

Intramolecular variations of Andreev reflection

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Andreev reflection is probed with a scanning tunneling microscope using a gold-coated normal-metal tip and a single nickel-phthalocyanine molecule adsorbed on superconducting Pb(111). Spectroscopy of the differential conductance at tip-molecule separations ranging from tunneling to contact distances unveils the evolution of Andreev reflection at the central Ni ion and its neighboring pyrrole moieties. Both molecular sites behave similarly in the tunneling range, while at contact separations deviations occur. The efficiency of Andreev reflection rises in a less pronounced manner for Ni than for the pyrrole groups. In addition, across Ni the Andreev reflection rate stays well below the maximal achievable value, while across the pyrrole groups it is nearly reached. This difference is associated with the energy shift of the lowest unoccupied molecular orbital, which reflects the progressive hybridization of the molecule with the approaching tip. The orbital energy remains above the Fermi level for Ni and dives below for the pyrrole groups, which is accompanied by the absence (Ni) and presence (pyrrole) of the molecular Kondo effect. A possible interplay of Andreev reflection and Kondo screening is suggested.

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I. INTRODUCTION

At the interface between a normal conductor (NC) and a superconductor (SC), electrons can be converted into Cooper pairs and vice versa due to Andreev reflection (AR) [1–3], which represents a theoretical picture of charge transport that was originally stimulated by the experimental observation of an anomalous heat flow in superconductors containing normal-metal phases [4–6]. An electron at the Fermi energy (E_F) of the NC cannot enter the SC because of the unavailability of electron states within the Bardeen-Cooper-Schrieffer (BCS) energy gap [7]. However, in the AR scenario a second electron of the NC can be supplied by the creation of a hole that is reflected in the opposite direction of the electron impinging on the interface. The coupling of the two electrons gives rise to a Cooper pair propagating in the SC. Analogously, a Cooper pair is transformed into one electron traveling in the NC and another electron that occupies a hole incident on the interface. These conversions take place in an interfacial region extending on the length scale of the SC coherence length. Therefore, AR is at the basis of the proximity effect [8], which describes the presence of the superconducting phase in the NC interfacing the SC. In other words, electrons of the NC turn into quasiparticles in this region where they are subject to an attractive interaction, which allows Cooper pair formation.

The AR picture remains valid for biased NC-SC junctions, i.e., for a net charge flow across the interface. For a bias voltage V giving rise to a current from the NC to the SC, electrons of the NC with energy $|eV| < \Delta$ (e , elementary charge; 2Δ , width of the BCS energy gap) can be converted into Cooper pairs via AR. The concomitantly created holes are retroreflected and flow into the opposite direction. Because of time-reversal symmetry, reversing the charge flow direction by inverting the polarity of V , AR likewise works for the conversion of Cooper pairs into electrons. To this end, holes of the NC are now incident on the NC-SC interface and retroreflected as electrons. In both cases, the net charge transferred per AR is $2e$, which entails a current for $|V| < \Delta/e$ that is two times as large as the current expected for a single transferred electron. The current due to AR is therefore often referred to as excess current [9].

So far, the AR process has convincingly been evidenced by experiments using macroscopic NC-SC point contacts [10] and quantum dot (QD) devices [11]. To theoretically describe the current-voltage characteristics of these studies, the Blonder-Tinkham-Klapwijk (BTK) model was put forward [12,13]. In this approach, the efficiency of AR is controlled by a Dirac- δ -function potential at the (one-dimensional) NC-SC interface ($x = 0$) of the form $H\delta(x)$, where H quantifies the height of the potential barrier and, thus, the transmission probability of the interface for charge transfer. The latter is given by $\tau = 1/(1 + Z^2)$ with $Z = H/(\hbar v_F)$ [$\hbar = h/(2\pi)$, h , Planck's constant; v_F , Fermi velocity]. The dependence of τ on v_F shows that AR can be optimized by well matching Fermi velocities of the materials at the interface. Another manner of modifying AR is the use of ferromagnet-SC interfaces, where the imbalance of majority and minority electrons in the magnet was reported to reduce AR [14–17].

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Surprisingly, despite its fundamental importance, atomic-scale properties of AR at NC-SC interfaces have only scarcely been studied. The scanning tunneling microscope (STM) appears to be an appropriate tool to this end. Indeed, spectroscopy of the differential conductance (dI/dV , I is the current) with an STM was first reported for contacts formed by Pt-Rh tips and polycrystalline Pb surfaces [18] as well as for junctions comprising Pt-Ir tips and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (110) surfaces [19], although spatial resolution at the atomic scale was not the prime target of these experiments. In both cases, a zero-bias resonance (ZBR) developed in dI/dV spectra for elevated junction conductance, which was interpreted as the spectroscopic signature of AR within the BTK model.

More than a decade later, spectroscopy of AR with an STM was revived by controlled contact experiments with W tips on compound superconductor V_3Si (100) [20]. Increasing the junction conductance on the order of the quantum of conductance ($G_0 = 2e^2/h$), the BCS energy gap was partly filled with spectral weight due to weak AR. In contrast, at considerably lower conductance, STM junctions comprising a W tip and a Nb(110) surface exhibited a clear ZBR caused by AR with a BTK transmission of $\tau = 1$ [21]. These experiments likewise revealed that AR depends on the orientation of adsorbed C_{60} molecules and permitted the interpretation of the BTK parameter Z in terms of the hybridization of C_{60} with the tip and with the substrate. Deviating from the observations for Nb(110) [21], a recent STM study on clean and C_{60} -covered Pb(111) reported only weakly developed AR [22], which strengthened the desire to understand the AR process at the atomic limit. A noncontact approach to AR with an STM was likewise introduced where the exponential evolution of the dI/dV signal with the tip-surface distance was compared for voltages inside and outside the spectroscopic signature of the BCS energy gap [23,24].

A first step toward the understanding of the strong difference in AR behavior of V_3Si (100) and Pb(111) on the one hand and Nb(110) on the other was the recently unveiled importance for AR of an electronic resonance close to E_F [25]. In a molecular junction where a single 2H-phthalocyanine (2H-Pc) was sandwiched between an Au-coated W tip and a Pb(111) surface, a molecular orbital was observed to shift toward and across the Fermi level as a response to the approach of the tip. Concomitantly, the efficiency of AR increased, reached its maximum when the orbital energy coincided with E_F , and decreased again upon further orbital shift below the Fermi level.

While these studies show that microscopic aspects of AR are becoming increasingly important for the understanding of charge transport across atomic-scale NC-SC interfaces, experiments that actually unveil the possible variations of AR on these length scales, e.g., at different intramolecular sites, are still missing. Such experiments are challenging because they require the stability of STM junctions across the molecule at elevated conductance, i.e., for tip-molecule separations close to chemical-bond distances. Undesired fluctuations of the junction geometry [26], displacements of the molecule [27], or even its decomposition [28] were reported under these harsh conditions. Moreover, for the reliable comparison of AR spectroscopy data acquired at different sites, the tip must remain invariant throughout the entire range of

probed tip-molecule distances and bias voltages in dI/dV spectroscopy.

In the work presented here, single Ni-Pc molecules adsorbed on Pb(111) enabled the sought-after spatially resolved dI/dV spectroscopy for junction conductances covering tunneling and contact ranges. Atop the central Ni ion as well as above the pyrrole moieties, AR is essentially irrelevant in a distance interval that spans tunneling and the tunneling-to-contact transition. The subsequent accelerated increase of AR is associated with the concomitant shift of the lowest unoccupied molecular orbital (LUMO) of Ni-Pc toward E_F and its ample overlap with the Fermi level. Further approach of the tip gives rise to AR at Ni with a BTK transmission of less than 0.6 while it reaches nearly unity at the pyrrole moieties. The different behavior of AR at the two intramolecular sites is assigned to the variation of the LUMO energy. While it stays above E_F for Ni, it shifts across and below E_F for the pyrrole groups. The LUMO energy below the Fermi level reflects the electron occupation of the orbital and the acquisition of a molecular spin, which is screened by the Kondo effect [29] as evidenced by the appearance of the Abrikosov-Suhl resonance (ASR) [30–32] at E_F .

II. EXPERIMENTAL DETAILS

The experiments were performed with an STM operated at low temperature (5 K) and in ultrahigh vacuum (base pressure 5×10^{-9} Pa). The preparation of atomically clean and crystalline Pb(111) surfaces was achieved by cycles of repeated Ar^+ ion bombardment and subsequent annealing. The solid phase of Ni-Pc (purity 98 %) was sublimated in a heated (550 K) Ta crucible and the clean Pb surface exposed to the resulting Ni-Pc molecular flux at room temperature. Chemically etched W wire (purity 99.99 %, diameter 250 μm) served as the tip material. Field emission on a gold surface likely coated the tip apex with a thin Au film. Imaging of the substrate surface and the molecular adsorbate was performed in the constant-current as well as in the constant-height mode with the bias voltage applied to the sample. Raw image data were further processed with the Nanotec Electronics WSxM software [33]. Constant-height spectra of dI/dV were acquired by a sinusoidal modulation (100–500 μV_{rms} , 360–700 Hz) of the dc bias voltage and measuring the first harmonic of the ac current response of the STM junction with a lock-in amplifier.

III. RESULTS AND DISCUSSION

A. Molecular superstructure

The adsorption phase of Ni-Pc on Pb(111) (Fig. 1) has not been reported before. Therefore, some structural aspects of the superstructure are briefly presented here. After room-temperature deposition of Ni-Pc on Pb(111) with sub-monolayer coverage, typical STM images are characterized by ordered molecular islands juxtaposed to clean surface areas [Fig. 1(a)]. Defining one monolayer (ML) as a closed molecular film covering the entire surface, the coverage of the sample is estimated as 0.4 ML from several large-scale STM images. The islands exhibit an apparent height of 150 pm, which indicates a monomolecular layer thickness. Within the range of applied voltages of $0.1 \text{ V} \leq V \leq 0.8 \text{ V}$ the apparent heights

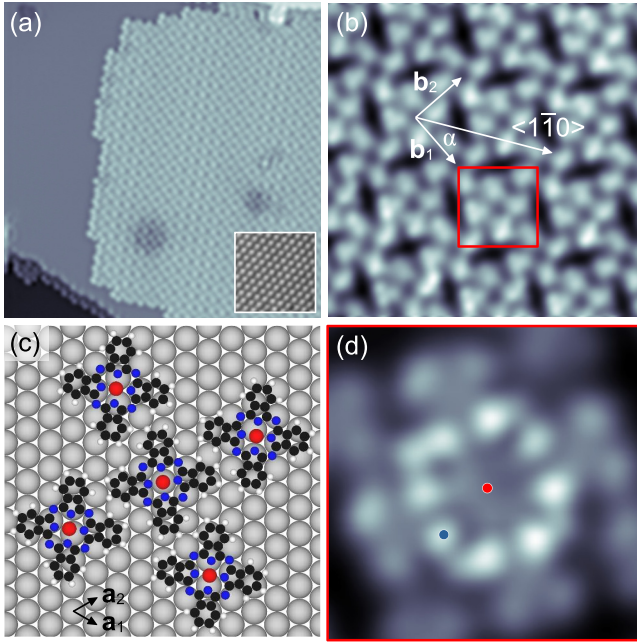


FIG. 1. (a) Constant-current STM image of a Ni-Pc island on Pb(111) [voltage: 100 mV, current: 50 pA, size: 40 nm $\times$ 40 nm, the gray scale covers apparent heights from 0 pm (black) to 640 pm (white)]. Inset: constant-current STM image recorded with an impurity-modified tip of the Pb(111) surface with atomic resolution [10 mV, 50 pA, 7.3 nm $\times$ 7.3 nm, the gray scale covers apparent heights from 0 (black) to 30 pm (white)]. (b) Constant-height close-up view of a Ni-Pc island interior [10 mV, 7 nm $\times$ 7 nm, the gray scale covers currents from 100 pA (black) to 400 pA (white)]. The Ni-Pc supercell is spanned by $\mathbf{b}_1$ and $\mathbf{b}_2$ where $\mathbf{b}_1$ subtends a compact $\langle 1\bar{1}0 \rangle$ direction of Pb(111) by $\alpha = 33^\circ$. (c) Sketch of the Ni-Pc supercell together with the Pb(111) lattice (gray dots) spanned by primitive unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. Atoms of Ni-Pc appear as red (Ni), black (C), blue (N), and white (H) dots. (d) Constant-height close-up view of the single Ni-Pc molecule marked by a square in (b) [10 mV, 1.8 nm $\times$ 1.8 nm, the gray scale covers currents from 1.6 nA (black) to 12 nA (white)]. The two dots indicate the central Ni ion and one neighboring pyrrole group where spatially resolved spectroscopy is performed.

remained invariant. Figure 1(a) likewise shows that step edges of the substrate are decorated with molecules, which hints at the step flow growth of the molecular islands. The shallow depressions visible within the Ni-Pc island are due to buried cavities [34,35], i.e., voids in the bulk lattice that result from the ion bombardment in the course of surface preparation and were likewise reported from Al [36], Cu [37–40], and Ag [41] surfaces.

Close-up views of the molecular clusters unveil an ordered superstructure [Fig. 1(b)]. The associated square unit cell is spanned by the vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ [Fig. 1(b)] with magnitudes $|\mathbf{b}_1| = |\mathbf{b}_2| = (1.4 \pm 0.1)$ nm. Molecules at adjacent corners of the adsorbate unit cell are rotated by $(14 \pm 1)^\circ$ with respect to each other. Defining the Ni-Pc orientation via the direction of two opposite isoindole moieties, one molecule of the unit cell subtends a crystallographic $\langle 1\bar{1}0 \rangle$ direction of the Pb(111) lattice by $(7 \pm 1)^\circ$ and the other by $(-7 \pm 1)^\circ$. With respect to the substrate primitive unit cell spanned by $\mathbf{a}_1$

and $\mathbf{a}_2$ [Fig. 1(c)], the matrix notation of the incommensurate molecular superstructure reads $\begin{pmatrix} 4.66 & -2.54 \\ 0.24 & 3.91 \end{pmatrix}$, which includes the angle $\alpha = (33 \pm 1)^\circ$ between $\mathbf{b}_1$ and $\langle 1\bar{1}0 \rangle$ [Fig. 1(b)]. Such molecular superstructures were likewise reported for Cu-Pc [42–44] and 2H-Pc [45] on Cu(111).

Individual Ni-Pc molecules exhibit a cloverlike shape where the central Ni ion appears as a depression and the isoindole groups as uniform protrusions. More intramolecular details can be achieved by imaging Ni-Pc at decreased tip–molecule distance [Fig. 1(d)]. The resulting submolecular pattern bears resemblance to the Ni-Pc LUMO [46]. The spatially varying electronic structure of Ni-Pc was the key impetus for the spatially resolved AR spectroscopy to be discussed next.

B. Spatially resolved spectroscopy

For accessing AR in spectroscopy experiments with an STM, the junction conductance must be increased, which entails the rising rate of AR events. To this end, the tip–molecule separation is reduced down to and even below the chemical-bond distance range. At intermediate tip excursions, dI/dV spectra were acquired in voltage ranges that cover the BCS energy gap and, if experimentally viable, the LUMO spectroscopic signature. For Ni-Pc these experiments were feasible at the Ni ion and the pyrrole moieties [dots in Fig. 1(d)]. The outer edges of the isoindole groups, however, gave rise to instabilities of the junction at elevated conductance. Therefore, the evolution of dI/dV with tip excursion Δz above Ni and pyrrole sites are discussed here. Importantly, while the observed trends to be discussed next were reproduced for many independently prepared Au-coated W tips, the data presented in this work result from a single tip that remained invariant for the entire set of distance-dependent spectroscopy, which is mandatory for the reliable comparison of the two intramolecular sites. The invariance of the tip was controlled by repeated imaging and spectroscopy in the tunneling range. Figures 2(a)–2(f) collect a representative subset of a sequence of dI/dV spectra obtained above Ni and a pyrrole group for increasing [from (a) to (f)] tip displacement Δz . The voltage range of the spectra was chosen such as to simultaneously access the evolution of the BCS energy gap and the spectroscopic signature of the Ni-Pc LUMO. In the tunneling range [Fig. 2(a)] the LUMO maximum is located at a voltage larger than 100 mV and only appears as a rising edge in the plotted spectra. The BCS energy gap [inset to Fig. 2(a)] is still unaffected. The best fit of the Bogoliubov quasiparticle density of states (DOS) (Appendix A) to the data [solid line in the inset to Fig. 2(a)] results in a width of the BCS energy gap of $2\Delta = 2.2$ meV, which is in agreement with expectations for Pb at 5 K [47]. In Fig. 2(b), for increased tip excursion, the LUMO line shape has entered the spectroscopy window. Its low-voltage tail weakly overlaps with $V = 0$ and, thus, with the dI/dV signal of the BCS energy gap giving rise to an asymmetry of the coherence peak heights. In particular, one can infer that the LUMO signature at the pyrrole groups is closer to $V = 0$ than at the Ni center. The actual evolution of peak positions and widths with the tip excursion will be analyzed in detail below. At $\Delta z = 450$ pm [Fig. 2(c)], the

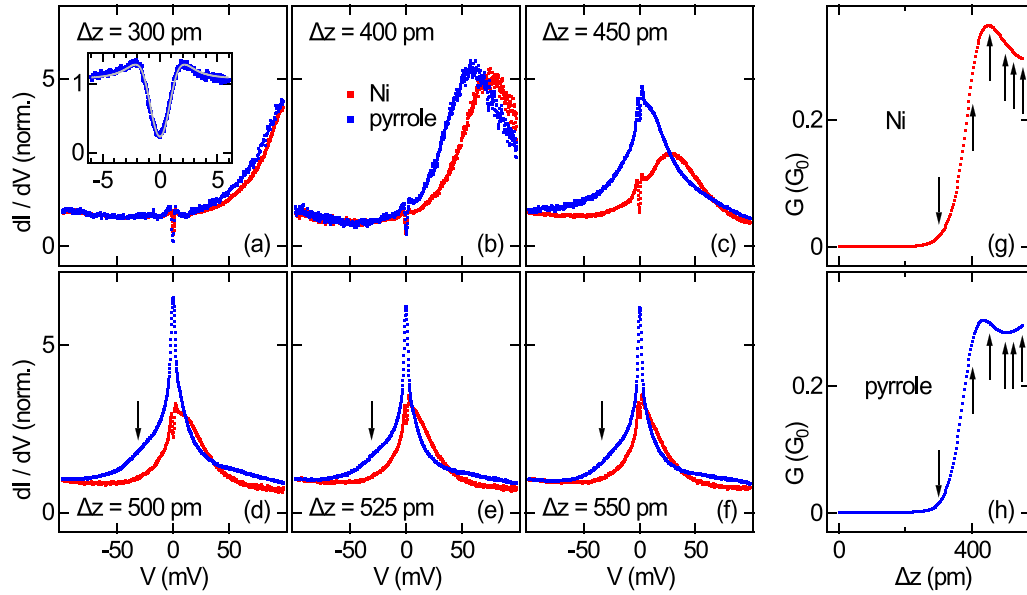


FIG. 2. (a)–(f) Spectra of dI/dV acquired atop the Ni ion and a pyrrole group of Ni-Pc [dots in Fig. 1(d)] at indicated tip excursions Δz . The data are normalized to unity at -100 mV. Inset to (a): close-up view of spectroscopic data close to $V = 0$ together with fit of the BCS energy gap (solid line). Arrows in (d)–(f) mark a shoulder to the ZBR, which is explained in the text. (g), (h) Conductance vs tip displacement acquired atop (g) Ni and (h) pyrrole of Ni-Pc. The arrows mark the junction conductance at which the spectra in (a)–(f) were recorded. The feedback loop parameters 100 mV and 50 pA define $\Delta z = 0$ for all presented data sets.

shift of the peaklike dI/dV feature toward $V = 0$ continues. Compared with $\Delta z \leq 400$ pm, both for Ni and pyrrole the peak associated with the LUMO has considerably sharpened. While the interpretation of this observation is unclear at present, it may reflect the change in hybridization of Ni-Pc with the substrate. Possibly, a partial lift of the molecule from the surface due to the attractive tip-molecule interaction tends to approach the free-molecule electronic structure with its sharp orbital texture. An additional explanation is suggested below in the context of the molecular Kondo effect. For both Ni and pyrrole, the BCS energy gap is still visible in the dI/dV spectra.

In the tip excursion interval $\Delta z \geq 500$ pm [Figs. 2(d)–2(f)], a strong qualitative spectroscopic difference of the two intramolecular sites is obvious. Above the Ni ion, dI/dV spectral data show that the LUMO-associated peak has further shifted toward $V = 0$ with its maximum remaining at positive V . In addition, the signature of the BCS energy gap is discernible on the LUMO spectroscopic line shape. In contrast, above the pyrrole group the dI/dV spectra exhibit a pronounced ZBR structure, where a sharper and higher resonance is superimposed on a wider and lower resonance, while the LUMO-associated signature has shifted to negative voltages and appears as a shoulder [arrows in Figs. 2(d)–2(f)] to the ZBR. The BCS energy gap has disappeared from the pyrrole spectra for these tip excursions. Increasing the tip displacement by another 50 pm does not alter this situation markedly for both Ni and pyrrole.

To relate the tip displacement to the junction conductance $G = I/V$, the evolution of G with Δz is shown for the junction atop Ni [Fig. 2(g)] and the pyrrole groups [Fig. 2(h)]. The accelerated increase of G between ≈ 300 pm and ≈ 400 pm signals the transition from tunneling to contact [48,49], while the weak variation of G for $\Delta z > 420$ pm is indicative of the

contact range. Notably, G does not simply level off in the contact range. Rather, after reaching a maximum it slightly decreases again. As in the case of 2H-Pc on Pb(111) [25], this behavior can be traced to the LUMO resonance shifting close to (Ni) and across (pyrrole) $V = 0$.

The interpretation of the spectroscopic data requires the identification of the contributions to the ZBR, in particular for the pyrrole case. Therefore, additional spectroscopic experiments were performed with the suppressed superconducting state of the sample (Fig. 3). To this end, an external magnetic field $B = 100$ mT $> B_c(5\text{ K}) = 42$ mT [$B_c(5\text{ K})$: critical magnetic field of Pb at 5 K [50,51]] was applied. Except for the expectedly missing BCS energy gap, the evolution of dI/dV [Figs. 3(a)–3(f)] as well as of G [Figs. 3(g) and 3(h)] with Δz is similar to the observations for $B = 0$ (Fig. 2). For example, the shift toward $V = 0$ of the LUMO feature for increasing Δz is comparable with the situation for $B = 0$, and so is its apparent sharpening upon reaching the contact range of tip-molecule distances. Moreover, while its maximum stays at $V > 0$ for Ni, it reaches $V < 0$ for pyrrole and appears as a shoulder to the ZBR [arrows in Figs. 3(d)–3(f)]. The latter, however, represents a single peak rather than the superposition of two resonances as observed for $B = 0$.

To analyze this notable deviation from the otherwise similar evolution of the spectra without and with magnetic field, Fig. 4 compares the spectra above Ni [Fig. 4(a)] and above pyrrole [Fig. 4(b)] for $B = 0$ and $B > B_c$ in a smaller voltage range. For Ni, the comparison of these spectra support the idea that the BCS energy gap for $B = 0$ is superimposed on the LUMO spectral line shape that is already present for $B > B_c$. For the pyrrole groups, the close-up view of dI/dV spectra at $B = 0$ corroborates the aforementioned superposition of a sharper ZBR on a wider ZBR, which is signaled by the strong change in the slope of the line shape [arrows in Fig. 4(b)].

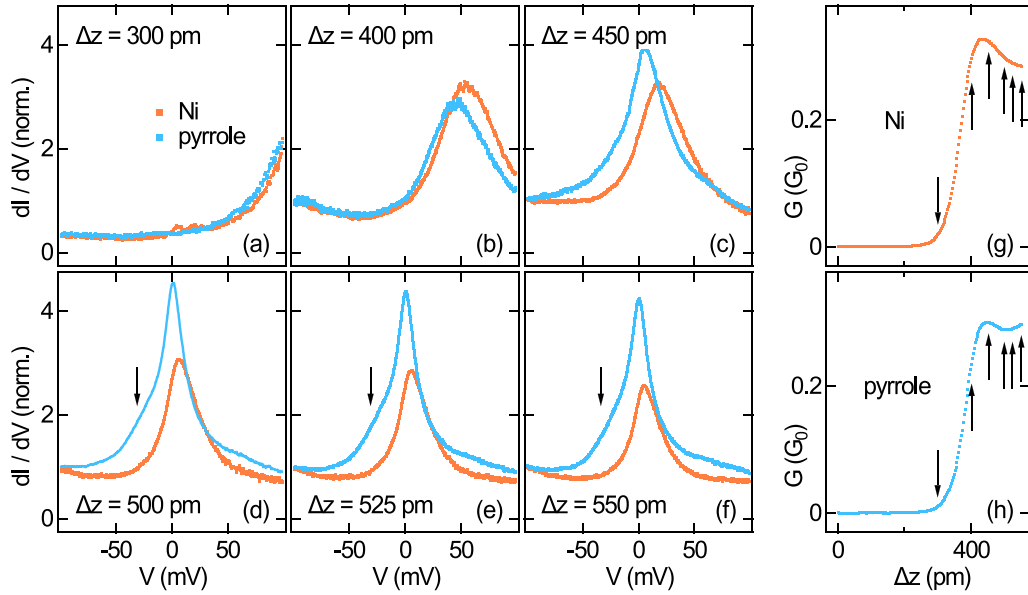


FIG. 3. As Fig. 2, for an applied external magnetic field of $B = 100 \text{ mT} > B_c$.

Since the wider ZBR is likewise present for $B > B_c$, the sharp ZBR must be related to the superconducting phase when $B = 0$. Consequently, the two resonances observed in contact dI/dV spectra above the pyrrole groups close to $V = 0$ are of different nature. While the sharp ZBR is supposedly due to AR, the wider ZBR likely represents the ASR [30–32] due to the Kondo effect [29]. The fits described in the following section show that AR occurs in junctions comprising the Ni ion, too, albeit to a reduced extent compared to the pyrrole moieties.

The assumption of the Kondo effect seems to be unjustified at first glance because Ni-Pc lacks a spin ($S = 0$) in the gas phase [52]. Moreover, dI/dV spectra in the tunneling range do not indicate the presence of the ASR, which rules out the acquisition of a molecular spin due to adsorption-induced charge transfer as observed for other phthalocyanine molecules [52,53]. Indeed, the suggested ASR appears only when the NC tip reaches chemical-bond distances to Ni-Pc. Concomitantly, the LUMO signature overlaps the Fermi level. One may therefore conclude that the hybridization of Ni-Pc with the tip causes charge transfer to the molecule, which is in line with the LUMO shift toward E_F , i.e., toward occupied states, and, at the same time, gives rise to a finite molecular spin. A similar scenario was put forward for a 2H-Pc molecule embedded in different 2H-Pc environments on Pb(100) [54]. Moreover, on noble metal Ag(100), the charge transfer from the substrate to adsorbed Ni-Pc was reported to be close to one electron with a resulting molecular spin of $S = 1/2$ [52,55]. In the present case, Ni-Pc hybridizes with the Au tip and charge transfer as well as the acquisition of spin are likely to be the same. These previous findings provide ample evidence for the presence of the Kondo effect of Ni-Pc in contact with the Au-coated tip.

The comparison of Ni and pyrrole dI/dV spectra indicate that at the Ni ion, in contrast to the pyrrole groups, the Kondo effect is not present. This conjecture relies on the energy and width of the peaklike background, which are both unusually

high for an ASR caused by the molecular Kondo effect. The hypothesis further implies that the molecular spin is delocalized in the π -electron system of the aromatic ligands rather than localized in Ni d -orbitals, which is in accordance with previous reports [52,55]. However, it remains elusive which electrode—tip or sample—actually takes the active part in the Kondo screening of the molecular spin magnetic moment. On the one hand, the NC tip in contact with Ni-Pc provides a nearly free electron gas for screening. The SC sample, on the other hand, impedes screening for $|eV| \leq \Delta$ due to missing electron states, while for $|eV| > \Delta$ quasielectrons with finite spin are available for the Kondo screening, in particular when the ASR width exceeds the width of the BCS energy gap [56]. In the following, in order to keep the model current as simple as possible, Kondo screening in the sample only is assumed.

C. Site-dependent Andreev reflection

The preceding paragraph motivates the matching of Ni spectroscopic data at $B = 0$ by two components, namely the LUMO and the BTK profile, while for $B > B_c$ only the LUMO is needed. For the pyrrole groups, the ASR has to additionally be taken into account. The tunneling current used for the simulations adopts the form

$$I \propto \int_{|E-E_F| \ll \Phi} \varrho_t(E - eV) \varrho_s(E) [f_t(E - eV) - f_s(E)] dE, \quad (1)$$

where ϱ_t and ϱ_s denote, respectively, the tip and sample DOS, while f_t and f_s are the Fermi-Dirac functions of tip and sample with known and, thus, fixed temperature. Since the current variation is relevant here only for small voltages $|V| \ll \Phi/e$ (Φ : arithmetic mean of tip and sample work functions), the transmission factor is assumed constant and does not appear in the integrand. Moreover, the tip DOS is likewise set constant, which reflects the use of a Au-coated s -wave tip and is in line

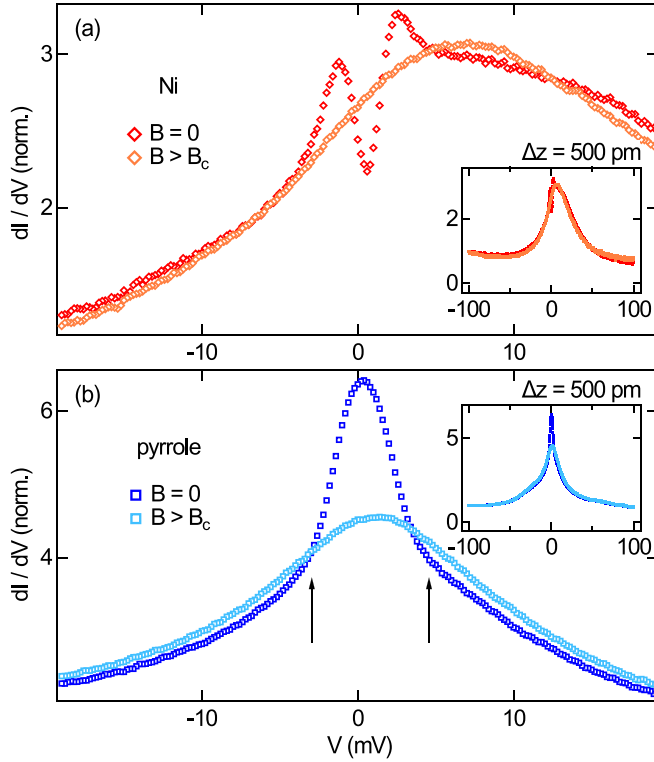


FIG. 4. (a) Close-up view of dI/dV spectra acquired atop the Ni ion of Ni-Pc at tip excursion $\Delta z = 500$ pm for $B = 0$ (dark) and $B = 100$ mT $> B_c$ (bright). (b) As (a) for a pyrrole group of Ni-Pc. The arrows mark the transition between two resonances centered at $V = 0$. Insets: wide-range dI/dV spectra of (a) Ni and (b) pyrrole from which the close-up views are extracted. For all spectra the feedback loop was deactivated at 100 mV, 50 pA and the tip subsequently displaced by Δz toward the two intramolecular sites.

with the Tersoff-Hamann model [57,58] as well as with the assumed Kondo screening in the sample alone. The sample DOS consequently reads

$$\varrho_s = (\varrho_{\text{LUMO}} + \varrho_{\text{ASR}})\alpha_{\text{BTK}}, \quad (2)$$

where the LUMO DOS ϱ_{LUMO} is described by an extended asymmetric pseudo-Voigt profile [59,60], the ASR line shape ϱ_{ASR} is best matched by the Frota function [61], and α_{BTK} represents the dimensionless BTK function [12]. The numerical derivative of I is convoluted with a function that considers the modulation broadening and is then fit to the data. The analytic expressions for all functions can be found in Appendix A.

Before presenting the fit results, a brief comment on the use of the Frota line shape for describing the ASR is appropriate. In a previous report, low modulation voltages in dI/dV spectroscopy were demonstrated to favor the Frota over the Fano profile [62]. The latter line shape was originally used for matching dI/dV spectra of atomic Kondo impurities obtained with an STM [63,64]. It highlights the coherent superposition of electron tunneling directly into the electron continuum of the substrate and via the discrete state of the impurity. For the applicability of the Frota profile a threshold modulation voltage exists that is a function of the voltage range for the fit. In the present case, the fit interval is given by $|V| \leq 50$ meV, for which staying below a modulation amplitude of 3 mV

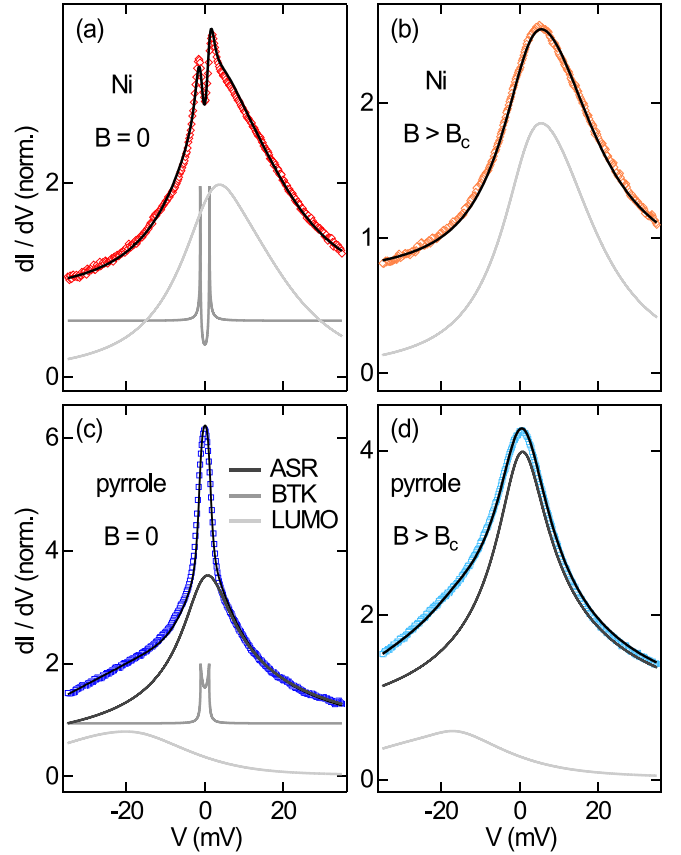


FIG. 5. Close-up views of raw dI/dV data (symbols) acquired above (a),(b) Ni and (c),(d) a pyrrole group for $B = 0$ and $B = 100$ mT $> B_c$ at a tip excursion of $\Delta z = 550$ pm. The resulting fit (black line) is composed of the ASR (dark gray), the BTK (gray), and the LUMO (light gray) profile.

gives rise to the Frota line shape as the most appropriate profile for the fit [62]. Therefore, because of root-mean-square values of the modulation voltage below 500 μ V, fits with the Frota function are justified.

Figure 5 shows exemplary fit results for Ni [Figs. 5(a) and 5(b)] and pyrrole [Figs. 5(c) and 5(d)] with $B = 0$ and $B > B_c$ using a tip excursion of $\Delta z = 550$ pm. The total fit (black line) follows closely the experimental data (symbols). The individual contributions to the fit are presented at the bottom of the plots (solid lines with different gray scales).

For instance, above the Ni ion for $B = 0$ [Fig. 5(a)] the best fit is achieved by considering ϱ_{LUMO} and α_{BTK} . The energy of the LUMO relative to E_F is $\varepsilon_{\text{LUMO}} \approx 6$ meV and its full width at half-maximum (FWHM) reads $\Gamma_{\text{LUMO}} \approx 30$ meV. The BTK transmission of this fit is $\tau \approx 0.58$. After quenching the Pb superconducting phase in $B = 100$ mT, only ϱ_{LUMO} with essentially identical $\varepsilon_{\text{LUMO}}$ and Γ_{LUMO} is needed for the best fit [Fig. 5(b)]. In particular, for both $B = 0$ and $B > B_c$ an additional contribution, such as the ASR, is not needed to describe the spectral data for Ni.

The situation is different for the pyrrole groups. Field-free spectroscopic data [Fig. 5(c)] are best described by including all contributions to ϱ_s [Eq. (2)]. The LUMO DOS for the best fit gives rise to $\varepsilon_{\text{LUMO}} \approx -20$ meV and $\Gamma_{\text{LUMO}} \approx 42$ meV.

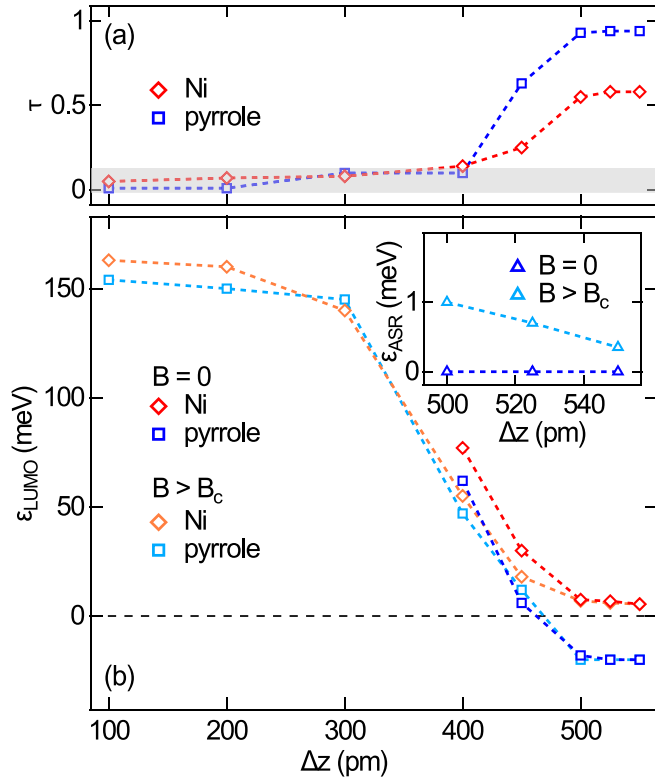


FIG. 6. Variation of (a) BTK transmission τ and (b) energy $\varepsilon_{\text{LUMO}}$ of the LUMO with the tip displacement Δz extracted from fits to dI/dV data above the Ni ion (diamonds) and a pyrrole group (squares). The shaded area in (a) marks a region, where the actual τ stays below the detection limit (see text). Dark (light) colors of the symbols in (b) refer to the presence (absence) of an external magnetic field. The horizontal dashed line indicates zero energy coinciding with E_F . Inset to (b): variation of the ASR energy ε_{ASR} with Δz for $B = 0$ (dark triangles) and $B = 100 \text{ mT} > B_c$ (light-colored triangles). Dashed lines connecting the data points in all plots are guides to the eye.

The FWHM is large enough for the LUMO profile to still straddle the Fermi level. In contrast to the Ni ion, the LUMO energy at the pyrrole groups is below E_F at the otherwise same tip excursion and a similar junction conductance. The Frota function ϱ_{ASR} likewise contributes to the fit with $\varepsilon_{\text{ASR}} \approx 0$ and an FWHM of $\Gamma_{\text{ASR}} \approx 28 \text{ meV}$. The ASR width corresponds to the Kondo temperature $T_K \approx \Gamma_{\text{ASR}}/(2k_B) \approx 162 \text{ K}$ (k_B is Boltzmann's constant) [65,66]. The BTK function is responsible for the sharp peak centered at $V = 0$, i.e., it shows a BCS energy gap that is strongly filled with spectral weight due to AR corresponding to a BTK transmission of $\tau \approx 0.94$. For $B > B_c$ [Fig. 5(d)], only the LUMO profile with the same $\varepsilon_{\text{LUMO}}$ and Γ_{LUMO} extracted from the field-free spectra as well as the ASR line shape ($\varepsilon_{\text{ASR}} \approx 0.4 \text{ meV}$, $\Gamma_{\text{ASR}} \approx 30 \text{ meV}$) are needed to describe the experimental data.

Fits such as the ones presented in Fig. 5 were performed for all dI/dV spectra acquired from the tunneling to and beyond the contact range of tip-molecule distances. The evolution of the most important fit parameters, i.e., the BTK transmission as well as the energy of the LUMO and the ASR, with the tip excursion is summarized in Fig. 6. In the tip excursion

range of $100 \text{ pm} \leq \Delta z \leq 400 \text{ pm}$, the BTK transmission remains below the detection limit for both the Ni ion and the pyrrole groups [Fig. 6(a)]. Rather than spectral weight due to AR, the intragap signal reflects spectroscopic background due to thermally excited electrons and feigns a finite BTK transmission. This region is indicated by the shaded area in Fig. 6(a). Starting from $\Delta z = 400 \text{ pm}$, which is assigned to the contact range of tip excursions [Figs. 2(g) and 2(h)], an accelerated increase of τ above the detection limit occurs, which is weaker for Ni than for the pyrrole moieties. Indeed, within a tip approach of 100 pm , τ reaches ≈ 0.6 above the Ni ion while it attains nearly unity above the pyrrole groups.

To understand this behavior, it is insightful to explore the evolution of the LUMO [Fig. 6(b)] and the ASR [inset to Fig. 6(b)] energy. For $B = 0$, LUMO spectroscopic data are available for $\Delta z \geq 400 \text{ pm}$, which is the range of tip excursions most relevant to the accelerated changes in τ . Moreover, the ASR exclusively appears for $\Delta z \geq 500 \text{ pm}$. Compared with $B > B_c$, where LUMO data are available for $\Delta z \geq 100 \text{ pm}$, the extracted energies $\varepsilon_{\text{LUMO}}$ and ε_{ASR} do not significantly deviate from observations in the field-free case. By comparing now the dependence of τ on Δz with the evolution of $\varepsilon_{\text{LUMO}}$ and ε_{ASR} two important conclusions can be drawn. First, the increase of τ for $400 \text{ pm} \leq \Delta z \leq 500 \text{ pm}$ coincides with the ample overlap of the LUMO with the Fermi level. In this tip excursion range the LUMO energy is very close to E_F and progressively shifts toward and, in case of the pyrrole groups, even across the Fermi level. This conclusion is in accordance with the findings for 2H-Pc [25]. Second, the BTK transmission above the Ni ion reaches a maximal value of $\tau \approx 0.6$ when the LUMO stays very close to E_F with $\varepsilon_{\text{LUMO}} \approx 6 \text{ meV}$ and $\Gamma_{\text{LUMO}} \approx 30 \text{ meV}$, which likewise agrees with previous conclusions for 2H-Pc [25]. Above the pyrrole groups, τ nearly adopts the maximum of 1 although the LUMO is clearly below E_F , i.e., $\varepsilon_{\text{LUMO}} \approx -20 \text{ meV}$. This observation is striking because it apparently contradicts the results obtained for 2H-Pc [25], where the efficiency of AR was attenuated again with the 2H-Pc LUMO shifting further below E_F . However, in spectra atop pyrrole the ASR appears as a resonance centered at E_F [inset to Fig. 6(b)]. Therefore, in the light of the previous report [25] it is tempting to associate the ASR with the required electronic resonance at E_F for enhancing AR. The apparently halted LUMO shift for $\Delta z \geq 500 \text{ pm}$ can tentatively be rationalized. The chemical-bond distance between the Au-coated tip and the Ni ion as well as a pyrrole moiety is reached for $\Delta z \geq 400 \text{ pm}$. The established bond then impedes further charge transfer and leaves the LUMO occupation—and with it the LUMO energy—unaltered. The remaining effect of further tip excursion is then a relaxation of the junction.

Before commenting on the possible interplay between AR and Kondo screening, the Kondo energy scale of $k_B T_K \approx 14 \text{ meV}$, which exceeds the Cooper pairing energy of $\Delta \approx 1.1 \text{ meV}$ by far, is discussed in the context of YSR states. The latter result from the same magnetic exchange interaction of the Kondo impurity with the substrate electron continuum and, thus, are expected to leave their fingerprints as intragap states. For Mn-Pc on Pb(111), the competition between Kondo screening and Cooper pair-breaking interaction was previously reported in a pioneering work [67]. Their binding energy

relative to E_F can be estimated in the classical-spin limit as $\varepsilon_{\text{YSR}} = \Delta(1 - a^2)/(1 + a^2)$ with $a = \pi S J \varrho_F$ (J , magnetic exchange coupling energy; ϱ_F , DOS at E_F in the normal state) [68,69]. Because of $k_B T_K \gg \Delta$, the underlying large value of J leads to $\varepsilon_{\text{YSR}} \approx -\Delta < E_F \equiv 0$, i.e., to an occupied YSR state, and to its position close to the BCS coherence peaks. The presence of the intragap states may be corroborated by an asymmetry of the BCS coherence peaks or a reduced width of the BCS energy gap in the spectra. However, the presence of the LUMO signal close to $V = 0$ already introduces an asymmetry of the coherence peak heights, which impedes the unambiguous assignment of an asymmetry due to YSR states. In addition, the joint action of AR-associated spectral weight and thermal broadening can feign a reduced gap width. Future work will be devoted to a similarly systematic study as presented here using a superconducting tip in order to push the energy resolution in spectroscopy beyond the Fermi-Dirac limit.

The role of the Kondo effect in AR may even go beyond the mere presence of the ASR. In QD experiments where an InAs QD was contacted to NC (Au) and SC (Al) wires, AR enhancement was reported and traced to the Kondo effect [70]. In a later related theoretical study [71] it was suggested that the Andreev bound states, which result from the coupling of the QD to the SC lead, not only take care of the conventional AR. They additionally contribute to the screening of the QD spin doublet. In this sense, Kondo screening represents a second charge transport channel via the Andreev bound states, which entails the enhancement of AR.

The presence of the Kondo effect together with AR is worth an extended discussion because it contributes to a tentative explanation of several observations reported in the present studies. Both experimental and theoretical work on charge transport across QD devices was dedicated to the understanding of the joint action of Kondo screening and AR [11], presumably stimulated by the appealing antagonistic interactions involved, i.e., the Coulomb repulsion of electrons in the Kondo effect and their attraction to Cooper pairs in AR.

Particular attention was paid to the coupling of the Kondo impurity to the electrodes, which likely plays an important role in the STM experiments reported here, too, because of Ni-Pc gradually changing its hybridization with the tip and the sample in the course of approaching the tip. Pioneering work using a QD connected to NC wires showed that by altering this coupling, the Kondo, the mixed-valence, and the empty-orbital regime could be engineered and probed [72]. The single-impurity Anderson model [73] characterizes these regimes by the ratio of the impurity level energy and its width. In the Kondo regime, this ratio adopts strongly negative values because the impurity energy level is clearly below E_F , while in the mixed-valence regime it is nearly zero and larger than zero in the empty-orbital regime. The suggested Kondo effect at the pyrrole groups of Ni-Pc and the assignment of the sharp ZBR to the ASR is therefore additionally corroborated because the LUMO takes the role of the Kondo impurity level, which is clearly below E_F [shoulders in the spectra of Figs. 2(d)–2(f)] and signals the Kondo regime. Furthermore, the absence of the Kondo effect at the Ni ion reflects in this picture the empty-orbital regime because the LUMO energy is above E_F . Also the mixed-valence regime is likely reproduced

in the experiments by the LUMO shift toward and across the Fermi level observed for the pyrrole groups of Ni-Pc. Additionally, the concomitant sharpening of the orbital resonance (Appendix B) is expected from theoretical grounds as $k_B T_K$ and the width of the Kondo impurity level are predicted to become comparable for the level energy approaching E_F [74].

While similar theoretical results were obtained for a QD attached to an NC and SC wire and, moreover, related to AR [75], it is most desirable to simulate the enhanced AR transport and its possible relation to the Kondo effect for the Au–Ni–Pc–Pb STM junction explored in the present studies.

IV. CONCLUSION

Andreev reflection in NC-SC junctions varies on atomic length scales. The efficiency of AR is locally controlled by the degree of overlap of electronic resonances with the Fermi level. Optimum AR with nearly unity BTK transmission is achieved when the resonance is centered at E_F . To obtain these results, a single-molecule contact proved sufficiently stable to sustain the progressive proximity of the STM probe at different intramolecular sites. Beneficial to the new findings is likewise the site-dependent energy shift of the LUMO, which is interpreted as the response to the increasing tip-molecule hybridization and concomitant charge transfer. The presented observations corroborate the importance of electronic resonances at E_F for AR. In addition they reveal that the ASR associated with the Kondo effect can mediate the resonant enhancement of AR. Whether the amplification of AR is due to an additional AR channel caused by the screening of the Kondo impurity spin via the underlying Andreev bound states remains to be explored by future simulations. Particularly helpful would be nonequilibrium charge transport simulations of a single-molecule STM junction including Kondo correlations and superconductivity, which are hopefully stimulated by the findings reported here.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: FIT FUNCTIONS

Equation (1) contains the Fermi-Dirac function

$$f(E, T) = \frac{1}{1 + \exp[\beta(E - \mu)]} \quad (\text{A1})$$

$[\beta = 1/(k_B T)$, μ : chemical potential] which causes the thermal broadening of spectral features. For the tip and the sample, the temperature $T = 5$ K was used as a fixed parameter. The numerical derivative of the simulated current [Eq. (1)] is then convoluted with

$$\chi_m = \begin{cases} \frac{2}{\pi} \frac{\sqrt{V_m^2 - V^2}}{V_m^2}, & |V| \leq V_m, \\ 0, & |V| > V_m, \end{cases} \quad (\text{A2})$$

in order to consider spectroscopic broadening due to the finite sinusoidal modulation amplitude V_m , which likewise enters the fit as a fixed parameter. The sample DOS [Eq. (2)] is expressed via the functions ϱ_{LUMO} , ϱ_{ASR} , and α_{BTK} whose analytic expressions are defined in the following.

1. Density of states of the lowest unoccupied molecular orbital

To match the spectroscopic signature of the Ni-Pc LUMO on Pb(111), an asymmetric line profile is needed. Since in the present studies, tracing the LUMO energy and width is most important, an heuristic approach to the best matching profile is chosen. The extended asymmetric pseudo-Voigt line shape (f_{pV}), which is often used for the description of x-ray photoelectron spectroscopy data [59,60], proved optimal in this respect. It represents the linear combination of Gaussian (f_G) and Lorentzian (f_L) profiles of the form

$$f_{\text{pV}}(E) = (1 - \eta)f_G(E) + \eta f_L(E) \quad (\text{A3})$$

with $0 \leq \eta \leq 1$ and

$$f_G(E) = \sqrt{\frac{4 \ln(2)}{\pi \gamma(E)^2}} \exp \left[-\frac{4 \ln(2)}{\gamma(E)^2} (E - \varepsilon_{\text{LUMO}})^2 \right] \quad (\text{A4})$$

and

$$f_L(E) = \frac{1}{2\pi} \frac{\gamma(E)}{4(E - \varepsilon_{\text{LUMO}})^2 + \frac{\gamma(E)^2}{4}}. \quad (\text{A5})$$

The width $\gamma(E)$ of f_G and f_L is energy-dependent in order to appropriately match the asymmetry of the experimentally observed line shape. A sigmoidal form was previously suggested [60] and applied here. It reads

$$\gamma(E) = \frac{2\gamma_{\text{pV}}^{(0)}}{1 + \exp[-a(E - \varepsilon_{\text{LUMO}} - b)]} \quad (\text{A6})$$

with $\gamma_{\text{pV}}^{(0)}$ the FWHM of the symmetric pseudo-Voigt profile. The FWHM of the resulting extended asymmetric pseudo-Voigt profile, which is referred to as Γ_{LUMO} in the article, is obtained numerically [60].

2. The Abrikosov-Suhl resonance

The ASR in dI/dV spectra acquired with an STM was initially [63,64] described with a Fano profile [76], which was later adopted in many other studies of the single-atom or single-molecule Kondo effect [77,78]. The asymmetry of the Fano profile reflects the interference of electrons tunneling via the magnetic impurity and directly via the electron continuum of the substrate. In the work presented here, the Frota line shape [61,79] is used instead. The Frota profile matches very

well the ASR obtained from numerical renormalization group calculations [80]. Its analytical form reads

$$\varrho_{\text{ASR}}(E) = \text{Im} \left[i \exp(i\varphi) \sqrt{\frac{i\gamma_{\text{ASR}}}{E - \varepsilon_{\text{ASR}} + i\gamma_{\text{ASR}}}} \right], \quad (\text{A7})$$

where $E = eV$, $i^2 = -1$, φ is a form factor reflecting the asymmetry of ϱ_{ASR} , ε_{ASR} is the ASR energy, and γ_{ASR} is related to the FWHM (Γ_{ASR}) of the ASR according to $\gamma_{\text{ASR}} = \Gamma_{\text{ASR}}/5.084$. The Frota line shape was successfully used for describing the ASR of buried magnetic atoms [81,82], magnetic atoms adsorbed on dielectric films [83,84], as well as for molecules on noble-metal surfaces [85–88].

3. The Blonder-Tinkham-Klapwijk function

As introduced in the main article, the BTK model [12] describes AR for a one-dimensional NC-SC interface where $\alpha_{\text{BTK}} = 1 + A - B$ with A (B) the probability for retro-reflected (normally reflected) electrons. These probabilities read

$$A = \begin{cases} \frac{\Delta^2}{E^2 + (\Delta^2 - E^2)(1 + 2Z^2)^2} & (E < \Delta), \\ \frac{u^2 v^2}{\gamma_{\text{BTK}}^2} & (E > \Delta), \end{cases} \quad (\text{A8})$$

$$B = \begin{cases} \frac{1 - A}{(u^2 - v^2)^2 Z^2 (1 + Z^2)} & (E < \Delta), \\ \frac{\gamma_{\text{BTK}}^2}{\gamma_{\text{BTK}}^2} & (E > \Delta), \end{cases} \quad (\text{A9})$$

with 2Δ the width of the BCS energy gap,

$$u^2 = \frac{1}{2} \left(1 + \frac{\sqrt{E^2 - \Delta^2}}{E} \right), \quad (\text{A10})$$

$$v^2 = \frac{1}{2} \left(1 - \frac{\sqrt{E^2 - \Delta^2}}{E} \right) \quad (\text{A11})$$

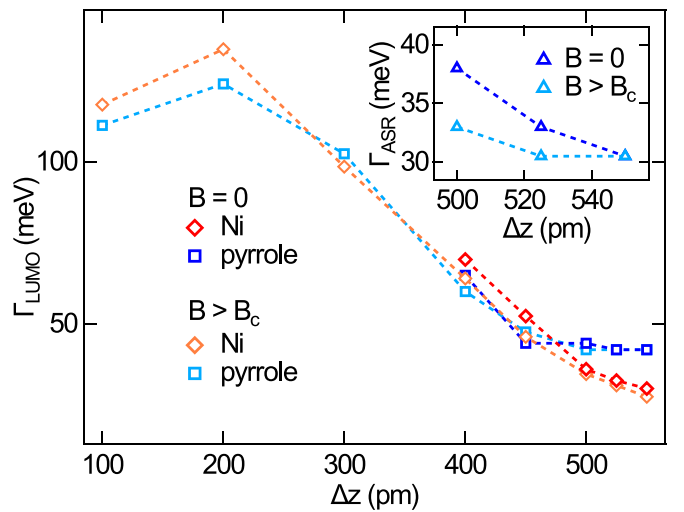


FIG. 7. Evolution of the FWHM of the LUMO at Ni (diamonds) and a pyrrole group (squares) with the tip displacement for $B = 0$ (dark symbols) and $B > B_c$ (light-colored symbols). Inset: variation of the FWHM of the ASR at a pyrrole group for $B = 0$ (dark triangles) and $B > B_c$ (light-colored triangles). Dashed lines connecting the data points in all plots are guides to the eye.

the probabilities for an unoccupied (u^2) and occupied ($v^2 = 1 - u^2$) Cooper pair, and

$$\gamma_{\text{BTK}}^2 = [u^2 + (u^2 - v^2)Z^2]^2, \quad (\text{A12})$$

where Z is related to the sought-after BTK transmission via $\tau = 1/(1 + Z^2)$.

The width of the BCS energy gap [inset to Fig. 2(a)] was obtained by solely using the Bogoliubov quasiparticle DOS for the sample DOS ϱ_s , i.e.,

$$\varrho_s(E) = \text{sgn}(E)\text{Re}\left[\frac{E - i\gamma_D}{\sqrt{(E - i\gamma_D)^2 - \Delta^2}}\right] \quad (\text{A13})$$

[$\text{sgn}(E) = \pm 1$ for $E > E_F$ (+) and $E < E_F$ (−), Re : real part, γ_D : Dynes parameter reflecting the finite quasiparticle lifetime [89]] and fitting the modulation-broadened numerical derivative of the resulting current I to experimental dI/dV data of the clean surface in the relevant voltage range. The resulting value of $\Delta = (1.1 \pm 0.1)$ meV is in good agreement with expectations [47] and kept fixed for subsequent fits.

APPENDIX B: VARIATION OF RESONANCE WIDTHS

Figure 7 summarizes the evolution of Γ_{LUMO} and Γ_{ASR} with the tip excursion. While Γ_{LUMO} strongly decreases from ≈ 130 meV to ≈ 30 meV in the tip excursion range of $200 \text{ pm} \leq \Delta z \leq 500 \text{ pm}$, the width of the ASR, which is exclusively present in the contact range ($\Delta z \geq 500 \text{ pm}$), exhibits a weak reduction from slightly below 40 meV to slightly above 30 meV. The reduction of Γ_{LUMO} with increasing Δz may partly be due to a lift of Ni-Pc from the surface induced by the attractive interaction with the tip. In addition, assigning to the LUMO the role of the Kondo impurity level, the narrowing of its line width with the orbital energy shift toward E_F is expected from theoretical grounds [74], where Γ_{LUMO} and Γ_{ASR} become comparable, which they do according to the data depicted in Fig. 7 and the inset. It is worth mentioning that the fit parameters of ϱ_{ASR} exhibit larger uncertainty margins for $B = 0$ than for $B > B_c$, which is supposedly due to the simultaneous presence of the ZBR due to AR. The fit of ϱ_{ASR} to the field-free data therefore solely relies on the tails of the ASR well apart from $V = 0$. As a consequence, the differences of ε_{ASR} [inset to Fig. 6(b)] and Γ_{ASR} (inset to Fig. 7) for $B = 0$ and $B > B_c$ are considered insignificant.

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