Quantitative sampling of atomic-scale electromagnetic waveforms

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Tailored nanostructures can confine electromagnetic waveforms in extremely sub-wavelength volumes, opening new avenues in lightwave sensing and control down to sub-molecular resolution. Atomic light-matter interaction depends critically on the absolute strength and the precise time evolution of the near field, which may be strongly influenced by quantum mechanical effects. Measuring atom-scale field transients, however, has been out of reach. Here, we introduce quantitative atomic-scale waveform sampling in lightwave scanning tunnelling microscopy to resolve a tip-confined near-field transient. Our parameter-free calibration employs a single-molecule switch as an atomic-scale voltage standard. While salient features of the far-to-near-field transfer follow classical electrodynamics, we develop a comprehensive understanding of the atomic-scale waveforms with time-dependent density-functional theory. The simulations validate our calibration and confirm that single-electron tunnelling ensures minimal back-action of the measurement process on the electromagnetic fields. Our observations access an uncharted domain of nano-opto-electronics where local quantum dynamics determine femtosecond atomic near fields.

The ability to map out the temporal shape of optical carrier waves, like an oscilloscope for light[1–4], has prompted a vibrant field of research exploring light-matter interaction faster than a cycle of light[5–11]. Electro-optic sampling and streaking techniques visualize lightwaves by stroboscopically scanning them with ultrashort gate pulses. When this idea is combined with scanning near-field optical microscopy[12,13], radiation scattered from the tip-confined near field can be detected electro-optically to monitor lightwaves with combined 10 nm spatial and subcycle temporal resolution. Meanwhile, sophisticated nanostructures including nanoantennas[14–17], nanoparticles[18], nanogaps[19–21], and tips[22–24] have facilitated near-field confinement, to volumes even smaller than the skin depth in metals[16,20,25]. Such tailored near fields have advanced (bio)chemical sensing[26], light harvesting[26], lightwave electronics[22–25,27–31], nanoimaging[12,13,27–31] and spectroscopy[12,13,32,33] down to sub-molecular resolution[28,34]. Importantly, atomic light-matter interaction depends critically on the absolute field strength and the precise temporal evolution of the oscillating carrier near field[12,15,16,22–25,27–32,35–39], both of which may be strongly influenced by quantum mechanical effects, such as tunnelling[36,39]. Yet, measuring electromagnetic transients on atomic length scales, where novel non-classical dynamics have been predicted to shape local fields[36,39], is highly challenging.

Lightwave-induced electron emission from sharp tips[22–24] has been used to reveal fascinating interferences of electron trajectories. The distribution of electron kinetic energies encodes complex dynamics including quiver motion and interferometric backscattering. While this approach has resolved tip-confined transients in a broad range of settings, the interaction between field-emitted electrons and a test waveform is not strictly localized in space, hence it is challenging to fully reconstruct the local near field. In lightwave-driven scanning tunnelling microscopy (STM)[27–31,38], conversely, terahertz (THz) pulses control local electron tunnelling with sub-cycle temporal resolution. Optical gating of semiconductor samples has been used to extract near-field waveforms under the assumption that the carriers relax extremely rapidly and that the steady-state conductance applies equally for femtosecond bursts of a tunnelling current[38]. Yet, detection of near-field waveforms with atomic resolution has remained an open challenge, let alone the measurement of calibrated absolute fields. State-selective

tunnelling in ultrafast single-molecule STM indeed combines sub-Å localization with spectroscopic orbital sensitivity[28], suggesting individual molecules as a quantitative atomic near-field sensor.

Quantitative waveform sampling with an atom-scale voltage sensor

Here, we introduce waveform sampling in ultrafast single-molecule STM as the first method to locally detect tip-confined near-field waveforms at combined sub-cycle temporal and atom-scale spatial scales. The detection scheme is quantitative without free parameters and builds on lightwave STM, where the oscillating carrier wave of ultrashort THz pulses serves as an ultrafast biasing voltage controlling single-electron tunnelling. To this end, the THz far field is focused onto the junction of an STM, consisting of a metallic probing tip (tungsten) located a few angstroms (Å) over a conductive substrate (Fig. 1a). This arrangement acts as a THz antenna (Fig. 1b), for which the confinement into the Å-scale tunnelling gap enhances the field by several orders of magnitude. While the coupling efficiency, plasmonic propagation and near-field screening as well as geometrical phase retardation could be described by classical electrodynamics, the tip-confined fields will also depend on atomic details of the geometry[21] and quantum effects like tunnelling. This currently renders a priori predictions of the near-field waveform inside the STM junction impossible.

To map out the actual waveform locally and quantitatively, we introduce an atomically small voltage gauge into the tunnelling gap: a single-molecule switch. It can be activated only if the voltage $V(t)$ that results from the local field $E(t)$ in the tunnelling gap exceeds a critical threshold. Ultrafast temporal resolution is obtained by superimposing the near-field waveform $V_{NF}(t)$, which is to be determined, with a THz gate pulse $V_{gate}(t)$. To this end, we generate pairs of identical THz waveforms with an adjustable delay time τ in a Michelson interferometer and strongly decrease the amplitude of one pulse in a pair using crossed polarizers. In Fig. 1c, $V_{NF}(t)$ is set five times weaker than the corresponding gate waveform $V_{gate}(t-\tau)$ (Fig. 1d). When the pulses interfere (Fig. 1e), the waveform of the test transient offsets the field crest of the gate. Because $V_{gate}(t)$ is much stronger than $V_{NF}(t)$, and thanks to the very nonlinear threshold behaviour of the switch, $V_{gate}(t)$ can be used as a subcycle probe for $V_{NF}(t)$. In fact, the peak of the sum

voltage $V_{peak}(\tau)$ traces out the instantaneous waveform V_{NF} (Fig. 1e, blue curve), as the delay time τ is varied (red curves labelled 1, 2, 3).

The single-molecule switch consists of a single magnesium phthalocyanine (MgPc) molecule adsorbed on a sodium chloride (NaCl) island on a copper substrate. As shown elsewhere[40], this molecule can be switched back and forth between two equivalent adsorption geometries by sufficiently strong THz fields (Fig. 2a) that trigger tunnelling into the lowest unoccupied molecular orbital (LUMO). We monitor a small non-resonant co-tunnelling current, which is driven by a small DC bias of ~150 mV (see Methods), to decide for every individual laser pulse whether or not the molecule has switched. This way we record the switching rate, p, with increasing waveform amplitude (Fig. 2b). When the THz peak voltage V_{peak} suffices to charge the LUMO, p rapidly rises (Fig. 2c, black dots). This onset behaviour follows an error function (black curve), the derivative of which (grey Gaussian curve) mimics the phonon-broadened (see Methods) LUMO resonance line at $V_{LUMO} = 1.2$ V. As this derivative dp/dV_{peak} is the ultrafast analogue of the differential conductance dI/dV in steady-state STM, we superimpose the resonance curves obtained by steady-state (blue) and femtosecond spectroscopy (grey) to gauge the tip-confined THz peak voltage V_{peak} in units of volts (vertical axis of Fig. 2c) without any free parameter. Consequently, when we couple the similarly shaped superposition waveforms $V_{sum,\tau}$ to the STM and detect the THz-induced switching rate, p, we retrieve the local peak voltage across the tunnelling junction by utilizing the inverted onset curve $V_{peak}(p)$. In particular, we note that the switching motion is triggered by a quasi-instantaneous electron tunnel event temporarily confined to the maximum of the gate pulse.

The amplitude of the gate pulse was chosen such that the superposition waveforms $V_{sum,\tau}$ covered the steepest region of $V_{peak}(p)$, to maximize the sensitivity. By monitoring the switching rate $p(\tau)$ of the molecular switch, we extracted the peak voltages of the superposition waveforms, $V_{peak}(\tau)$, and thus obtained the first time-resolved atomic-scale femtosecond waveform $V_{NF}(t)$ (Fig. 3). For the incident far-field transient detected electro-optically (Fig. 3a) and centred at a frequency of 0.9 THz (Fig. 3a, inset), we retrieve the tip-confined voltage waveform shown in Fig. 3b. These waveforms differ quite markedly.

The tip-confined pulse is longer and exhibits a different carrier-envelope-phase (CEP). Compared to the far-field, the near-field spectrum peaks at a lower frequency around 0.5 THz and exhibits a subtle oscillatory structure (Fig. 3c). The near-field spectral phase (Fig. 3d) is almost as flat as that of the far-field waveform, but the tip-confined pulse exhibits a CEP shift of approximately $-\pi/3$. The accumulated amplitude and phase effects upon coupling and propagation of a far-field waveform into the tip-confined atomic near field are summarized in a frequency-dependent complex-valued transfer function (Fig. 3e).

Plasmonic coupling of the far field to the tunnelling junction

To scrutinize salient characteristics of this transfer function that arise from classical electrodynamics, we simulated the field propagation by numerically solving Maxwell's equations with a finite-element calculation (see Methods for details). We apply the calculated transfer function (Fig. 3e, solid curves) to the far-field spectrum and obtain a simulation of the tip-confined voltage waveform via an inverse Fourier transform (Fig. 3b, black curve). The shape of the amplitude spectrum is reproduced very well (Fig. 3c). Even the frequency-periodic structure, which stems from a resonator for surface plasmon waves formed by the etched tip geometry (see Methods), is matched. The experimentally observed redshift of the near-field spectrum is caused by the $1/f$-scaling of the field enhancement. Also, the simulated phase agrees with the measurement remarkably well, including both the curvature of the phase function and the prominent CEP shift of approximately $-\pi/3$ (Fig. 3d). Comparing the measured and simulated time-domain waveforms (Fig. 3b), the overall shape and even subtle features like the small kink after the main peak match, opening the door to predictive design of coherent control in near-field nanooptics.

The transient bias voltage in the simulations is calculated as the product of the field E_{NF} in the middle of the tunnelling junction times the tunnelling distance d. In the regime in which the field enhancement is inversely proportional to the gap size $E_{\mathrm{NF}} \propto 1/d$, as predicted by the classical antenna theory (see Methods), the voltage drop between tip and substrate $V_{\mathrm{ts}} = E_{\mathrm{NF}}\, d$ does not depend on the tip height providing the absolute scale to the tip-confined voltage waveform $V_{\mathrm{NF}}(t)$. With this gauge, the classical simulation predicts the correct tip enhancement of as much as 2×10^5. Voltage waveforms acquired at different tip heights (Extended Data Fig. 1a) support this picture and illustrate the reproducibility of our

near field detection. We also note that the shape of the near-field transients we record is robust against mechanical modification of the atomistic tip apex (Extended Data Fig. 1b).

Local femtosecond quantum dynamics

Nonetheless, our experimental approach relies on two implicit assumptions that are questioned if electron tunnelling takes place: (i) The voltage gauge from steady-state spectroscopy requires ultrafast lightwave biasing to drive tunnelling at the same local field strength required for steady-state tunnelling. (ii) The tunnelling-based measurement process should exhibit minimal back-action on the instantaneous voltage, which is to be measured. Recent theoretical simulations of light-matter interaction at atomic scales have shown that light-driven tunnelling currents can significantly modify near fields and lead to retardation effects, owing to accumulating charge imbalance[39]. In this light, the good agreement of our experimental results with classical-electrodynamics simulations that do not even take the presence of the molecule in the junction into account calls for a thorough analysis of the role of generated ultrafast tunnelling currents. Hence, we developed a full quantum mechanical description of the ultrafast dynamical scenario with time-dependent density functional theory (TDDFT). The tip is modelled as a tetrahedral cluster of metal atoms and the molecule is placed at distances of 6 and 9 Å from the tip and the substrate, respectively (Fig. 4a). Time domain simulations at a centre frequency of 0.9 THz used in the experiment are computationally prohibitively expensive. However, we verified (see Supplementary Information for details) that the relevant physical effects can be captured by simulating a much faster waveform oscillating at 40 THz (and 20 THz), for which the Keldysh parameter remains well below one and the photon energy well below any electronic excitation in the system. We computed the transient current and static and dynamical molecular screening for different field strengths reaching the onset of electron tunnelling into the molecule (around 0.2 V/Å). In what follows, all local observables were plane averaged (see Methods for details).

The self-consistent local screening in the molecule as well as electron tunnelling between tip and molecule is shown to significantly alter the local potential and, hence, the near field in the junction, as shown in Figs. 4a,b. The calculated Hartree potential difference with and without the molecule in the

junction vary locally very strongly (Supplementary Video 1). Following the longitudinal near-field strength averaged in the molecular region over time (Fig. 4c), we find strong retardation effects: The first section of the transient is barely modified but drives tunnelling from the tip into the molecule. The charge accumulation in the molecule together with the hole left behind in the tip leads to an electric field opposite to the one of the largest half-cycle, strongly modifying the remaining near-field transient.

In our experiment, the voltage transient is probed by the tunnelling of electrons, which drive the molecule to repeatedly switch its orientation. Thus, it is important for the interpretation of the experimental data, whether the tunnelling currents are driven at similar voltage thresholds as in steady-state spectroscopy with quasi-static biasing. Remarkably, our first principles TDDFT simulations predict an almost unchanged onset behaviour for the tunnelling currents as a function of the voltage drop across the junction (Fig. 4d), which is exactly what our sensor probes. In addition, retardation effects are not strong enough to drive an appreciable current in the opposite direction and, therefore, do not alter the current-to-peak-voltage relation, which our experiments rely on. Thus, we conclude that, while the near field in the junction is distributed very inhomogeneously, the total peak voltage across the tunnelling junction is probed very accurately by our atomic-scale sensor.

Finally, in our sampling scheme the test waveform only adds a small offset to this peak field, which is sensed via single-electron tunnelling. Exploiting this quantum process to gauge the near field is robust: First, the quasi-instantaneous tunnel process is not affected by the subsequent fields or the way they are perturbed by local dynamics. Second, our experiment benefits from the quantum mechanical principle that a particle does not alter its own potential. When one isolated electron tunnels through a potential barrier (Fig. 4e), it leaves its energy landscape unchanged. Nevertheless, an external observer or other particles would sense the electric field of the tunnelling electron and observe a potential being modified by the tunnelling electron. This fundamental contemplation leads us to the conclusion that different regimes have to be discriminated in such experiments: In a regime where less than one electron tunnels on average per laser pulse, we sense a voltage transient that is unperturbed by the tunnelling process itself. This is the limit in which the present experiments have been conducted. On the other hand, if many

electrons tunnel during every single pulse transient, the tunnelling electrons may act back on all other electrons, giving rise to a vastly modified potential. In this scenario, the behaviour may not be quasi-static. In an intermediate regime of few tunnelling electrons, even pulse-to-pulse quantum fluctuations may have to be taken into account.

Outlook

Our novel approach opens several new doors across nanoscience and nanophotonics at once. Most fundamentally, with this local sampling scheme, atomic-scale near fields can now be spatio-temporally mapped. We expect precisely calibrated movies of sub-Å field distributions to reveal the limits of classical nanooptics and directly visualize the quantum nature of atomic-scale light-matter interaction. Moreover, state-of-the-art simulations that bridge the gap between macroscopic light and atomic waveforms can now be gauged by experiment, and thereby revolutionize the design of nanotechnology such that novel metamaterials and atomic-scale devices make use of precisely tailored coherent near fields, faster than a cycle of light.

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Author Contributions D.P., C.R., L.Z.K., T.B., A.N., J.H., J.R. and R.H. conceived, set up and carried out the experiments. D.P. and A.N. implemented and carried out the classical finite-element simulations. F.B., D.S., M.R., and A.R. conceived, implemented and carried out the TDDFT simulations. All authors analysed the data and wrote the manuscript.

Data Availability The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

Additional Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to A.R. (angel.rubio@mpsd.mpg.de) or R.H. (rupert.huber@physik.uni-regensburg.de).

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Acknowledgements We thank Christian Meineke, Andreas Pöllmann, Christoph Rohrer, and Martin Furthmeier for assistance and Ferdinand Evers, Heiko Appel and Sebastian Ohlman for discussions. Financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through Project-ID 314695032 – SFB 1277 (Subproject B02), Research Grants HU1598/3 and HU1598/8, the Cluster of Excellence "Advanced Imaging of Matter" (AIM, EXC 2056, ID 390715994) and from Grupos Consolidados (IT1249-19), the European Research Council (ERC-2015-AdG694097), the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 895747, and the Flatiron Institute, a division of the Simons Foundation is gratefully acknowledged.

Methods

STM setup. The homebuilt STM[28] operates at ultrahigh vacuum (UHV; pressure ~7×10^{-11} mbar) and cryogenic (7 K) conditions. The bias voltage is applied to the sample. A homebuilt high-gain ($G = 2.5 \times 10^{10}$ V/A) preamplifier (*I*-*V*-converter) is mounted close to the STM head. The collimated THz beam enters the vacuum chamber through a sapphire viewport and is focused onto the tunnel junction by a parabolic mirror that is mounted on the STM head.

THz optical setup. Phase-locked THz pulses (centre frequency, 0.9 THz) are generated by tilted-pulse-front optical rectification of femtosecond near-infrared pulses (1028 nm centre wavelength, 250 fs pulse duration FWHM) from a regenerative laser amplifier (repetition rate tuneable from 0.61 MHz down to single shot) in lithium niobate. 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, τ. Crossed wire grid polarizers allow us to continuously tune the THz field amplitude, for both pulses individually, without changing the waveform. To retrieve the far-field waveforms that are incident in the STM junction, we mimic the aperture of the vacuum chamber on the optical table.

Single-molecule switch. Sodium chloride (NaCl) is evaporated thermally onto a clean Cu(111) surface under UHV conditions at ~275 K. Subsequently, at a sample temperature below 15 K, magnesium phthalocyanine molecules are deposited to adsorb on chlorine sites of a NaCl surface such that the molecular and substrate symmetry directions are rotated with respect to each other, resulting in two degenerate, stable adsorption geometries[41]. As studied elsewhere, transient charging of the molecule by lightwave-induced injection of a single electron into the LUMO induces switching events between the two adsorption geometries with a certain probability[40]. The onset of LUMO tunnelling, which depends on the material composition of the substrate[41], has been shown to remain the same for terahertz-induced and DC electron tunnelling[40]. Here, the differential conductance associated to LUMO tunnelling is peaked around a bias voltage of 1.2 V and strongly Gaussian-broadened owing to Coulomb coupling between the temporary excess charge in the molecule and the ions in the NaCl thin film – a phenomenon well known

from steady-state STM experiments[42]. Furthermore, it has been demonstrated that the lightwave-driven switching probability is proportional to the rate of lightwave-triggered electron tunnelling into the LUMO[40]. At specific tip positions, the ultrafast atomic force associated with the near field can also be used to trigger a coherent librational motion of the molecule, which can coherently modulate the switching rate[40]. By performing the experiments at a selected spatial location over the molecule, we managed to minimize this influence[40], which is undesirable in the present context, to below the uncertainty margin. Varying the THz field strength allows us to spectroscopically access the phonon-broadened LUMO resonance and detect peak-field-dependent switching rates as shown in Fig. 2c and when sampling near-field waveforms.

During each THz transient, the electric field remains far below the bias threshold for resonant tunnelling, except for a time window of ~100 fs during the field crest of the most intense half-cycle of the gate transient. After this time window has passed, no further resonant tunnelling occurs that could possibly be influenced by the previous event. Hence, this restriction to a maximum of one single tunnelling event per THz transient ensures minimal back-action.

We monitor every switching event by a non-resonant detection current to directly retrieve the switching probability. The detection current is induced by a small bias voltage on the order of 150 mV, far below the voltage required for LUMO tunnelling and therefore too small to charge the molecule[40]. Hence this current stems from electrons tunnelling directly between tip and substrate, a process also denoted “non-resonant cotunnelling”.

We note that the presented sampling scheme can in principle be employed in many other scenarios where an observable depends monotonically on the tip-confined field. Instead of the MgPc molecular switch, which we utilized as a near-field detector due to its very strong response, for example a tunnelling current into any conductive sample exhibiting a spectrally sharp nonlinear response, or photoluminescence detected externally could be considered as alternative sensing strategies. For the detection of particularly low field strengths even a superconducting sample could be conceivable as a detector.

Statistical uncertainty in the detection of the switching probability. In order to resolve the switching probability – and therefore the near-field waveform – with high precision, the experiments are repeated numerous times to observe a sufficient number of events for every set of parameters (field strength for the calibration curve, delay time for the near-field waveform). In Fig. 3b, for example, every data point represents statistics extracted from an observation period where a total of around 1 million pulse pairs were coupled to the STM. This sequence triggered about $np = 1000$ switching events. Statistically, every laser shot represents a Bernoulli trial and every sequence follows a binomial distribution. This yields a shot-noise limited signal-to-noise (SNR) ratio of $\sqrt{np} = 33$ corresponding to a relative statistical uncertainty of 3%, which is the dominating source of experimental uncertainty. By increasing the number of observed events the uncertainty margin could be reduced even further.

Classical finite-element simulations of the sampled near-field THz waveforms. We performed numerical simulations using the frequency-domain finite element solver COMSOL. Maxwell's equations are solved for complex-valued electromagnetic fields on a discrete mesh, providing a self-consistent three-dimensional map of amplitude and phase distributions. All classical wave propagation, plasmonic coupling to the tip shaft, screening and localization in the Å-sized tip-sample gap are accounted for via the complex-valued dielectric properties of the materials used in the experiment.

The geometry is modelled within a cuboid cell where the incident electromagnetic radiation is implemented as oscillatory boundary conditions on one side of the simulation volume. The shape of the tungsten tip is chosen based on actual electron microscope images (Extended Data Fig. 2a,b). It consists of a cylindrical wire with a diameter of 200 µm and a conical, etched region with a 15° taper and a height of 200 µm. The apex features a radius of curvature of 300 nm. A flat gold sample is placed at a distance of 1nm below the tip. The dielectric functions used for tungsten and gold are adopted from the literature[43,44]. The physical simulation volume is surrounded by perfectly matched layers (PML) as boundaries on 4 sides imitating an infinite world by suppressing all back-reflections of radiation. The beam enters the simulation volume through one cell wall at an angle of 40° relative to the sample surface.

The excitation boundary absorbs plane waves leaving the simulation volume by fulfilling the scattering boundary condition.

In order to resolve the propagation of electromagnetic waves with millimetre wavelength from the far field down to Å-scale localized near fields, the simulation cell is partitioned into a graded mesh consisting of tetrahedrals with sizes between 25 µm and 5 Å. At all metal surfaces, the mesh is chosen fine enough to resolve skin depth effects. The boundary PMLs are meshed with hexahedra and the tip and sample extend vertically through them. The junction was meshed with at least two grid points in between tip and sample surface. A direct matrix solver computes the solution to a predefined tolerance level for each frequency. To cover the entire spectrum of the transient, the simulated frequencies range from 0.33 THz to 3.33 THz with a linear spacing of 33 GHz.

Extended Data Figure 2c shows the simulated field distribution about the tip upon plane-wave excitation. In the top left corner of the panel, the incident plane waves propagate towards the junction with constant amplitude, hardly influenced by the geometry. Closer towards the substrate, the wave fronts appear transversally structured, which stems from an interference with the reflection off the flat metal substrate. In proximity to the tip apex, pronounced field enhancement and phase retardation effects manifest. Directly in the tunnelling gap, we find a field enhancement factor of $\sim 2 \times 10^5$ for a tip-sample distance of 1 nm (Extended Data Fig. 2d). According to classical antenna theory, the field enhancement is inversely proportional to the gap size $E_{\mathrm{NF}} \propto 1/d$ (ref. 45).

To remove artefactual diffraction from the simulation, we performed a second calculation with the same simulation volume and mesh, but we replaced the entire geometry with bare vacuum. Comparing the complex electric field of both scenarios allowed us to obtain the complex transfer function shown in Extended Data Figure 2e. The field-enhancement amplitude (black solid line) approximately scales with the inverse frequency, f^{-1}. Both amplitude and phase of the simulated transfer function exhibit a minor oscillatory structure with a periodicity of ~1.3 THz, the origin of which is revealed by the simulated pattern of spatial field distribution (Extended Data Fig. 3). The curved part of the tip that converges towards the apex has been manufactured by electrochemical etching. For the employed tip shown in

Extended Data Figure 2a,b, this process created a sharply curved edge at the circumference where etching began. As this edge serves as a reflector for surface plasmons, a standing-wave pattern can form vertically across the ~250 μm etched region, giving rise to a periodic structure of frequencies with slightly amplified or attenuated coupling efficiency (Extended Data Fig. 3b-d).

Ab initio TDDFT simulations. We performed the real-time TDDFT calculations with the Octopus code[46,47] employing the adiabatic local density approximation (LDA)[48] to describe exchange-correlation effects. In order to obtain an efficient and accurate description of the relatively long-range interactions between substrate, tip and molecule, the averaged density self-interaction correction was applied[49]. To ensure the stability of our time-propagation, we solved the time-dependent Kohn–Sham equations self-consistently at every time step using the enforced time-reversal symmetry propagator[50]. We employ norm-conserving pseudo-potentials to describe the core-valence interactions. We constructed a microscopic model system consisting of a sodium substrate-tip geometry with and without the confined MgPc molecule according to Fig. 4a and b, respectively. The substrate was modelled as a finite slab of 256 atoms, and a tetrahedral structure of 55 atoms was used to represent the STM tip, located on top of a phenyl H atom of the MgPc molecule. The use of Na instead of Cu and W considerably reduces the computational cost, but we confirmed that it reproduces the proper physical description of a metallic STM junction under a non-resonant, THz-range perturbation, giving access to the longer time-scale dynamics. The MgPc geometry was optimized on a NaCl island to account for the presence of the distance spacer[40]. In the dynamical simulations the NaCl layers were replaced by vacuum space of the same height (9 Å). Local observables (electric fields, charge and current) were averaged over the whole *x*-*y* plane and in a 3.7-Å region in the z-axis around the centre of the molecule.

Numerically, the system was represented on a real space grid with 0.4 atomic units spacing and time-propagated with using a time-step of 2.15 as until a total time of 55 fs was reached. The external perturbation was represented by a 40 THz waveform (period of 25 fs), modulated by a Gaussian envelope (FWHM = 18 fs), considering different peak field strengths. The field strength range was such that it spanned values lower and higher than the onset for electron tunnelling into the molecular orbitals, which

is around 0.2 V/Å. A higher frequency than in the experiment was considered to run simulations in a reasonable computation time at the affordable computational cost (320 cores). However, as vibrational excitations are supressed (ions are clamped in our simulations), and the plasmonic modes have energies[39] of the order of 1 eV, our approximated approach is accurate. The transient current under a (quasi) DC external bias was obtained considering a static external field with a smoothed switch-on ramp of 3 fs duration, modulated by a sine-squared envelope. This microscopic approach to obtain the DC response from real-time dynamics has been proposed and applied previously[51]. The orbital current is calculated by linear regression of the charge dynamics after the end of the initial ramp, subtracting the reference charge dynamics of the junction without molecule.

Methods References

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Figure 1 | Near-field waveform sampling by superposition. When a THz waveform is coupled to a nanotip tunnelling junction (**a**), its magnitude and shape change drastically in the near field such that the transient voltage $V_{NF}(t)$ induced at atomistic distances is a priori unknown (**b**). When a weak test waveform $V_{NF}(t)$ (**c**) and a delayed, comparatively strong gate waveform $V_{gate}(t–\tau)$ (**d**, labelled 1, 2, 3 for different delay times τ) interfere in the near field, the test waveform is imprinted on the sum waveforms $V_{sum}(t)$ (**e**, red curves labelled as in **d**) as an envelope for the sub-cycle waveform crests (blue curve).

Figure 2 | Quantitative single-molecule peak-voltage sensor. a, A single-molecule switch is used for detection and parameter-free calibration of the near-field peak voltage. When the peak field accesses an orbital resonance, electron tunnelling statistically causes a switching event, which is registered for every laser shot. Due to the phonon-broadened linewidth of the tunnelling resonance, tip-confined voltage waveforms with different peak fields (**b**) induce different electron tunnelling rates, such that the resulting switching probability p directly encodes the localized peak voltage V_{peak} (**c**, data points). This calibration curve describes an error function (black line), the derivative of which ($\mathrm{d}p/\mathrm{d}V_{\mathrm{peak}}$, grey Gaussian curve) represents the ultrafast analogue of steady-state $\mathrm{d}I/\mathrm{d}V$-spectroscopy (blue curve). Relating the LUMO resonance peaks centred at 1.2V allows us to quantify the tip-confined peak voltage directly in units of Volts without any free parameter. For every waveform measurement, a separate calibration curve similar to Fig. 2c was acquired.

Figure 3 | Calibrated atomic-scale near-field waveform. a, A cosine-like far-field waveform with a spectrum centred at 0.9 THz and a flat phase of ~0 rad (inset) is coupled to the nanotip. **b**, The evolution of the induced near-field voltage is remarkably different (data points). Its overall shape possesses a different CEP and subtle sub-cycle features like a kink at $t = 0.6$ ps are resolved, indicating a more structured spectrum. **c**, Indeed, the spectral amplitude of the measured near-field waveform (data points) is shifted to lower frequencies and possesses a minor oscillatory structure with a period of 1.3 THz. **d**, A similar slight modulation is visible in the spectral phase (data points), which is otherwise flat at approximately -1 rad. **e**, Relating the near-field and far-field spectra and assuming a locally homogeneous electric field across a tip-sample distance of 10 Å yields the complex transfer function that visualizes the f^{-1}-like field enhancement and CEP shift of approximately $-\pi/3$ rad. A classical electrodynamic simulation qualitatively reproduces these results including fine details, without any free parameter (black lines in **b**-**e**, see Methods for details).

Figure 4 | Quantum-mechanical simulation of atomic-scale light-matter interaction. In the time-dependent DFT calculations, the junction is modelled as a tetrahedral tip above four atomic substrate layers with and without the phthalocyanine molecule. Lightwaves are modelled as an ultrafast *z*-polarized external field transient (see Methods for details). **a**,**b**, A vertical cross section of the dynamical Hartree potential at the field maximum (relative to the potential at the apex atom at $t = -25$ fs) reveals inhomogeneous near fields, strongly localized around the front-most apex atom. Including the molecule (**a**) alters the near-field distribution at angstrom scales. **c**, The time-dependent vertical electric field component, E_z, averaged across the molecular plane, is, thus, also modified by the presence of the molecule by roughly a factor of 2. Accumulation of transferred charge leads to retardation effects and a trailing field offset. **d**, Despite this back-action on the local fields, the onset behaviour of lightwave-driven tunnelling and of steady-state tunnelling are similar, confirming that our experimental calibration of the local transient voltage remains valid. **e**, A schematic picture of tunnelling (symbolic electron wavefunction in blue) illustrates that deeply in the single-electron tunnelling regime, the electron wave packet does not affect its own potential landscape (black), warranting minimal back-action of our field-measurements on the near field.