Tracking the ultrafast motion of a single molecule by femtosecond orbital imaging

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Watching a single molecule move on its intrinsic timescale has been one of the central goals of modern nanoscience, and calls for measurements that combine ultrafast temporal resolution1–8 with atomic spatial resolution9–30. Steady-state experiments access the requisite spatial scales, as illustrated by direct imaging of individual molecular orbitals using scanning tunnelling microscopy9–11 or the acquisition of tip-enhanced Raman and luminescence spectra with sub-molecular resolution26–28. But tracking the intrinsic dynamics of a single molecule directly in the time domain faces the challenge that interactions with the molecule must be confined to a femtosecond time window. For individual nanoparticles, such ultrafast temporal confinement has been demonstrated18 by combining scanning tunnelling microscopy with so-called lightwave electronics1–8, which uses the oscillating carrier wave of tailored light pulses to directly manipulate electronic motion on timescales faster even than a single cycle of light. Here we build on ultrafast terahertz scanning tunnelling microscopy to access a state-selective tunnelling regime, where the peak of a terahertz electric-field waveform transiently opens an otherwise forbidden tunnelling channel through a single molecular state. It thereby removes a single electron from an individual pentacene molecule’s highest occupied molecular orbital within a time window shorter than one oscillation cycle of the terahertz wave. We exploit this effect to record approximately 100-femtosecond snapshot images of the orbital structure with sub-Ångström spatial resolution, and to reveal, through pump/probe measurements, coherent molecular vibrations at terahertz frequencies directly in the time domain. We anticipate that the combination of lightwave electronics1–8 and the atomic resolution of our approach will open the door to visualizing ultrafast photochemistry and the operation of molecular electronics on the single-orbital scale.

We investigate the π-conjugated organic molecule pentacene with low-current9, low-temperature terahertz scanning tunnelling microscopy (THz-STM). In our experiments, we focus phase-stable, single-cycle THz pulses5,8 onto the STM junction. There, the electric field of the THz waveform adds to the static electric potential between tip and sample, resulting in an ultrafast modulation of the applied bias voltage. To preserve the inherent electronic properties of pentacene, the molecules are adsorbed on monolayer islands of NaCl, which electronically decouple the pentacene molecules from the underlying Au(110) surface8 (Fig. 1a; see Methods for further details of sample preparation and microscope set-up).

Figure 1b depicts the novel ultrafast, energy-selective tunnelling regime at the heart of this study. It builds on the orbital-specific tunnelling of conventional STM that is enabled by the use of insulating films6, where the double-barrier (salt, vacuum) geometry leads to two very distinct tunnelling mechanisms (Fig. 1b, left). For low bias voltages, tunnelling electrons cannot access the molecular orbitals and must tunnel between the tip and the metal substrate in a single step. Conversely, once the voltage reaches a threshold such that either the lowest unoccupied molecular orbital (LUMO) or the highest occupied molecular orbital (HOMO) is inside the bias voltage window, sequential tunnelling sets in. In this two-step process, for example, an electron will temporarily localize in the LUMO after having tunnelled through the first barrier, and before tunnelling through the second barrier. The alignment of the LUMO or HOMO transport level with the Fermi energy of the tip thus opens up a new tunnelling channel, and consequently appears as a peak in the differential conductance (Fig. 1b, centre).

To understand how this situation enables a new regime in THz-STM, we now consider the dynamic analogue of this process, where a THz pulse replaces the steady-state bias (Fig. 1b, right). Light–matter interactions with intense THz fields are often characterized by different competing quantum effects4–6, occurring at the crossover of the photon versus classical-field regimes. The semi-classical picture discussed in the following is justified by the experimental results presented further below, but cannot be assumed a priori. To facilitate the discussion, however, we will introduce the new regime directly in the context of this picture, in which the THz waveform is viewed as a transient bias voltage and hence a transient modification to the level alignment of the system. Thus, it is expected to temporarily open an otherwise forbidden tunnelling channel through the HOMO when the peak of the waveform matches the corresponding transport level.

This concept of THz-induced sequential tunnelling has the potential to yield optimally short current responses that are ultimately limited only by the linewidth of the resonance. Moreover, the asymmetry of the THz waveform should allow us to drive tunnelling out of the HOMO without accessing the LUMO, and create a unipolar current burst with a duration defined by the width of the THz waveform crest. Finally, we note that sensitivity to rectified currents below one electron per THz pulse is a prerequisite for exploring this new ultrafast, state-selective tunnelling regime. In the experiment, we position the STM tip over a pentacene molecule, turn off the STM feedback loop as well as the bias voltage, and measure the net THz-induced tunnel current through the molecule as a function of the THz peak field. We observe a rectified current onset in the negative bias direction (Fig. 1c) and currents approaching one electron per THz pulse. The threshold peak field is about 0.25 kV cm⁻¹, corresponding to a peak bias voltage of about –1.65 V, owing to the large field enhancement19–30 at the tip.

The ultimate test of whether this signal is due to THz-induced sequential tunnelling is the spatial distribution of the rectified current. Steady-state STM imaging with the bias set to the HOMO transport level directly reveals the HOMO density contours of the free molecule9. Figure 2a shows such a steady-state, constant-current STM image of a pentacene molecule, recorded at a voltage near the HOMO level (bias voltage, \( V_{\text{DC}} = –1.7 \) V), and features the ten lobes of the HOMO protruding towards the tip9. In contrast, these lobes are absent from the steady-state STM image when the bias voltage window does not include a molecular resonance (shown in Fig. 2b, \( V_{\text{DC}} = +6 \) mV) and only one-step tunnelling is permitted. The THz-STM image recorded

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Figure 1 | Ultrafast THz-induced tunnelling of a single electron out of a single molecule. a, Our experimental set-up. Two THz pulses separated by a variable delay time, $\tau$, are coupled into the STM junction, which includes a tungsten tip and a pentacene molecule that is electronically decoupled from the Au(110) substrate by a monolayer NaCl film. The net current produced by the THz pulses was measured as a shift in the DC tunnel current, $I$. The bias voltage, $V_{\text{DC}}$, refers to the voltage of the metal substrate relative to the tip. Likewise, positive currents correspond to electrons tunnelling from the tip into the sample. b, Concept of steady-state and ultrafast tunnelling out of the HOMO of a single molecule. For low bias voltages (far left, top), tunnelling electrons cannot access the molecular resonances. In contrast, for voltages exceeding the LUMO or HOMO transport levels (far left, bottom), sequential tunnelling sets in. c, The time resolution of the snapshot in Fig. 2 can be extracted from a THz autocorrelation measurement over a central pentacene HOMO lobe (data points in Fig. 3a), where the rectified current is recorded as a function of the delay, $\tau$, between two identical THz pulses (Fig. 3a, top). To simulate the experimental trace, we account for the tunnelling conductance (see Methods for details), under the assumption that the voltage transient equals the THz electric field.
positive and far from either molecular resonance. d, Simulated THz-STM image calculated on the basis of the Tersoff–Hamann approximation, with the tip position following the topography shown in b. e, THz-STM image (close-up of the blue rectangle in c) measured at constant height, with \( V_{\text{DC}} = 0 \) V, \( V_{\text{THz}} = 2.05 \) V, and a time resolution of 115 fs. The THz-induced current is calibrated in units of rectified electrons per THz pulse.

f, g, DFT-derived HOMO (f) and LUMO (g) contours of the free pentacene molecule. h, Molecular structure of pentacene. i, Simulated constant-height THz-STM image (close-up of blue rectangle in d).

multiplied by a scaling factor, which acts as the only fit parameter. Good agreement is found between the simulated (Fig. 3a, black curve) and measured (Fig. 3a, data points) autocorrelations for a peak voltage of \( -2.22 \) V \( \pm 0.07 \) V at \( \tau = 0 \) fs, supporting our assertion that THz pulses tuned to the HOMO resonance drive sequential tunneling. Yet more fundamentally, this result verifies that the THz waveform modulates the bias voltage of the junction quasi-instantaneously, even on the sub-cycle scale. In this regime, the simulations allow us to retrieve the average temporal shape of the rectified current pulse. As shown in Extended Data Fig. 3, the rectified current is generated within a time window as short as 130 fs for a voltage peak of \( -2.22 \) V. Furthermore, we estimate that the THz peak was only \( -2.05 \) V during THz-STM imaging (Fig. 2; see Extended Data Fig. 3 for details), so the temporal window for tunneling in the single-orbital snapshot image (compare Fig. 2c and Fig. 2e) is determined to be only 115 fs (see Extended Data Fig. 3).

Femtosecond control over the tunneling time window can be used to capture the ultrafast dynamics of an individual molecule following a single tunneling event (Fig. 3b). To this end, we introduce a new quantum pump/probe scheme, where two successive, identical THz pulses are individually tuned in resonance with the pentacene HOMO (Fig. 3b, top). Ultrafast dynamics driven by the first field transient (pump) thus potentially modify the rectified current, \( I_{\text{THz2}} \) (see Methods), induced by the second (probe). Remarkably, this probe current measured as a function of the pump–probe delay, \( \tau \) (Fig. 3b), indeed exhibits a marked oscillation at a frequency of 0.5 THz (Fig. 3c).

We interpret this behaviour as a coherent vibration of the molecule, which may be understood as a manifestation of the Franck–Condon principle at the single-molecule level: the pump stimulates tunneling of an electron from the HOMO to the tip, leaving the molecule temporarily charged. The abrupt change to the Coulomb and van der Waals forces on the molecule imparts an impulse that prepares a dominantly vertical vibration of the molecular frame over the salt layer\(^9\). We expect the HOMO to be refilled on the \( \approx 100-\)fs timescale (see Methods), so vibrations occur about the equilibrium position of the neutral molecule. The probe pulse subsequently samples the resulting oscillation of the molecule’s position (Fig. 3d), which is well defined because the time window for tunneling out of the molecule is much shorter than the vibrational period of the relatively heavy molecular frame. Assuming that the \( \pm 10\% \) oscillations of the probe current (Fig. 3b) originate from a modulation of the tunneling-barrier thickness owing to the molecule’s motion, its average oscillation amplitude can be estimated to be \( \pm 4 \) picometres from the tunneling decay rate (current versus barrier thickness).

The oscillatory mode of the molecule is characteristic of the specific van der Waals interaction between pentacene and the substrate. To demonstrate this, we prepared monolayer salt islands at a higher temperature (see Methods), thereby removing the missing-row reconstruction of the Au surface underneath (Fig. 4a, b). Pump/probe measurements recorded over an adsorbed pentacene molecule (at the position indicated by the red circle in Fig. 4c) reveal a molecular oscillation frequency of 0.3 THz (Fig. 4d), which is different from the oscillation frequency observed for pentacene on the previous substrate (Fig. 3b, c). The shift is a direct result of altering the Au reconstruction underneath the decoupling layer, as this modifies the adsorption potential of pentacene. Furthermore, under identical experimental conditions to those in Fig. 4d, we observe a different oscillation frequency (Fig. 4e) for a copper phthalocyanine molecule adsorbed on the same salt island (recorded at the blue circle in Fig. 4c), excluding alternative mechanisms as the origin of the observed current oscillations (see Methods). In each case, we coherently stimulate and resolve
Ultrafast dynamics of a single molecule. a, Bottom, THz-pulse autocorrelation for two identical THz pulses, in units of rectified electrons per THz pulse pair, measured with the STM tip located over a pentacene HOMO lobe. Each individual THz pulse (solid line in the diagram above) is too weak (THz far-field amplitude = 0.12 kV cm$^{-1}$) to enable sequential tunnelling through the HOMO. Upon perfect overlap ($\tau = 0$), however, the resulting transient does reach the HOMO level (dashed line). The experimental $I_{THz,1}$ versus $\tau$ values (dots in graph) are fit (solid line) by a simulation based on rectifying the electro-optically measured THz waveform using a $dI/dV$ representation of the sum of two Gaussians. The best fit yields a time resolution of 130 fs here and 115 fs for the settings used for imaging. b, Measurement of a single pentacene molecule’s time dynamics in a pump/probe experiment. Here, each individual THz pulse is strong enough (THz far-field amplitude = 0.22 kV cm$^{-1}$) to facilitate HOMO tunnelling. The current due to the second pulse exhibits coherent oscillations as a function of delay time, $\tau$. This pump-induced variation, $\Delta I_{THz,2}$, about the average current, $I_{THz,2}$, originating from the second pulse is shown (dark green points and curve). A second scan taken on the same molecule confirms a fixed phase relation (light green points and curve). c, The Fourier spectra of the measurements in b exhibit sharp peaks at $\sim$0.5 THz. d, Illustration of the pump/probe measurement. The first THz pulse excites a vertical vibration by removing an electron from the HOMO. The second pulse detects the instantaneous height of the oscillating molecule as a change in the net current. Error bars indicate the standard deviation from the fitted sinusoidal oscillations as a function of delay time, $\tau$. e, Quantum pump/probe measurements recorded over the pentacene molecule (d, red) and the copper phthalocyanine molecule (e, blue). Although the experimental conditions were identical for d and e, the results show coherent oscillations at different frequencies (0.3 THz and 0.5 THz, respectively). Error bars indicate the standard deviation from the sinusoidal fits to the oscillations (black lines in d, e), which identify the dominant spectral component in each case. Tracing each fit back to $\tau = 0$ reveals a consistent absolute phase with a temporal offset of less than 130 fs (vertical purple belt). Sinusoidal fits to the oscillations in Fig. 3b also give the same phase.

Influence of substrate surface and molecular species on ultrafast single-molecule dynamics. a, b, Constant-current DC-STM images of NaCl/Au(110) islands with (a) and without (b) the missing-row Au(110) reconstruction beneath the monolayer NaCl film. Greyscale range = 2.0 Å. c, Constant-current DC-STM image of a pentacene molecule HOMO (top left) and a copper phthalocyanine molecule HOMO (bottom right), which are adsorbed next to one another on the same NaCl monolayer island shown in b ($V_{DC} = -1.75$ V, $I = 0.83$ pA). Greyscale range = 3.0 Å. The red and blue circles indicate the positions at which the pump/probe dynamics shown in d, e were measured on each molecule. d, e, Quantum pump/probe measurements recorded over the pentacene molecule (d, red) and the copper phthalocyanine molecule (e, blue). Although the experimental conditions were identical for d and e, the results show coherent oscillations at different frequencies (0.3 THz and 0.5 THz, respectively). Error bars indicate the standard deviation from the sinusoidal fits to the time-domain oscillations (black lines in d, e), which identify the dominant spectral component in each case. Tracing each fit back to $\tau = 0$ reveals a consistent absolute phase with a temporal offset of less than 130 fs (vertical purple belt). Sinusoidal fits to the oscillations in Fig. 3b also give the same phase.
The development of ultrafast THz-STM of well-defined quantum states opens the door to a qualitatively new experimental domain in nanoscience. Now, the femtosecond-scale quantum motion of molecules—ranging from vibrations to electronic excitations—can be probed on the scale of a single electronic orbital. Furthermore, the dynamics of the energy landscape associated with single electrons and phonons can be traced directly by ultrafast tunnelling, providing a way of exploring few-particle quantum statistics in single molecules with sub-cycle time resolution. Moreover, combining an optical pump pulse with the THz-STM probe will provide access to a multitude of optical excitations, including those in the time window immediately following the pump pulse (τ < 2 ps). In the near future, we envisage watching single-electron lightwave electronics in molecular circuits, single-molecule movies, and chemical reactions in four dimensions, visualizing the initial reaction steps of key elementary processes in chemistry and biology.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

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Additional Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to J.R. (jascha.repp@physik.uni-regensburg.de) or R.H. (rupert.huber@physik.uni-regensburg.de).

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METHODS
THz optical set-up. Intense, phase-locked THz pulses are generated by tilted-pulse-front optical rectification of femtosecond near-infrared pulses (centre wavelength 1,028 nm, pulse duration (full width at half-maximum) 250 fs) from a regenerative ytterbium-doped potassium gadolinium tungstate (Yb:KGW) laser amplifier (repetition rate 0.61 MHz) in lithium niobate. The waveform of the generated single-cycle THz transients is directly measured by electro-optic sampling in a 0.5-mm-thick (110)-cut zinc telluride crystal using femtosecond near-infrared gate pulses (centre wavelength 800 nm, pulse duration 106 fs). Pairs of mutually delayed THz transients are prepared by transmitting the THz pulses through a Michelson interferometer, in which the computer-controlled position of one end mirror sets the delay time, \( \tau \). The field amplitude can be continuously scaled without changing the waveform using wire-grid polarizers. We note that the precise field enhancement at the tip depends on the local tip preparation for a specific experiment, but is constant for a given tip position as long as the tip shape is maintained.

STM set-up and sample preparation. The homebuilt STM is based on a Besocke design\(^\text{32}\) and operates in ultra-high vacuum (UHV; pressure \( \sim 7 \times 10^{-11} \) mbar) and at low temperatures down to 11 K. The bias is applied to the sample, and the bias voltage window refers to the energy region between the tip and sample Fermi levels. A homebuilt, low-temperature (~100 K), high-gain (\( G = 2.5 \times 10^{10} \)) preamplifier is used that is mounted in close proximity to the STM head. THz radiation enters the vacuum chamber through a sapphire viewport as a collimated beam and is focused onto the tip by a parabolic mirror that is fixed to the STM scan unit. NaCl is evaporated thermally onto the clean Au(110) sample under UHV conditions at a sample temperature of ~295 K (missing-row reconstruction) and ~400 K (no missing-row reconstruction), in two different preparations. Pentacene or copper phthalocyanine molecules are deposited onto the cold sample (\( T < 15 \) K) while it is located inside the STM.

THz-STM measurements. To detect the THz-induced current, we modulate the THz pulses at 475 Hz with an optical chopper (faster than the STM feedback loop bandwidth), and measure the AC tunnel current with lock-in detection. We note that the average current due to the THz pulse train is small relative to the DC setpoint current, which is typically of the order of 1 pA, and can be in the opposite direction. The average THz-induced current, \( I_{\text{THz,average}} \), in units of amps, can be converted into the number of electrons per pulse by: \( I_{\text{THz,average}} \left( \text{e}^- - \text{pulse}^{-1} \right) = I_{\text{THz,average}} \left( A \right) \left( n \right) \), where \( f \) is the repetition rate of the THz pulses and \( e \) is the elementary charge. For example, if only one THz pulse is produced per laser shot, 98 fA corresponds to 1 electron per pulse. The combination of our low-noise preamplifier, laser repetition rate, and lock-in detection therefore allows us to measure THz-induced currents down to 0.01 electrons per pulse.

In an autocorrelation measurement (for example, Fig. 3a), each generated THz pulse is split in two and separated by a variable delay time, \( \tau \), in the Michelson interferometer. The peak fields of the two identical THz pulses focused onto the tip are adjusted such that the combined peak field reaches the HOMO only when the pulses fully overlap (\( \tau = 0 \)). The optical generation beam is modulated, so the measured AC current corresponds to the total THz-induced current created by the two pulses.

Conversely, pump/probe measurements (for example, Figs. 3b and 4d, e) are made by modulating one of the two THz pulse trains in a pair independently (that is, one arm of the Michelson interferometer contains a chopper). Additionally, in quantum pump/probe measurements, we adjust the peak field of each THz pulse in a pair such that the pulses access a particular orbital independently when separated (that is, for large values of \( \tau \)). We then compare the AC tunnel current, \( I_{\text{THz,1}} \), induced by the first pulse only, the corresponding current \( I_{\text{THz,2}} \) caused solely by the second pulse, and the current \( I_{\text{THz,total}} \), measured when both THz fields act on the junction. Finally, we define \( I_{\text{THz,1,2}} \left( \text{e}^- - \text{pulse}^{-1} \right) = I_{\text{THz,1,2}} \left( A \right) \left( n \right) \), where \( \Delta \) represents the difference between \( I_{\text{THz,1}} \) and \( I_{\text{THz,2}} \).

In the measurements shown here, we avoid the range \( \tau < 2 \text{ ps} \), because of interference. To obtain a detectable THz-induced current, the tunnelling rate between tip and molecule has to be large enough to ensure that an electron has an appreciable probability of tunnelling during the ultrashort tunnelling time window at the THz peak. This high tunnelling rate is facilitated by a close tip–molecule distance and will—outside the THz peak—lead to an electron tunnelling from the tip, thereby refilling the HOMO at a similar rate. This process competes with the HOMO being refilled from the substrate, where extrapolation of the results in ref. 32 indicates a tunnelling time of the order of 100 fs through a NaCl monolayer. The net tunnel current that is observed stems from those instances only for which the HOMO is refilled from the substrate. Signals similar to the oscillations shown for \( \tau > 2 \text{ ps} \) are observed at negative delay times, when the roles of the identical THz pump and probe pulses are interchanged. Finally, we note that we observe a small tip expansion owing to heating by the THz pulse train, but it is on the order of 10 picometers and occurs on a timescale of seconds (which is far slower than our chopping frequency) and therefore has no effect on our measurements.

Simulations. To simulate the spatial distribution of the HOMO in the THz-STM images (Fig. 2d, i), we adopt the Bardeen model\(^\text{33}\), where the tunnel current is proportional to the square of the matrix element between the relevant tip and sample wavefunctions. As in the Tersoff–Hamann approach\(^\text{34}\), we approximate the tip wavefunction as an s-wave, whereas we use the DFT-derived HOMO of the free molecule as the sample wavefunction (calculated using the ‘TURBOMOLE’ computational framework\(^\text{35}\) in version 6.2, with the B3-LYP functional in the def2-TZVP basis set). To model the spatial dependence of the tunnel current, we evaluate the convolution of the HOMO with the s-wave tip for the experimentally measured topography (Fig. 2b). The best agreement between the simulations and the THz-STM images is obtained for s-waves with 1/e decay lengths of <0.5 Å, which is consistent with the spatial resolution of the experimental image (0.6 Å; see Extended Data Fig. 1).

Origin of different oscillation frequencies. For pentacene molecules adsorbed on NaCl monolayer islands on Au(110) with the missing-row reconstruction, we observed a consistent oscillation frequency of 0.5 THz (Fig. 3). We also investigated copper phthalocyanine (CuPc) molecules on the same substrate and observed a higher oscillation frequency of 0.7 THz (data not shown). For pentacene and CuPc adsorbed on NaCl islands on Au(110) without the missing-row reconstruction, we found oscillation frequencies of 0.3 THz (Fig. 4d) and 0.5 THz (Fig. 4e), respectively. The higher frequency observed for CuPc molecules is consistent with the slightly polar character of the bonds inside CuPc, which results in an increased electrostatic interaction with the underlying ionic NaCl film that stiffens the binding to the substrate. Generally, though, the weak interaction of a relatively large \( \pi \)-conjugated organic molecule with an insulating substrate is very difficult to model and to predict with theory or corresponding simulations.

On the experimental side, vibrational frequencies of 1.5–2 THz have been reported for hydrocarbons directly adsorbed on Cu(100)\(^\text{36}\) and Ru(0001)\(^\text{37}\). It is expected that the interaction of the \( \pi \)-conjugated molecules with the substrate is substantially weakened by introducing an insulating film. Hence, for pentacene and CuPc on NaCl/Au(110), frequencies well below 1.5 THz are expected, in qualitative agreement with our observations. Most importantly, the occurrence of different oscillator frequencies for different molecular species and different surface reconstructions with otherwise identical conditions rules out many other potential causes of the observed oscillations: namely, plasmonic resonances of the junction; THz resonances of the entire tip that influence the THz coupling; interference effects of potential trailing oscillations of the THz waveform; and coherently excited surface modes that change the substrate–molecule tunnelling probability as a function of \( \tau \).

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Extended Data Figure 1 | Spatial resolution of THz-STM imaging.

**a, b.** Line-scan cuts (a) through a constant-height, zero-bias THz-STM image (b), where the THz-induced current $I_{\text{THz}}$ is shown in units of rectified electrons per THz pulse. The pixel size in the image is 0.25 Å $\times$ 0.25 Å and the white scale bar is 1 Å long. The image contains edges where the signal rises from the background level to a maximum within 0.75 Å. The signal rise from 10% to 90% in these cases occurs over approximately 0.6 Å, which provides an upper bound for the spatial resolution of the image. This estimate agrees with simulations of the spatial distribution of the rectified current (Fig. 2d, i). There, we calculate the square of the matrix element between the pentacene HOMO and the tip wavefunction (Bardeen model). The tip wavefunction, which ultimately determines the attainable spatial resolution, is modelled as an s-wave (as in the Tersoff–Hamann approach) and the spatial decay of this wavefunction is used as a fitting parameter, as is the tip height. The best agreement between the experimental and simulated images is found for s-waves with decay lengths of $\leq 0.5$ Å, consistent with our spatial resolution estimate of 0.6 Å based on the line scans in **a**.
Extended Data Figure 2 | Ultrafast THz-STM imaging of the lowest unoccupied orbital of pentacene. a, When Au(110) is replaced with Cu(100) as the substrate, the HOMO and LUMO levels realign with respect to the Fermi level of the substrate in such a way that the LUMO can be probed by THz-induced currents. This situation is depicted schematically here, in analogy to Fig. 1b. Left, steady-state differential conductance measured on a pentacene molecule adsorbed on NaCl/Cu(100). Right, THz electric-field waveform measured by electro-optic sampling. Although the THz waveform is the same as that in Fig. 1b, it now induces sequential tunnelling into the pentacene LUMO at the most intense positive half-cycle, while the negative half-cycle is too weak to allow for HOMO tunnelling. b, Steady-state constant-current STM image of three pentacene molecules side-by-side at $V_{DC} = 100$ mV and $I = 1.4$ pA. Greyscale range = 2.4 Å. c, Constant-height THz-STM image of the same sample area as in b, with $V_{DC} = 0$ mV and the maximum positive THz voltage set to $V_{THz,peak} = 1.3$ V. The spatial distribution of the THz-induced current closely resembles the LUMO density for each molecule, indicating state-selective THz-induced LUMO tunnelling. The onset field for this process agrees with the modified alignment of the orbitals. Specifically, the peak THz voltage in the positive direction that is predicted based on the field enhancement determined from HOMO tunnelling is consistent with the new LUMO transport level voltage observed in the steady-state $dI/dV$ curve here. This agreement lends further support to the proposed mechanism for THz-STM in this regime.
Extended Data Figure 3 | Modelling ultrafast terahertz-induced tunnelling out of a pentacene HOMO. a, Terahertz voltage waveforms used in the simulations. We approximate the time trace of the THz voltage with the THz electric-field waveform measured in the far field by electro-optic sampling. In all plots, the pink curve corresponds to a waveform with a peak of $-2.05\,\text{V}$ and the navy-blue curve corresponds to a waveform with a peak of $-2.22\,\text{V}$. The scaling factor and resulting peak voltages are determined by fitting the shape of the experimental autocorrelation (Fig. 3a) as follows. We simulate the autocorrelation by taking the sum of two THz pulses and calculating the total rectified current from the resulting transient as a function of the delay time between the pulses. b, The $dI/dV$ characteristic needed for the simulation is obtained by modelling the HOMO and LUMO molecular-resonance peaks in the experimental $dI/dV$ curve (Fig. 2b, centre) with two Gaussians. This $dI/dV$ curve is then scaled up to account for the significantly lower tip height for THz-STM imaging. Note that the scaling factor does not affect the shape of the autocorrelation. Blue line, centre of HOMO Gaussian, $-1.93\,\text{V}$ (0.62 V full width at half-maximum, FWHM). Red line, centre of LUMO Gaussian, $2.06\,\text{V}$ (0.58 V FWHM). c, Resulting current response induced by the THz voltage waveform in a when applied to a junction with a $dI/dV$ relation defined by b. The asymmetry of the THz voltage pulse leads to a much larger current response in the negative bias direction than in the positive bias direction. Inset, induced current response during the negative crest of the THz voltage waveform. Pink curve, 120-fs FWHM; navy-blue curve, 140-fs FWHM. d, Total number of electrons that have tunnelled across the junction, calculated from the integral of c. Negative numbers refer to the negative bias direction, that is, electron tunnelling from the HOMO to the tip. Inset, rise of the rectified electron signal during the negative crest of the THz voltage waveform. The rise time from 10% to 90% of the maximum signal is 115 fs for the pink curve and 130 fs for the navy-blue curve. The simulated autocorrelation for the $-2.05\,\text{V}$ peak (pink curve) provides the best fit to the shape of the measured autocorrelation. The $dI/dV$ curve is scaled such that the autocorrelation peak at $-2.22\,\text{V}$ matches the measured peak of approximately $-0.75\,\text{electrons per THz pulse}$. The peak voltage of the THz pulses used in the imaging configuration is then determined by finding the THz peak for which the simulations yield this number of rectified electrons per THz pulse. For example, in Fig. 2e the maximum observed signal is approximately $-0.58\,\text{electrons per THz pulse}$, and the best agreement is found for $-2.05\,\text{V}$ (pink curve). We note that the simulations are based on the assumption that the THz pulse modulates the bias of the junction quasi-instantaneously. In our simulations we disregard any blocking of tunnelling or other effects resulting from the finite time until an electron from the substrate refills the molecular state. This blocking is expected to become important if the THz current reaches or even exceeds one electron per pulse.