Disentangling the electronic structure of an adsorbed graphene nanoring by scanning tunneling microscopy

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Graphene nanorings are promising model structures to realize persistent ring currents and Aharonov-Bohm effect at the single molecular level. To investigate such intriguing effects, precise molecular characterization is crucial. Here, we combine low-temperature scanning tunneling imaging and spectroscopy with CO functionalized tips and algorithmic data analysis to investigate the electronic structure of the molecular cycloarene C108 (graphene nanoring) adsorbed on a Au(111) surface. We demonstrate that CO functionalized tips enhance the visibility of molecular resonances, both in differential conductance spectra and in real-space topographic images. Comparing our experimental data with ab-initio density functional theory reveals a remarkably precise agreement of the molecular orbitals and enables us to disentangle close-lying molecular states only separated by 50 meV at an energy of 2 eV below the Fermi level. We propose this combination of techniques as a promising new route for a precise electronic characterization of complex molecules and other physical properties which have electronic resonances in the tip-sample junction.

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Molecular adsorbates are characterized by electronic resonances that can be spectroscopically detected. Scanning tunneling microscopy (STM) with its submolecular imaging resolution and its ability to probe the local density of states (LDOS) by recording the differential conductance $dI/dV$ spectra yields spatially resolved images of molecular states. Since scanning tunneling spectroscopy (STS) can access occupied as well as unoccupied molecular states, it has become a valuable tool to unveil the electronic structure of molecular adsorbates.

So far, the spatial mapping of molecular resonances has been conducted mostly in the following way: The tunneling bias of the junction is set to the energy value at which the resonance occurs and, while the molecule is scanned by the STM tip, the $dI/dV$ signal is recorded. Such scanning procedure can be performed in two distinct modes: constant-height or constant-current. The obtained $dI/dV$ map is commonly interpreted as a two-dimensional visualization of the molecular state. This approach has been successfully employed to molecular systems on which electronic resonances are well-separated from each other and in many cases decoupled from the metallic substrate by ultrathin insulators, revealing a clear correspondence between calculated molecular orbitals and the measured electronic resonances. However, for the cases when the molecular resonance spectrum is denser and the detected electronic resonances have contributions from different molecular states, the interpretation of the $dI/dV$ data becomes a difficult problem which has in general not been solved yet.

In this work, we use a graphene nanoring, the cycloarene C108 adsorbed on Au(111), as a model system. Cycloarenes are considered as ideal test cases for studying electron delocalization in extended aromatic systems. The C108 possesses a rich energy spectrum in which several molecular states are only separated in energy by a few meV, making it particularly interesting for disentangling the contributions from the different molecular orbitals in the STM images.

To access, map and have a complete understanding of the C108 electronic structure, we use an approach that aims to overcome the limitation of common $dI/dV$ imaging. For that, we combine CO functionalized tips, shown to provide sub-molecular resolution particularly on sp$^2$-hybridized carbon nanostructures as well as sub-atomic resolution of metal clusters and metal adatoms, with feature-detection scanning tunneling spectroscopy (FD-STS), a statistical analysis tool that allows the unbiased detection of electronic resonances. We find that this combination enables us to classify, resolve and separate orbitals lying close in energy, providing experimental information on the electronic structure of a cycloarene in unprecedented detail.

**Results and Discussion**

**Synthesis of Cycloarene C108 on Au(111).** We synthesize the cycloarene C108 on a Au(111) surface via Ullmann coupling followed by cyclohydrogenation of a bromoarene precursor containing 9 phenyl moieties ($5''''$-(1,1'-biphenyl)-2-yl)–$5''''$-dibromo-1,1'-2,1'''-3,1''''-3,1''''''-3,1''''''''-2-yl)-septiphenyl (DBSP) (Fig. 1a–c). The first step, on-surface Ullmann coupling, leads to the cyclodimerization of the precursor into a nonplanar macrocycle, which subsequently forms C108. This new on-surface cyclodimerization reaction is more efficient than the on-surface cyclotrimerization used in previous work for the first synthesis of C108. Details of the C108 precursor synthesis can be found in Supplementary Note 1 in the supplementary information.

**STM and STS Characterization.** We image C108 at a base temperature of 10 K using a tungsten tip functionalized with a single CO molecule (CO tip), enabling sub-molecular resolution of the geometrical structure (Fig. 1d). Using the same tip, we also perform $dI/dV$ spectroscopy revealing several electronic resonances in the energy range between $-2$ eV and $+2$ eV around the Fermi energy $E_F$ (Fig. 1e). The CO tip impacts the measured images and spectra compared to a bare metallic s-wave tip in two
ways: first, at biases close to $E_p$, it allows to achieve structural submolecular resolution, similar to previous reports, and, second, it enhances significantly the intensity of the electronic resonances. We identify the four main features as positive (PIR) and negative ion resonances (NIR) (orange dots in Fig. 1e). Compared to previously published results, with the increased resolution of the CO tip, we additionally identify four secondary features shifted by ~150 mV from the main features to higher absolute bias (green dots in Fig. 1e).

Density functional calculations. To understand the origin of the resonances, we perform density functional theory (DFT) calculations that use the B3LYP hybrid functional to calculate the density of states (DOS). From the gas-phase DFT calculation (Fig. 2a, b) and by comparing with a representative $d/dV$ spectra, we compute the lock-in detection, which limits the energy resolution. Therefore, the good agreement between theory and experiment, we must consider the electronic broadening due to the bias modulation $V_{\text{mod}} = 20$ mV (peak to peak) used for the lock-in detection, which limits the energy resolution. Therefore, we compare $|V_{\text{mod}} \frac{d \Psi}{d \Omega} |^2$ with $\nabla r$, as the in-plane gradient and $\Psi(r)$ as the DFT-calculated wavefunction and sum up those molecular orbitals, which lie within the broadening range of the detection method (Fig. 3a–c). The computed p-wave images and the measured constant current $d/dV$ maps match very well. The good agreement between theory (Fig. 3a–c) and experiment (Fig. 3d–f) stems from a low hybridization between the C108 and the metallic surface and the energetically well-separated resonances, so that the constant current $d/dV$ maps do not capture contributions from other states, avoiding intermixing. We note however, that the slight

**Fig. 2** DFT-calculated DOS and molecular orbital energy levels of the cycloarene C108. a) Simulated DOS of C108 in the gas phase (black curve). b) Energetic positions of the gas-phase orbitals as found in the DFT calculation (black dots), overlaid with typical experimental $d/dV$ spectra, red and gray, taken at the positions of the red and gray dots, respectively, in Fig. 1d. Spectroscopy parameters prior to opening the feedback: $V = 200$ mV, $I = 80$ pA, $V_{\text{mod}} = 20$ mV. In both graphs, the region between $-0.8$ V and 1.2 V is omitted for a better visualization of the resonances.

**Fig. 3** Calculated gas-phase p-wave molecular orbitals and constant-current $d/dV$ maps of C108 obtained with a CO tip. a–c Visualization of the molecular wavefunctions as calculated by DFT using a p-wave tip at the resonance energies $V_{\text{PIR2}} = -1.52$ V, $V_{\text{PIR1}} = -1.06$ V, and $V_{\text{NIR}} = 1.8$ V.

d–f Constant-current $d/dV$ maps performed with CO tip at the bias voltages $V_{\text{PIR2}} = -1.47$ V, $V_{\text{PIR1}} = -1.05$ V, and $V_{\text{NIR}} = 2$ V, and current setpoints of $I_{\text{PIR2}} = 5$ nA, $I_{\text{PIR1}} = 3$ nA and $I_{\text{NIR}} = 50$ nA, $V_{\text{mod}} = 10$ mV. Image sizes are $2.5 \times 2.5$ nm².
deformation of the $dI/dV$ maps at the rim of the molecule might stem from a deflection of the CO at the apex of the tip\textsuperscript{22}.

Remarkably, we find that the obtained constant current $dI/dV$ maps of PIR\textsubscript{1} and NIR (Fig. 3e, f) look very different compared to the constant height $dI/dV$ maps obtained by Fan et al. at presumably significantly larger tip-sample separation\textsuperscript{11}. These differences are due to the CO tip’s p-wave character at low tunneling resistances, i.e., small tip-sample separations, which is sensitive to the nodal planes of the molecular wavefunction\textsuperscript{23}. The metallic s-wave character of the CO tip can be recovered by increasing the tip-sample distance and therefore the tunneling resistance on which the s-wave character predominates over the faster decaying p-wave character\textsuperscript{24} (Supplementary Fig. 1).

We continue by investigating PIR\textsubscript{3} which has contributions from H\textsubscript{−5} and H\textsubscript{−6}. Because in this case H\textsubscript{−5} and H\textsubscript{−6} are separated by an energy difference of 55 meV, slightly higher than the modulation voltage, we compute p-wave images of the molecular orbitals for H\textsubscript{−5} and H\textsubscript{−6} separately (Fig. 4a, b) as well as for the sum of H\textsubscript{−5} and H\textsubscript{−6} (Fig. 4c). Comparing with the constant current $dI/dV$ image, we find that it resembles more the sum of the two orbitals (Fig. 4d). Apparently, we see here the limit of constant current $dI/dV$ map which do not allow to discern between two energetically neighboring molecular orbitals.

**Feature detection scanning tunneling spectroscopy method.**

Until here, we have only explored the traditional way of how electronic properties of molecules have been characterized by STM. Now, we would like to utilize a method which gives a more complete picture of the molecular electronic properties even at larger tip-sample separations where the high resolution of the CO tip is no longer predominant.

For this purpose, we measure $dI/dV$ spectra on a grid of $64 \times 64$ points covering an area of $2.4 \times 2.4 \text{ nm}^2$ centered on an isolated C108 molecule with the CO tip. At each grid point, we regulate the tip height prior to opening the feedback loop to a tunneling current of $I = 80 \text{ pA}$ at a bias of $V = 200 \text{ mV}$. The bias lies inside the energy gap between PIR and NIR to avoid the influence of molecular orbitals on the tip height and thus the resulting spectroscopic intensities. We then analyze the corresponding matrix of spectra using a recently developed FD-STS algorithm\textsuperscript{17}.

The feature detection enables one to find and classify spectral features in a large set of individual $dI/dV$ spectra. This method circumvents the necessity of using a model describing the physical processes and its subsequent time-consuming least-square fits. Because we are mainly interested in finding molecular states which are smeared out by hybridization with the substrate and by thermal broadening, the task is to detect broadened peaks on an unknown background (see the methods section for more details of the peak detection procedure).

To each detected peak in the raw $dI/dV$ signal, we assign a weight $W$ by finding the next lying extrema in the derivative of the signal, i.e., the second derivative $d^2I/dV^2$ (Fig. 5a). Note that even though $W$ is not identical to the peak intensity in $dI/dV$, it is a measure commonly used, for instance, in Auger and ESR spectroscopy. By adjusting a threshold $W_\text{c}$, we disregard spurious noise peaks as well as peaks clearly originating from the substrate only (Fig. 5b).

The statistical evaluation of the features detected by FD-STS allows us to plot the (weighted) occurrence center energies $E_p$ of the detected peaks in a certain energy range across the grid in an energy distribution histogram (EDH) (Fig. 5c), or to explicitly map the (weighted) occurrence of spectroscopic features in a feature distribution map (FDM). Finally, it is possible to map the

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**Fig. 4 Calculated gas-phase p-wave molecular orbitals and constant-current $dI/dV$ maps of C108 obtained with a CO tip of PIR\textsubscript{3}.** a, b Visualization of the molecular wavefunctions as calculated by DFT using a p-wave tip of H\textsubscript{−5} and H\textsubscript{−6} (Supplementary Fig. 1). c Constant-current $dI/dV$ map performed with CO tip at the bias voltage $V_{\text{mod}} = 1.95 \text{ V}$ and current setpoint of $I_{\text{mod}} = 40 \text{ nA}$, with $V_{\text{mod}} = 10 \text{ mV}$. Image sizes are $2.5 \times 2.5 \text{ nm}^2$.

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\textsuperscript{17}Fan et al. (2015) J. Phys. Chem. C 119, 20423–20429.
energy position of a given feature, yielding an energy distribution map (EDM).

Energy of the molecular states. We start our analysis by normalizing each individual spectrum to the intensity sum of the 3 PIRs that are the result of occupied molecular orbitals in the C108. This normalization compensates for the different tunneling probabilities occurring at different locations on the C108 (red and gray curves in Fig. 2b) assuming an approximately constant total electron density within the spatial extension of the molecule. By applying the FD-STS algorithm, we are able to detect the center of the peaks in each spectrum. The EDH in Fig. 6a reflects the PIR and NIR main energies and intensities (red in Fig. 6a) as well as a series of side peaks (cyan in Fig. 6a) separated by bias voltages ranging from 140 to 210 meV.

As we will show, FDMs and EDMs are particularly useful for the classification and visualization of molecular orbitals that are very close in energy and are present in different regions of the molecule. In combination with the enhanced spatial resolution of the CO tip’s p-wave nature,23,25 this results in better understanding of the electronic structure than conventional dI/dV maps.

We start by selecting the energy range of the EDH that will be used for the FDM and EDMs (yellow boxes in Fig. 6b–d). The sharpness of the selected peaks suggests that only a single resonance is contributing, despite originating from the contributions of more than one molecular orbital. The produced EDMs use a linear scale to visualize the energy distribution of the selected resonance over the previously defined energy range (Fig. 6e–g). Additionally, the EDMs confirm that the resonances are energetically monodisperse varying approximately only by the energy of the modulation broadening within the molecule. In other words, we do not observe different resonances merged to a larger resonance. Unlike in previous work,17 for the FDMs we plot the intensity at the center of each detected peak of the normalized dI/dV (Fig. 6h–j). We notice that even by adjusting $W_c$ to zero, i.e., no filtering any peak attributed to spurious noise, or by using different window widths we obtain qualitatively the same EDH and FDM with the caveat of being noisier (Supplementary Figs. 2, 3).

Next, we proceed to relate the spatial distribution of the detected features with FD-STS to molecular orbitals. In contrast to Figs. 3 and 4, we consider here an equal contribution of s and a p-wave orbitals from the CO tip due to the increased tip-sample distance at the higher tunneling setpoint $R = 2.5$ GΩ. The FDMs reproduce the main features of the calculated s + p wave images (Fig. 6). For instance, the FDM obtained for PIR1 (Fig. 6i) shows lobes situated at the corners of the C108 molecule, in agreement with the corresponding DFT calculations (Fig. 6l).

We note that the molecular resonances decay in their intensity as the tip moves towards the inner part of the ring either in the constant-current dI/dV maps or in the normalized spectra used for the FDM. This effect can be compensated by decreasing the tip-sample distance as shown in Figs. 3 and 4. However, often this is not feasible due to the fragility of adsorbed molecules. This reveals the limits of not only our approach but also to similar experiments conducted on many different molecular systems probed both with metallic s-wave8,26 and CO tips27, in which the molecular states are observed extending beyond the rim of the molecular structure, while the interior of the molecule tends to be electronically transparent. We observe in Fig. 6 that at larger absolute bias voltages (i.e., larger tunneling barriers) the FDMs tend to concentrate the features closer to the periphery of the molecule.

Remarkably, and contrary to the DFT calculation, the FDM as well as constant-current dI/dV maps (Figs. 3, 4 and Fig. 6) show an increased intensity in the central hole of the C108 nanoring. In this position, the tip is placed above the Au(111) surface, which is why we attribute the detection of these electronic resonances to a closer tip-sample distance caused by the directional sharper CO tip that is able to pick up the tails of electronic contributions from the molecular orbitals. On the contrary, such intensity in the center of
the C108 molecule is not observed when the same set of measurements is performed with a metallic s-wave tip (Supplementary Fig. 4) due to its relative bluntness compared to a CO tip.

**Vibronic replicas.** We now focus on the side peaks separated by bias voltages ranging from 140 to 210 meV from the main peaks. We attribute these peaks to vibronic replica28–30 of the C108 electronic states. This conjecture is supported by a calculation of the vibrational spectrum based on a finite-difference approach at DFT-PBE level; the observed vibronic replica stem most likely from a family of vibrational modes found at frequencies ranging from 1100 to 1600 cm$^{-1}$ (Supplementary Fig. 5), equivalent to 140 to 200 meV.

A close inspection of the vibrational replica (Supplementary Fig. 6) reveals a substantial broadening of the EDH compared to the main peak, understood in terms of the symmetry dependence of the vibration assisted tunneling31. Additionally, by analyzing the resulting FDMs in Supplementary Fig. 6, we observe that the maps reproduce qualitatively the main resonance to which it belongs, confirming that these peaks are the result of vibrational replicas.

**Disentanglement of nearby molecular orbitals.** Finally, we focus on the PIR$_3$. In contrast to the maps of Fig. 6e–g, the EDM shows a resonance that is composed of two separable regions with slightly different energies: Yellow/green areas with higher peak energy and red/orange areas with lower peak energy (Fig. 7a). A closer look at the EDH reveals that a peak which appears to be monodisperse at first glance is a composition of two separate peaks whose energetic centers are located at $-2.00$ and $-1.95$ V (Fig. 7b). The strong additional maximum in between the two peaks is an artifact of the FD-STS algorithm: if none of the two resonances is dominant, the superposition of both will result in an apparent single peak close to the intermediate energy, artificially creating an extra peak in the histogram. Remarkably, our DFT calculations predict two non-degenerate molecular orbitals (H$_{-5}$ and H$_{-6}$) at approximately $-2$ eV with a separation of only 55 meV (Fig. 7e, f).

To separate these two orbitals, we now fit this part of the dI/dV spectra with a sum of two Lorentzians with fixed energies at $-1.95$ and $-2.00$ eV as determined by the EDH. The resulting intensity maps (Fig. 7c, d) are in remarkable agreement with the DFT calculations (Fig. 7e, f), showing the potential of FD-STS to...
identify energetically overlapping molecular orbitals that can be separated to obtain a reliable image of the molecular orbitals in contrast to constant-current dI/dV maps showing contributions of both molecular orbitals (Fig. 4d).

Since also NIR contains two orbitals, we follow the same procedure. In this case, the resonance is the contribution of \( L_0 \) and the degenerate \( L_{1+1} \) and \( L_{1-2} \) with an energy difference of 90 meV (Fig. 2b). We fix Lorentzian centers at an energy of 1.84 and 1.98 V, corresponding to the positions on which the central peak and the peak shoulders are found (Fig. 1b). In contrast to Fig. 7, however, we do not observe any significant difference in their intensities (Supplementary Fig. 7) in agreement with the EDH (Fig. 6d), that only shows a single peak. We relate this to the lack of differences in the wavefunction intensities between the \( L_0 \) and the degenerate \( L_{1+1} \) and \( L_{1-2} \).

### Conclusion

We have shown that the combination of a CO tip and FD-STS is a powerful tool to identify, classify and map the molecular states of the cycloarene C108 in good agreement with theoretical calculations. With this combination, we reach a level of detail in the understanding of the molecule's electronic properties that is neither achievable by constant-current dI/dV maps nor by using a metallic tip and applying FD-STS alone. In particular, our method shows its potential by experimentally identifying and disentangling the closely lying molecular states at -2 V only separated by an energy difference of 50 mV. We note that this method could also be applied to systems on which different types of electronic excitations are observed, e.g., superconductivity, spin excitations or to molecular systems such as those incorporating transition metals or rare earth atoms, on which theoretical calculations are limited due to their complexity. Furthermore, we expect that the methodology presented here will make the studies of the complex electronic structure of larger nanostructures more efficient. In the case of C108, the unambiguous identification of molecular resonances may help in future experiments exploring the intriguing effects of high magnetic fields such as persistent ring currents and the Aharonov–Bohm effect.

### Methods

**Feature-detection algorithm.** We implement the feature-detection method in the following way: The spectra containing the bare signal \( S \) are in our case dI/dV spectra obtained by modulating the swept bias voltage \( V \) with a small sinusoidal modulation voltage \( V_{mod} = 20 \text{ mV} \) (peak to peak) and recording the first derivative dI/dV of the tunneling current \( I(V) \) with the help of a lock-in detection scheme. Because these spectra are equally spaced with respect to \( V \), we can smooth out their intrinsic noise by using the well-established Savitzky-Golay method, which does a polynomial fit on a sliding window with very little computational effort. Since we are mainly interested in finding peaks, a second order Savitzky-Golay filter, which uses local quadratic fits of the form \( S(x) = a + bx + cx^2 \) on each point of all spectra is sufficient. The Savitzky-Golay filter provides us not only with the smoothed \( S = a \), but also directly with the smoothed first and second derivative \( S' = b \) and \( S'' = c \) of the signal \( S \). To avoid filtering out meaningful signal components we use a sliding window of ~100 mV width, less than the full-width half-maximum of the expected peak structures. Furthermore, we check that the residuals, \( R = S - a \), of the spectra do not significantly exceed the standard deviation \( \sigma \) of all residuals.

To find peaks (dips) in the spectra, we search for zero crossing in \( S' \) by evaluating \( \text{sign}(S'(n)) = \text{sign}(S(n+1)-S(n)) \), with \( \text{sign}(x) = x/|x| \) as the signum function and \( n \) as the bin of the linearly increasing bias \( V \). Note that the method can be straightforwardly extended to also detect steps as well as “shoulders”: masked peaks which due to some nearby larger structures do not develop a local maximum.

**Density Functional Theory calculations.** We performed Density Functional Theory (DFT) calculations using the Fritz-Haber-Institute ab initio molecular simulation package (FHI-aims). The geometry of the graphene nanoring was optimized using Becke’s three parameter hybrid exchange functional and the Lee Yang Parr correlation functional (B3LYP). Applying the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm, we relaxed the structure via two consecutive steps; first by expanding the Kohn–Sham wavefunction with the default numerical “light” basis sets, applied to all atomic species. Once finished, all basis sets were replaced with the default numerical “tight” basis sets and the relaxation was resumed. We continued the relaxation until the maximum force on each atom, in either setup, was less than 10−3 eV/Å. To aid the convergence in either relaxation step, we applied a 0.05 eV broadening to all states, using...
a Gaussian occupation smearing scheme. It was later reduced to 0.01 eV for precisely calculating the molecular orbitals and density of states. Pair-wise intramolecular dispersion effects were included using the Tkatchenko-Scheffler (TS) approach and relativistic effects were accounted for via scaled zeroth-order regular approximation (ZORA). To obtain a well converged electronic description of the systems, a threshold of $10^{-6}$ eV for the total energy, $10^{-4}$ eV for the sum of eigenvalues and $10^{-6}$ eV/Å² for the charge density was applied during all self-consistent field (SCF) cycles.

The vibrational spectrum was computed using a finite displacement approach and assuming harmonic approximation. In order to reduce the computational costs, the semi-local exchange-correlation functional of Perdew, Burke and Ernzerhof (GGA-PBE) was used to treat the electronic exchange and correlation. First the graphene nanoring was fully relaxed at DFT-PBE/tight-bs level with lowered force threshold of $10^{-4}$ eV/Å for improved accuracy. Subsequently, the Hessian matrix was determined numerically by finite displacements of all atomic positions in six directions $\pm (x, y, z)$ by $25 \times 10^{-3}$ Å, and then diagonalized to obtain the vibrational modes. The corresponding intensities are obtained by taking the derivative of the dipole moments along these modes and broadened with Lorentzian function for visual enhancement and comparison with experimental data.

**Data availability**

The references that support the findings of this study are available in Julich Dataset Repository with the identifier https://doi.org/10.26165/JUELICH-DATA/ONOVYK.

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**Author contributions**

J.M.-C., R.T. and F.S.T. conceived the project. J.M.-C. and R.B. performed the experiments. J.M.-C., R.B., T.E. and M.T evaluated the data. H.H.A. and C.W. performed the DFT calculations. S.W. and J.S. synthesized the C108 precursor. Q.F. and J.M.G. developed the on-surface synthesis protocol. All authors discussed the results. J.M.-C and M.T. wrote the paper with significant contributions from all authors.

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