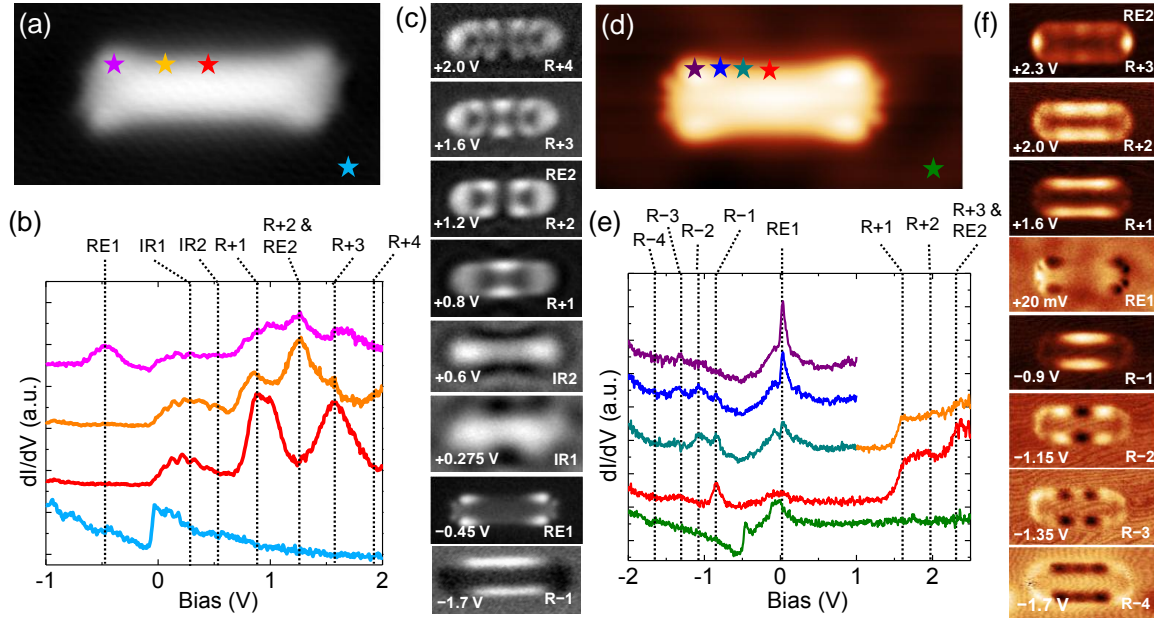


FIG. 2. Electronic tunneling excitation resonances of a 5-monomer-unit long 7-aGNR on Ag(111) and Au(111). (a) STM image of a 5-monomer-unit long 7-aGNR on Ag(111) surface ($V_{\text{bias}} = +20$ mV, $I = 20$ pA). (b) Corresponding dI/dV spectra recorded at different positions (marked with colored stars in (a)) along the armchair side. Several electronic resonances of the 7-aGNR are resolved and highlighted with vertical dotted lines. (c) Corresponding dI/dV maps recorded at the tunneling resonance voltages revealed in (b). They showcase the electronic behavior of 7-aGNR on the Ag(111) surface. **RE1 and RE2 represent the low-bias and high-bias ESs of the 7-aGNR, respectively.** IR1 and IR2 represent the interface resonances. (d-f) STM image and dI/dV characteristics revealing the electronic behavior of the same length (5-monomer-unit long) 7-aGNR on the Au(111) surface similar to that on the Ag(111) surface presented in (a-c), respectively. Scan sizes are $8 \text{ nm} \times 4 \text{ nm}$ (length \times height). Ag(111) and Au(111) reference dI/dV spectra are presented in blue and green curves in (b) and (e), respectively.

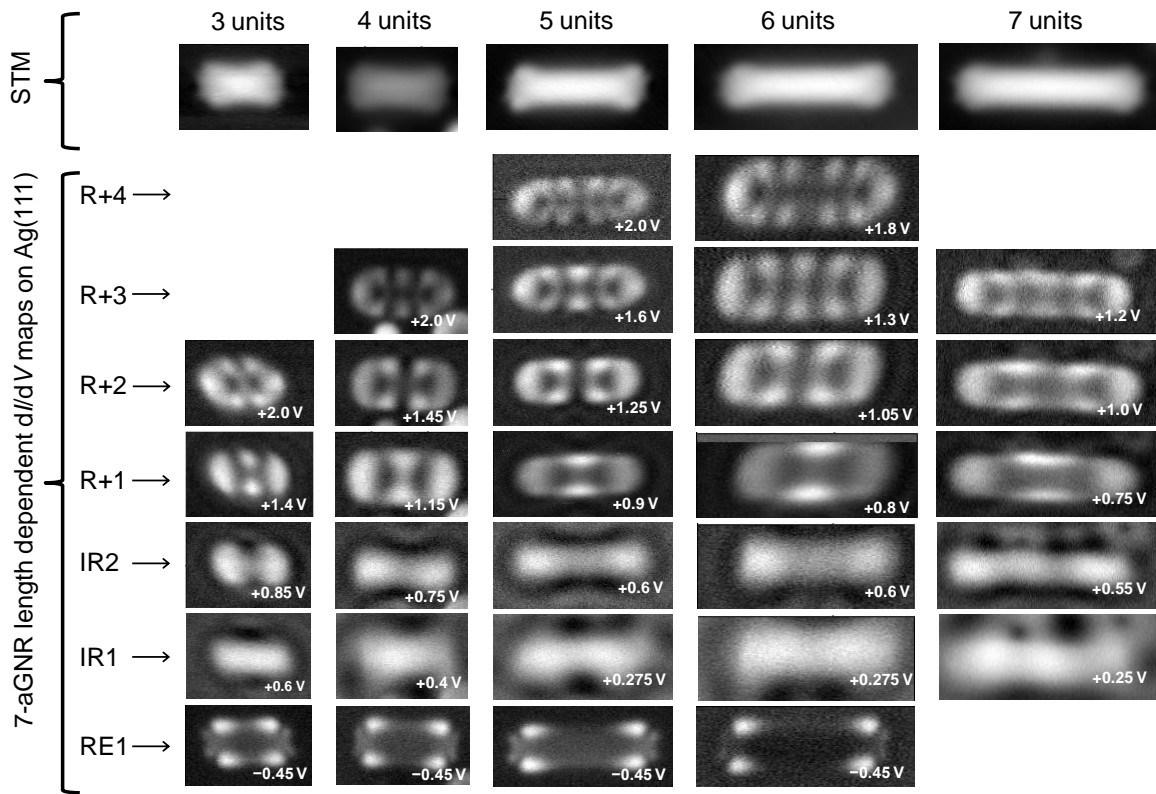


FIG. 3. Spatial dI/dV mapping of tunneling electronic excitations in 7-aGNRs on Ag(111). A matrix view presentation of STM images (top row) and dI/dV maps (columns) recorded for different lengths of 7-aGNR on Ag(111) surface. Corresponding 7-aGNR lengths are given in number of DBBA monomer units on top of STM images. Different electronic eigenmodes (R+n, IRn and RE1) are indicated in the figure. Tunneling bias voltage for each dI/dV map is indicated in the inset of the corresponding map.

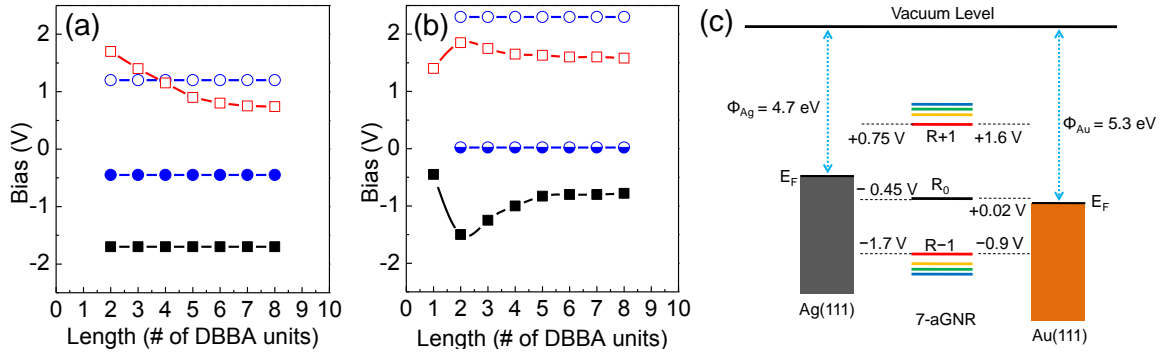


FIG. 4. Electronic energy level structure of a 7-aGNR on Ag(111) and Au(111) surfaces. Electronic stabilization behavior visualized for the quasi-particle resonances of R+1 (open red squares) and R-1 (filled black squares) which contribute the quasi-particle-electronic bandgaps of a 7-aGNR, (a) on Ag(111) and (b) on Au(111), respectively. ES resonance positions of 7-aGNR, RE1 ((half) filled blue circles) and RE2 (open blue circles), are also presented in the figures for reference. (c) Schematic illustration of the relative positioning of different tunneling electronic excitation energies extracted from the dI/dV spectra of a stabilized 7-aGNR visualized with respect to the Fermi levels of Ag(111) and Au(111) surfaces.

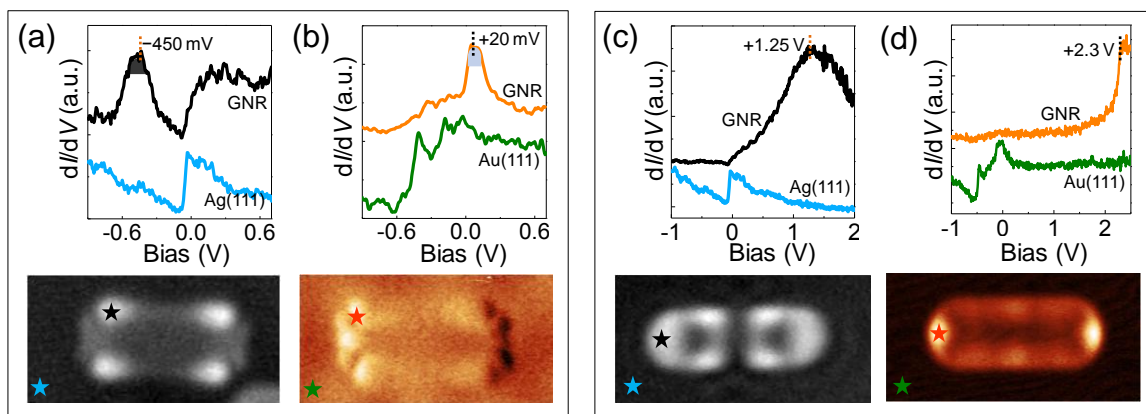


FIG. 5. Edge localized electronic characteristics of 7-aGNRs. (a) A typical dI/dV spectrum (upper panel, black curve) and corresponding dI/dV map (lower panel) showing the low-bias ES around -450 mV of a 5-monomer-units long 7-aGNR on Ag(111) surface. Similarly, the dI/dV spectrum and map presented in (b) illustrate the same low-bias 7-aGNR ES characteristic (orange curve) located at $+20$ mV on Au(111) surface. (c,d) Wide range dI/dV characteristics revealing a new high-bias ES of 7-aGNR located at $\sim +1.25$ V on Ag(111) surface (c, black curve) and at $+2.3$ V on Au(111) surface (d, orange curve). Corresponding dI/dV maps in the lower panels show the characteristic appearance of high-bias ESs of 7-aGNR on Ag(111) and Au(111) surfaces, respectively. Scan areas are $8 \text{ nm} \times 4 \text{ nm}$ (length \times height). Ag(111) and Au(111) reference dI/dV spectra are presented in blue and green curves, respectively.

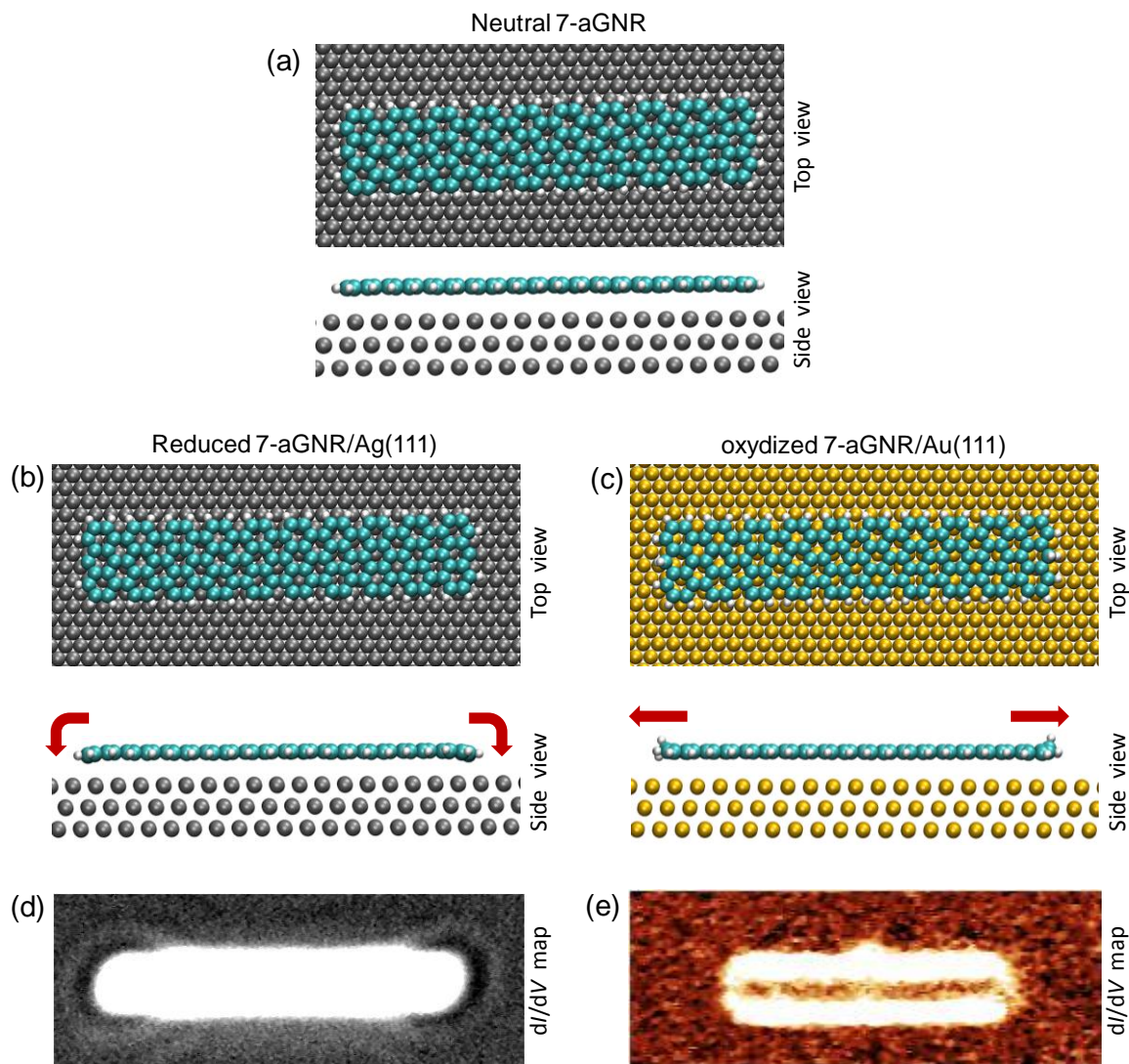


FIG. 6. 7-aGNR conformation on Ag(111) and Au(111). (a) Minimum energy configuration of a neutral 5-monomer-units long 7-aGNR revealing a flat conformation after relaxing its structure on the Ag(111) surface calculated by ASED+. The flat conformation shown in top (top panel) and side (bottom panel) views is used here as a reference. (b) Calculated minimum energy conformation of a reduced 7-aGNR on Ag(111) surface after removing one H atom at each zigzag termini. It shows a marked downward curvature at both termini. (c) Calculated minimum energy conformation of oxidized 7-aGNR on Au(111) after adding one H atom at each zigzag termini. (d,e) Experimental dI/dV maps corresponding to the (b) and (c) configurations that reveal the presence, in (d), and absence, in (e) of circular patterns at the 7-aGNR edge positions on Ag(111) and Au(111), respectively. Scan parameters are: $\sim +600$ mV/100 pA. Scan sizes are $15 \text{ nm} \times 5.5 \text{ nm}$ (length \times height)

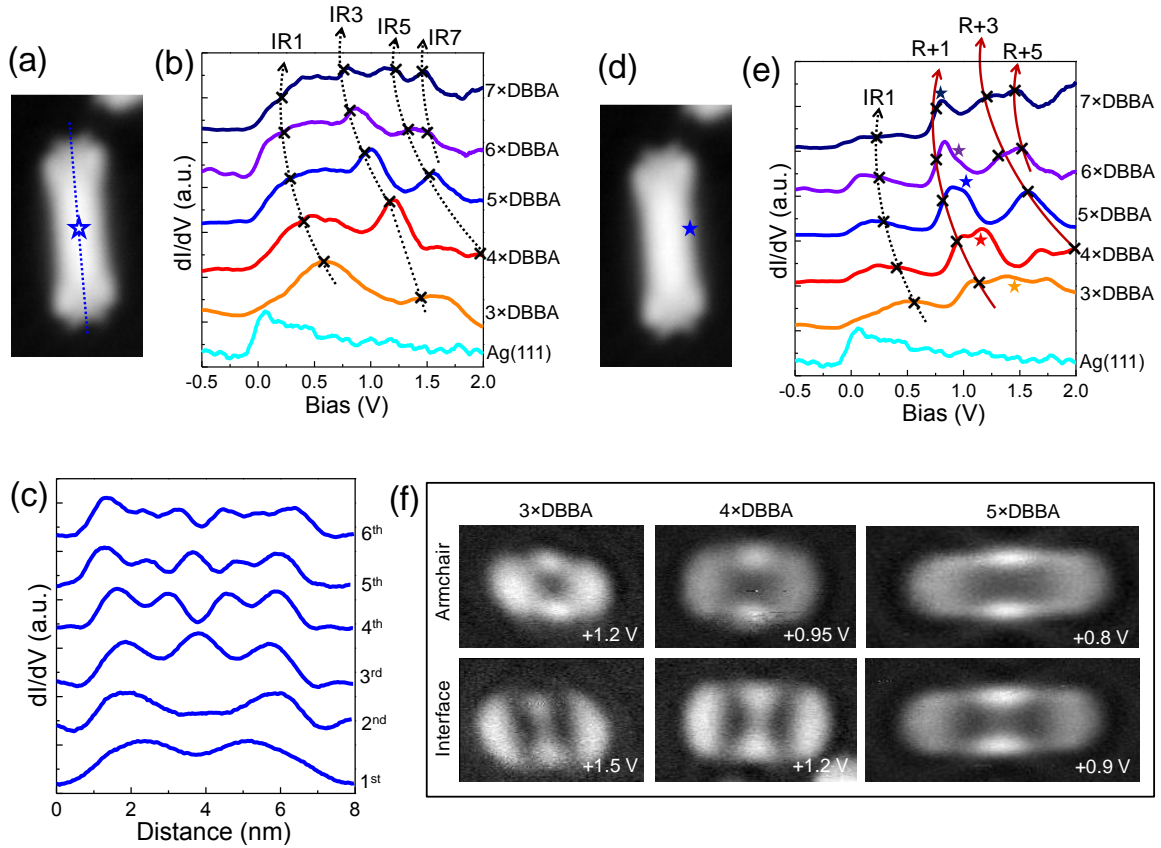


FIG. 7. Shockley surface state lateral quantization at the interface of 7-aGNR and Ag(111) surface. (a) STM image showing the spectroscopic position (open blue star symbol) and (b) corresponding dI/dV spectra reveal the length dependency of several electronic interfacial resonances (IRs). In (b) each electronic resonance can be followed as a function of the 7-aGNR length as indicated by the dotted arrows. (c) Line profiles extracted from the dI/dV maps of 5-monomer-units long 7-aGNR (from Fig. 1(c)) along the central axis as indicated by dotted line in (a). These profiles reveal the laterally quantized standing-wave-like behavior of IRs. (d) STM image showing the spectroscopic position at the armchair side center (closed blue star symbol) and (e) Corresponding dI/dV spectra of 7-aGNR revealing the intrinsic armchair side electronic eigenmode resonances ($R+1$, $R+3$, etc.) and their GNR length dependency. In (e) the shift of each armchair mode electronic resonance is indicated by the solid arrows. The shoulder peak (indicated with filled colored stars) represents the 3rd quantized IR. An energetically isolated interface mode (IR1) was indicated with dotted arrow. (f) dI/dV maps recorded at different voltages comparing the 1st armchair resonance (top panels) and 3rd quantized IR (bottom panels) for different 7-aGNR lengths revealing the well isolated and non-hybridized armchair and IR modes.