

Coexisting Spin, Vibrational, and Orbital Excitations in Conductance Spectra

Arnab Banerjee,^{1,*} Roberto Robles², Nicolás Lorente², Richard Berndt¹, and Alexander Weismann^{1,†}

¹*Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, 24098 Kiel, Germany*

²*Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU), 20018 Donostia-San Sebastián, Spain*



(Received 12 January 2026; accepted 30 July 2026; published 11 September 2026)

First-principles predictions of excitation energies and cross sections in inelastic tunneling spectroscopy are challenging, making it difficult to assign experimental features to specific excitations. There is, however, a need for a reliable identification of conductance features. We investigated the spin-1/2 molecule cobaltocene on superconducting Pb(110) and employ Yu-Shiba-Rusinov states combined with a superconducting tip to detect a large number of sharp spectral features. From an analysis of the peak heights at both bias voltage polarities along with model calculations and density-functional theory results we identify spin, vibrational, and orbital excitations that coexist within a single conductance spectrum. The peak height asymmetry turns out to be a useful indicator to determine the type of excitation.

DOI: 10.1103/mwl6-8nzi

Tunneling spectroscopy probes low-lying excitations of materials and provides access to spin and vibrational degrees of freedom with sub-meV energy resolution [1–8]. When superconducting electrodes are involved, spectroscopy benefits from the absence of thermal broadening as well as increased sensitivity and spectral resolution due to resonance enhancement [9–14]. The response of these excitations to external stimuli such as magnetic fields [15] or the presence of the scanning tunneling microscope (STM) tip [16,17] provides valuable insight into their origin. Because of their many-body nature, inelastic conductance features are not captured by mean-field approaches and not reflected in the local density of states obtained from density-functional theory (DFT). They may, however, be added through postprocessing using perturbation theory [18,19]. Conversely, single-particle spectral functions computed with many-body methods only contain inelastic contributions if the relevant degrees of freedom are explicitly included in the underlying model [20,21]. Furthermore, as the first-principles prediction of excitation energies and cross sections is challenging, assigning experimental features to specific excitations is particularly difficult when many excitations are resolved. The coexistence of different excitations, including orbital excitations, has been reported from strongly correlated materials through momentum-resolved resonant inelastic

x-ray scattering [22–25]. Orbital excitations have rarely been probed in real space with scanning tunneling spectroscopy [16,17].

Transition-metal complexes such as cobaltocene [Co(C₅H₅)₂, hereafter **Cc**; Fig. 1(a)], possess a partially filled Co 3*d* shell [3,26–32]. The degeneracy between the Co-*d*_{xz} and *d*_{yz} frontier orbitals [33], hosting one electron in total, is lifted due to Jahn-Teller distortion and coupling to the substrate [27,34,35]. In addition, intermolecular exchange was found to induce spin alignment within a honeycomb lattice [36].

Here, monolayer islands of **Cc** molecules are investigated on a superconducting Pb(110) surface using scanning tunneling spectroscopy with superconducting Pb tips. An unusually large number of spectral features is observed. Based on the spectral intensities and the influence of a magnetic field, we identify these features as being due to Yu-Shiba-Rusinov (YSR) states, and the excitations of vibrational, spin, and orbital degrees of freedom.

The experiments were carried out with an STM (UNISOKU USM-1300) at temperatures between $T = 1.6$ and 3.8 K in ultrahigh vacuum. STM tips were cut from Pb wire (0.25 mm diameter). The Pb(110) single crystal and the tips were cleaned by Ar-ion bombardment and annealing. **Cc** molecules (Sigma Aldrich) were deposited from a tantalum crucible at ambient temperature. For deposition, the sample was precooled in the STM, then kept on a manipulator at ambient temperature for a few minutes, and immediately transferred into the STM after deposition. The precise substrate temperature during deposition is unknown.

The deposition of a submonolayer amount of **Cc** onto the Pb(110) surface leads to the formation of **Cc** islands with monolayer height as shown in the constant current topograph in Fig. 1(b). The island's perimeter is disordered

*Contact author: banerjee@physik.uni-kiel.de

†Contact author: weismann@physik.uni-kiel.de

and appears slightly lower than the central area. This effect is presumably caused by **Cc** fragments or contaminants, similar to an earlier report on nickelocene on coinage metals [37]. In the ordered part of the island, a hexagonal arrangement of **Cc** molecules with a nearest neighbor distance of 570 pm is resolved [Fig. 1(c)]. Two edges of the hexagonal cell are parallel to the close-packed $[1\bar{1}0]$ substrate direction. The superstructure appears to be commensurate with the Pb surface lattice resolved in separate measurements (not shown) and may be denoted as (13×2) . A model of the superstructure is proposed in Supplemental Material (Fig. S1) [38]. Figure 1(d) shows differential conductance spectra (dI/dV ; I current, V sample voltage) from a narrow range around the Fermi level recorded on the substrate (gray) and a **Cc** molecule (blue). The substrate spectrum reproduces the characteristic coherence peaks of superconducting lead at $\approx \pm 2.7$ mV, whose shape is affected by the two-band nature of Pb superconductivity [51,52]. The molecular spectrum reveals two pairs of peaks at ± 2.7 and ± 3.0 mV. To quantify the different peak heights at negative (A^-) and positive (A^+) polarity, we define an asymmetry parameter $\chi = A^+/A^-$ [53]. Compared to the coherence peaks measured on the substrate, the 2.7 mV peaks on **Cc** are slightly shifted toward lower energies and exhibit an asymmetry $\chi \approx 0.8$. We assign these features to YSR resonances, similar to previous observations on many molecules [54]. In contrast, the peaks near ± 3.0 mV have almost identical heights ($\chi \approx 1$), and are outside the superconducting energy gap, indicating inelastic tunneling processes [14]. Notably, these spectral signatures are found exclusively in molecules within islands, but not in isolated molecules (Supplemental Material, Fig. S2 [38]).

Figure 2 shows dI/dV spectra of **Cc** measured slightly displaced from the top of the molecular contrast, covering a wider voltage range. The blue curve was measured using a superconducting tip and substrate, whereas the red curve was obtained after suppressing superconductivity with a 1 T magnetic field. The most intense structures in the zero-field spectrum are the double peaks near ± 3 mV discussed earlier, which are better resolved in Fig. 1(d). Furthermore, bulk phonon modes of Pb give rise to a broad conductance decrease at $\approx \pm 6$ mV. In addition, the spectrum exhibits 14 sharp features marked by vertical lines and arrows. The spectrum acquired with a normal-conducting tip and substrate (red) shows a pronounced zero-bias dip flanked by two peaks ($\uparrow$, upper right inset of Fig. 2) and steplike features appearing symmetrically at higher positive and negative voltages.

To categorize the spectral features, we determined their asymmetries χ (Table I). On the superconducting substrate, most peaks (marked by $\downarrow$) exhibit $\chi \lesssim 1$, similar to the YSR peaks. These peaks resemble replicas of the YSR states shifted by the inelastic excitation energy [9]. In two cases (marked by $\uparrow$ and $\downarrow$), however, χ strongly exceeds 1, with

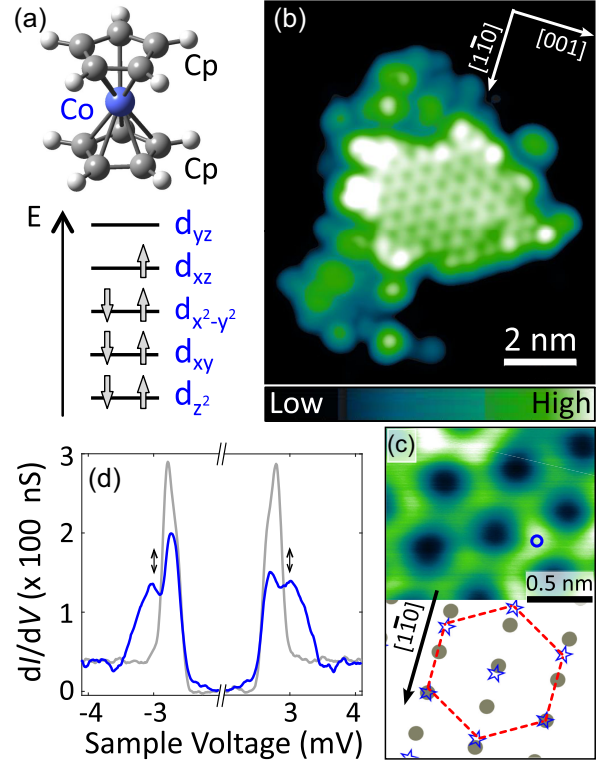


FIG. 1. (a) Eclipsed conformer of free **Cc** with two parallel cyclopentadienyl (Cp) moieties (gray, carbon; white, hydrogen) sandwiching a cobalt ion (blue) along with a scheme of the Co 3d orbitals. The ligand field leads to a $S = 1/2$ ground state of **Cc** in gas phase. (b) Topograph ($V = 80$ mV) of a **Cc** island. Arrows indicate high-symmetry directions. (c) Magnified view of the island interior ($V = 50$ mV) with proposed hexagonal arrangement of **Cc** molecules (blue stars) on the Pb surface atoms (gray dots). The color scales span 560 and 22 pm in panels (b) and (c), respectively. (d) dI/dV spectra of Pb(110) (gray line) and **Cc** (blue line) acquired over the location marked by the blue circle in (c). While the substrate spectrum exhibits coherence peaks marginally above ± 2.7 mV, the molecular spectrum consists of YSR resonances at ± 2.7 mV and additional peaks at ± 3 mV. The bias range between ± 2 mV (not shown) was featureless. For spectroscopy (1.6 K), the tip was stabilized at $V = 6$ mV and $I = 200$ pA and a voltage modulation of $60 \mu\text{V}_{\text{pp}}$ was applied.

larger conductance changes at positive voltages. Apparently, these excitations are more likely to be excited by electron injection than by extraction. The energy of the excitation near 10 mV varies between neighboring molecules (Supplemental Material, Fig. S4 [38]), with the feature marked by $\downarrow$ (upper right inset of Fig. 2) arising from an adjacent molecule. On normal-conducting Pb (red curves in Fig. 2), the asymmetries of the features marked by $\uparrow$ and $\downarrow$ persist, while the remaining inelastic features ($\downarrow$) become symmetric ($\chi \approx 1$) as the YSR resonances vanish. Below, we attribute these differences to different excitation mechanisms.

We first address the presence of the YSR state. From our DFT calculations of **Cc** on Pb(110) (Supplemental Material, Fig. S5 [38]) we find that the gas-phase electronic

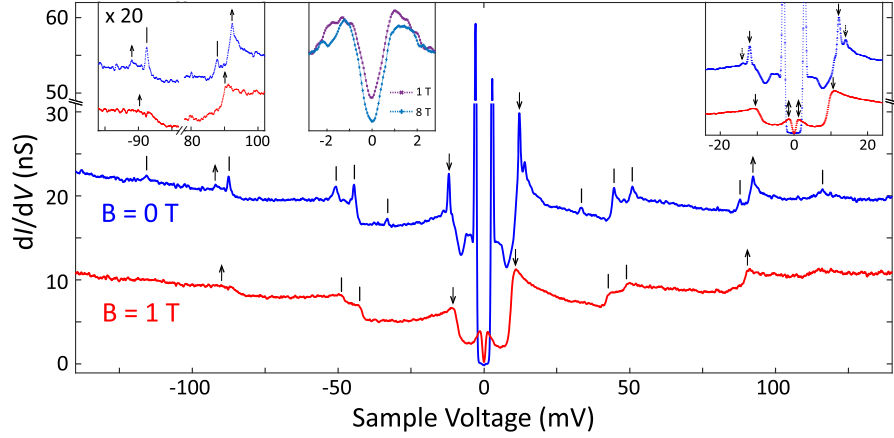


FIG. 2. Wide-range dI/dV spectra of **Cc** measured without (blue lines) and with (red lines) a magnetic field $B = 1$ T perpendicular to the substrate surface. The red spectrum was shifted downward by 10 nS for clarity. Vertical markers indicate vibrational ($|$), orbital ($\uparrow$, $\downarrow$, $\downarrow\downarrow$), and spin flip ($\uparrow\downarrow$) excitations, respectively. The top right and left inset shows spectra within ± 25 mV and for $78 \text{ mV} \leq |V| \leq 102 \text{ mV}$, respectively. The middle inset shows the spectra within ± 2.8 mV under magnetic field 1 T (violet) and 8 T (blue). For spectroscopy (1.6 K), the tip position was frozen at $I = 4$ nA and $V = 205$ mV and a voltage modulation of $500 \mu\text{V}_{\text{pp}}$ was used.

structure shown in Fig. 1(a) is preserved. The d_{xz} orbital is singly occupied, thereby inducing a localized spin $S = 1/2$ in **Cc** and leading to YSR states. The close proximity of the YSR states to the superconducting gap edge (YSR energy $E_{\text{YSR}} \approx 1.34$ meV) reflects a weak exchange interaction between **Cc** and the substrate electrons [55].

We attribute the 10 peaks marked by $|$ in Fig. 2 to five vibrational excitations [9]. In the superconducting case, the YSR states are the predominant final states for inelastic tunneling. Consequently, the associated inelastic spectral features exhibit a peak-height asymmetry that reflects that of the YSR resonances ($\chi_{\text{YSR}} = 0.8$). Based on this criterion, the excitation energies 30.7, 41.8, 48.1, 85.0, and 113.4 mV are attributed to molecular vibrations. The

individual asymmetries match χ_{YSR} quite well, while the small deviations are likely caused by difficulties in accurately determining the background conductance in the presence of nearby inelastic features.

The identification of vibrational excitations is corroborated by the fact that χ approaches unity when the superconductivity is suppressed. In this case, the inelastic signatures are replicas of the substrate's Fermi edge. The lack of YSR-state-mediated enhancement renders the less intense modes at $|V| = 30.7, 85.0$, and 113.4 mV insufficiently resolved to determine χ when superconductivity is suppressed. The symmetry-based origin of the restricted set of observable molecular vibrations is discussed in Supplemental Material [38].

Next, we analyze the peaks at ± 3.0 mV [Fig. 1(d) and top right inset to Fig. 2, indicated by $\uparrow\downarrow$]. Their heights are comparable to those of the YSR resonances, in contrast to the less intense vibrational peaks. Such a large inelastic cross section is indicative of spin excitations [14,56]. In addition, χ is close to one, with and without magnetic field, as expected for a spin-flip excitation (SFE) with a spin-unpolarized tip [46,57]. To further test the magnetic origin, spectra were recorded at fields up to 8 T (middle inset of Fig. 2) and fitted using a model based on third order perturbation theory (Supplemental Material, Fig. S6 [38]) [46]. Starting from an excitation energy of $\approx 250 \mu\text{V}$ at 1 T, the data surprisingly show a shift far smaller than the Zeeman splitting expected for $S = 1/2$, reaching $\approx 320 \mu\text{V}$ at 8 T. However, such a behavior is reproduced by a model assuming antiferromagnetic coupling between neighboring molecules (details in Supplemental Material, Fig. S7 [38]), which is also energetically favored in our DFT calculations (Supplemental Material, Fig. S5).

Finally, we consider the peaks with large asymmetries (marked by $\downarrow$, $\downarrow\downarrow$ and $\uparrow$ in Fig. 2), which significantly

TABLE I. Energies and asymmetries of molecular excitations with and without magnetic field. SFE, spin-flip excitation; VIB, vibrational mode; OE, orbital excitation; DOE, orbital excitation involving doubly occupied states; —, insufficiently resolved modes under B field. Excitation energies at 0 T are determined from the voltage differences between the spectral features and the YSR resonances.

Energy (meV)	$\chi = A^+/A^-$		Type	Symbol
	at 0 T	at 1 T		
0.3	1.01	0.99	SFE	$\uparrow\downarrow$
9.4	1.95	2.1	OE	$\downarrow$
(11.0)	2.21	—	OE	$\downarrow\downarrow$
30.7	0.79	—	VIB	$ $
41.8	0.77	0.98	VIB	$ $
48.1	0.92	1.0	VIB	$ $
85.0	0.61	—	VIB	$ $
89.5	5.69	4.89	DOE	$\uparrow$
113.4	0.98	—	VIB	$ $

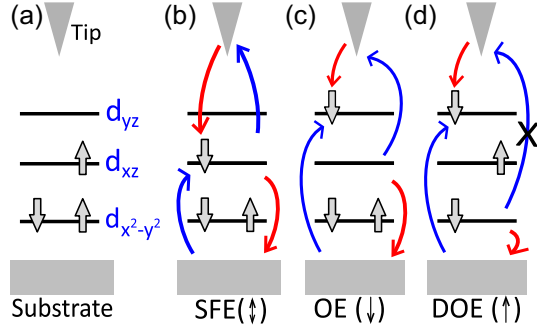


FIG. 3. Schematic illustration of excitation processes (curved arrows) involving three Co d states (horizontal lines). Red and blue arrows indicate electron injection ($V > 0$) from the tip and extraction ($V < 0$) of electrons from the substrate. (a) Initial state. (b) Spin-flip excitation (SFE). (c) Orbital excitation (OE) involving a partially occupied d orbital. (d) Orbital excitations involving a doubly occupied Cc orbital (DOE). The cross symbol indicates that tunneling from this state to the tip is suppressed.

deviate from χ_{YSR} . For both normal and superconducting electrodes, the conductance changes are approximately twofold (9.4 mV) and fivefold (89.5 mV) larger at positive sample voltage.

Figure 3 displays a heuristic model of excitation pathways that are consistent with the observed asymmetry, representing processes involving a virtual propagation of d electrons through a charge-excited state. Panel (a) shows the initial state with the tip, the substrate, and three Co d levels. Two further fully occupied levels have been omitted for simplicity. The subsequent panels (b)–(d) present final states. At positive sample voltage (red arrows), an SFE [panel (b)] is achieved by injecting a spin-down electron from the tip while the spin-up electron from d_{xz} level moves to the substrate. At negative bias (blue arrows), the same excitation occurs when the spin-up electron from level d_{xz} is extracted by the tip and replaced by a spin-down electron from the substrate. When the tip and the substrate are not spin-polarized, the probabilities of both processes are similar. Panel (c) displays an orbital excitation (OE) process involving the d_{xz} and d_{yz} orbitals. At negative bias (blue arrow), extracting the d_{xz} electron with the tip induces a reoccupation of d_{yz} by a substrate electron of either spin. At positive bias, two injection pathways into the empty d_{yz} orbital trigger the excitation that releases the initial d_{xz} electron to the substrate. This accounts for the approximately twofold larger amplitude near 10 mV at positive polarity.

An orbital excitation with $\chi \gg 1$ is consistent with a doubly occupied orbital that couples to the substrate but only weakly to the tip [Fig. 3(d)]. As the $d_{x^2-y^2}$ orbital is singly occupied in the final state, excitation at negative bias is suppressed because tunneling from this level to the tip is unlikely. In contrast, electron injection from the tip into the d_{yz} orbital at positive bias and subsequent electron escape

from $d_{x^2-y^2}$ orbital to the substrate are both favorable. In this case, very large values of χ may be expected.

Next we analyze the transitions leading to the inelastic signatures near 9.4 and 89.5 meV. Excitations between different d -orbital configurations of identical occupation number are not represented by Kohn-Sham energies, which describe single-particle charge excitations. Such rearrangements are intrinsically multiconfigurational and require advanced quantum-chemical methods. We therefore employed time-dependent DFT (TDDFT) as implemented in *Gaussian* [47] using the LanL2DZ basis set and B3LYP exchange correlation functional [58] to estimate the relevant excitation processes and energies for a gas-phase Cc molecule. These calculations serve to reveal the orbitals involved in the lowest excitations that leave the electron number unchanged along with their spatial accessibility.

TDDFT predicts that the lowest-energy excitation promotes a majority-spin electron from d_{xz} to d_{yz} . Both orbitals are strongly hybridized with the Cp ligand and contain a large admixture (65.1% and 49.9%, respectively) of π states (Supplemental Material, Fig. S10 [38]). The next higher excitation promotes a minority-spin electron from a doubly occupied state of predominantly Co $d_{x^2-y^2}$ and d_{z^2} character and only weak π admixture (11.9%) to the d_{yz} orbital. The corresponding excitation energies varied during structural optimization, i.e., for slightly different molecular geometries, ranging from 37–316 meV for the first and 0.35–1.06 eV for the second excitation. These values are significantly lower than the differences between the Kohn-Sham energies of the involved orbitals. The lowest excitation is particularly sensitive to the Jahn-Teller distortion, which is expected to differ between the gas phase and the adsorbed molecules. Furthermore, the energies of different d -level configurations are strongly affected by the intraorbital Coulomb interaction, which is screened by the substrate and only incompletely captured by gas-phase TDDFT. Although the gas-phase excitation energies should be regarded as estimates, the TDDFT calculations confirm that the lowest excitation involves orbitals with substantial π -electron character that are accessible to the STM tip, whereas the second excitation involves the more localized $d_{x^2-y^2}$ orbital.

Further support for our assignment of the 10-mV feature to an orbital-flip excitation between the d_{xz} and d_{yz} states may be obtained from maps of the differential conductance dI/dV measured at $V = 2.55$ and 10.0 mV [Figs. 4(a) and 4(b)]. These voltages correspond to the YSR state and the lowest orbital excitation, respectively. By comparison with a topograph of the same area [Fig. 4(c)], we find that the spatial distributions of the YSR state and the orbital excitation of each molecule (example highlighted by yellow contours) are orthogonal to each other. The partially occupied Co d_{xz} orbital induces the YSR states, while the d_{yz} orbital is involved in tunneling processes that lead to the lowest orbital excitation [Fig. 3(c)]. This is consistent with

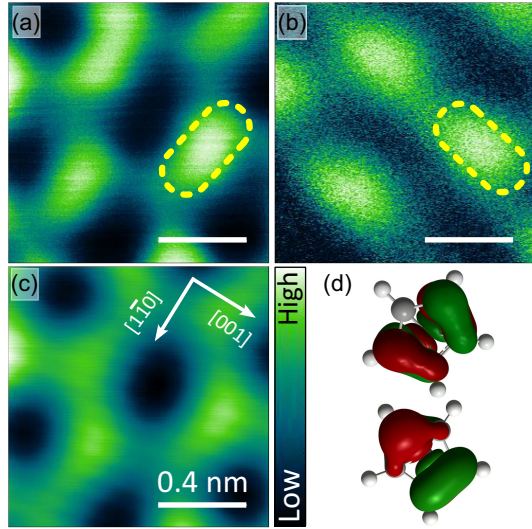


FIG. 4. Differential conductance maps of **Cc** molecules measured at (a) 2.55 and (b) 10 mV. (c) Topograph of the same area ($V = 20$ mV, $I = 50$ pA at 3.8 K). Scale bars indicate 0.4 nm. (d) Wave function isosurfaces of **Cc** molecular orbitals, labeled according to the d states, d_{yz} (top) and d_{xz} (bottom), that contribute to the orbital excitations and the YSR states, respectively.

the calculated spatial distribution of the relevant wave functions [Fig. 4(d)].

In conclusion, we observed the coexistence of spin, vibrational, and orbital excitations in tunneling spectra of cobaltocene molecules on Pb(110). We show that the peak-height asymmetries of the spectral features reflect the excitation processes. The coexistence of spin and orbital degrees of freedom—each independently tunable by magnetic and electric fields—may enable the realization of an entangled two-qubit system within a single molecule.

Acknowledgments—A. B. acknowledges support by Kiel Nano, Surface and Interface Science (KiNSIS). R. R. and N. L. are grateful for financial support from Project No. PID2021-127917NB-I00 funded by MCIN/AEI/10.13039/501100011033, from Project No. IT-1527-22 funded by the Basque Government, and from Project No. ESiM 101046364 funded by the European Union.

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.

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