

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.

22 The ability to map out the temporal shape of optical carrier waves, like an oscilloscope for light¹⁻⁴,
23 has prompted a vibrant field of research exploring light-matter interaction faster than a cycle of light⁵⁻¹¹.
24 Electro-optic sampling and streaking techniques visualize lightwaves by stroboscopically scanning them
25 with ultrashort gate pulses. When this idea is combined with scanning near-field optical microscopy^{12,13},
26 radiation scattered from the tip-confined near field can be detected electro-optically to monitor lightwaves
27 with combined 10 nm spatial and subcycle temporal resolution. Meanwhile, sophisticated nanostructures
28 including nanoantennas¹⁴⁻¹⁷, nanoparticles¹⁸, nanogaps¹⁹⁻²¹, and tips²²⁻²⁴ have facilitated near-field
29 confinement, to volumes even smaller than the skin depth in metals^{16,20,25}. Such tailored near fields have
30 advanced (bio)chemical sensing²⁶, light harvesting²⁶, lightwave electronics^{22-25,27-31}, nanoimaging^{12,13,27-31}
31 and spectroscopy^{12,13,32,33} down to sub-molecular resolution^{28,34}. Importantly, atomic light-matter
32 interaction depends critically on the absolute field strength and the precise temporal evolution of the
33 oscillating carrier near field^{12,15,16,22-25,27-32,35-39}, both of which may be strongly influenced by quantum
34 mechanical effects, such as tunnelling^{36,39}. Yet, measuring electromagnetic transients on atomic length
35 scales, where novel non-classical dynamics have been predicted to shape local fields^{36,39}, is highly
36 challenging.

37 Lightwave-induced electron emission from sharp tips²²⁻²⁴ has been used to reveal fascinating
38 interferences of electron trajectories. The distribution of electron kinetic energies encodes complex
39 dynamics including quiver motion and interferometric backscattering. While this approach has resolved
40 tip-confined transients in a broad range of settings, the interaction between field-emitted electrons and a
41 test waveform is not strictly localized in space, hence it is challenging to fully reconstruct the local near
42 field. In lightwave-driven scanning tunnelling microscopy (STM)^{27-31,38}, conversely, terahertz (THz)
43 pulses control local electron tunnelling with sub-cycle temporal resolution. Optical gating of
44 semiconductor samples has been used to extract near-field waveforms under the assumption that the
45 carriers relax extremely rapidly and that the steady-state conductance applies equally for femtosecond
46 bursts of a tunnelling current³⁸. Yet, detection of near-field waveforms with atomic resolution has
47 remained an open challenge, let alone the measurement of calibrated absolute fields. State-selective

48 tunnelling in ultrafast single-molecule STM indeed combines sub-Å localization with spectroscopic
49 orbital sensitivity²⁸, suggesting individual molecules as a quantitative atomic near-field sensor.

50 **Quantitative waveform sampling with an atom-scale voltage sensor**

51 Here, we introduce waveform sampling in ultrafast single-molecule STM as the first method to
52 locally detect tip-confined near-field waveforms at combined sub-cycle temporal and atom-scale spatial
53 scales. The detection scheme is quantitative without free parameters and builds on lightwave STM, where
54 the oscillating carrier wave of ultrashort THz pulses serves as an ultrafast biasing voltage controlling
55 single-electron tunnelling. To this end, the THz far field is focused onto the junction of an STM,
56 consisting of a metallic probing tip (tungsten) located a few angstroms (Å) over a conductive substrate
57 (Fig. 1a). This arrangement acts as a THz antenna (Fig. 1b), for which the confinement into the Å-scale
58 tunnelling gap enhances the field by several orders of magnitude. While the coupling efficiency,
59 plasmonic propagation and near-field screening as well as geometrical phase retardation could be
60 described by classical electrodynamics, the tip-confined fields will also depend on atomic details of the
61 geometry²¹ and quantum effects like tunnelling. This currently renders a priori predictions of the near-
62 field waveform inside the STM junction impossible.

63 To map out the actual waveform locally and quantitatively, we introduce an atomically small voltage
64 gauge into the tunnelling gap: a single-molecule switch. It can be activated only if the voltage $V(t)$ that
65 results from the local field $E(t)$ in the tunnelling gap exceeds a critical threshold. Ultrafast temporal
66 resolution is obtained by superimposing the near-field waveform $V_{\text{NF}}(t)$, which is to be determined, with a
67 THz gate pulse $V_{\text{gate}}(t)$. To this end, we generate pairs of identical THz waveforms with an adjustable
68 delay time τ in a Michelson interferometer and strongly decrease the amplitude of one pulse in a pair
69 using crossed polarizers. In Fig. 1c, $V_{\text{NF}}(t)$ is set five times weaker than the corresponding gate waveform
70 $V_{\text{gate}}(t-\tau)$ (Fig. 1d). When the pulses interfere (Fig. 1e), the waveform of the test transient offsets the field
71 crest of the gate. Because $V_{\text{gate}}(t)$ is much stronger than $V_{\text{NF}}(t)$, and thanks to the very nonlinear threshold
72 behaviour of the switch, $V_{\text{gate}}(t)$ can be used as a subcycle probe for $V_{\text{NF}}(t)$. In fact, the peak of the sum

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

75 The single-molecule switch consists of a single magnesium phthalocyanine (MgPc) molecule
76 adsorbed on a sodium chloride (NaCl) island on a copper substrate. As shown elsewhere⁴⁰, this molecule
77 can be switched back and forth between two equivalent adsorption geometries by sufficiently strong THz
78 fields (Fig. 2a) that trigger tunnelling into the lowest unoccupied molecular orbital (LUMO). We monitor
79 a small non-resonant co-tunnelling current, which is driven by a small DC bias of ~ 150 mV (see
80 Methods), to decide for every individual laser pulse whether or not the molecule has switched. This way
81 we record the switching rate, p , with increasing waveform amplitude (Fig. 2b). When the THz peak
82 voltage V_{peak} suffices to charge the LUMO, p rapidly rises (Fig. 2c, black dots). This onset behaviour
83 follows an error function (black curve), the derivative of which (grey Gaussian curve) mimics the
84 phonon-broadened (see Methods) LUMO resonance line at $V_{\text{LUMO}} = 1.2$ V. As this derivative dp/dV_{peak} is
85 the ultrafast analogue of the differential conductance dI/dV in steady-state STM, we superimpose the
86 resonance curves obtained by steady-state (blue) and femtosecond spectroscopy (grey) to gauge the tip-
87 confined THz peak voltage V_{peak} in units of volts (vertical axis of Fig. 2c) without any free parameter.
88 Consequently, when we couple the similarly shaped superposition waveforms $V_{\text{sum},\tau}$ to the STM and
89 detect the THz-induced switching rate, p , we retrieve the local peak voltage across the tunnelling junction
90 by utilizing the inverted onset curve $V_{\text{peak}}(p)$. In particular, we note that the switching motion is triggered
91 by a quasi-instantaneous electron tunnel event temporarily confined to the maximum of the gate pulse.

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

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

104 **Plasmonic coupling of the far field to the tunnelling junction**

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

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

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

126 **Local femtosecond quantum dynamics**

127 Nonetheless, our experimental approach relies on two implicit assumptions that are questioned if
128 electron tunnelling takes place: (i) The voltage gauge from steady-state spectroscopy requires ultrafast
129 lightwave biasing to drive tunnelling at the same local field strength required for steady-state tunnelling.
130 (ii) The tunnelling-based measurement process should exhibit minimal back-action on the instantaneous
131 voltage, which is to be measured. Recent theoretical simulations of light-matter interaction at atomic
132 scales have shown that light-driven tunnelling currents can significantly modify near fields and lead to
133 retardation effects, owing to accumulating charge imbalance³⁹. In this light, the good agreement of our
134 experimental results with classical-electrodynamics simulations that do not even take the presence of the
135 molecule in the junction into account calls for a thorough analysis of the role of generated ultrafast
136 tunnelling currents. Hence, we developed a full quantum mechanical description of the ultrafast
137 dynamical scenario with time-dependent density functional theory (TDDFT). The tip is modelled as a
138 tetrahedral cluster of metal atoms and the molecule is placed at distances of 6 and 9 Å from the tip and the
139 substrate, respectively (Fig. 4a). Time domain simulations at a centre frequency of 0.9 THz used in the
140 experiment are computationally prohibitively expensive. However, we verified (see Supplementary
141 Information for details) that the relevant physical effects can be captured by simulating a much faster
142 waveform oscillating at 40 THz (and 20 THz), for which the Keldysh parameter remains well below one
143 and the photon energy well below any electronic excitation in the system. We computed the transient
144 current and static and dynamical molecular screening for different field strengths reaching the onset of
145 electron tunnelling into the molecule (around 0.2 V/Å). In what follows, all local observables were plane
146 averaged (see Methods for details).

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

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

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

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

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

180 **Outlook**

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

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192 out the experiments. D.P. and A.N. implemented and carried out the classical finite-element simulations.
193 F.B., D.S., M.R., and A.R. conceived, implemented and carried out the TDDFT simulations. All authors
194 analysed the data and wrote the manuscript.

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

197 **Additional Information** Reprints and permissions information is available at www.nature.com/reprints.
198 The authors declare no competing financial interests. Correspondence and requests for materials should
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287 **Methods**

288 **STM setup.** The homebuilt STM²⁸ operates at ultrahigh vacuum (UHV; pressure $\sim 7 \times 10^{-11}$ mbar) and
289 cryogenic (7 K) conditions. The bias voltage is applied to the sample. A homebuilt high-gain
290 ($G = 2.5 \times 10^{10}$ V/A) preamplifier (*I-V*-converter) is mounted close to the STM head. The collimated THz
291 beam enters the vacuum chamber through a sapphire viewport and is focused onto the tunnel junction by
292 a parabolic mirror that is mounted on the STM head.

293 **THz optical setup.** Phase-locked THz pulses (centre frequency, 0.9 THz) are generated by tilted-pulse-
294 front optical rectification of femtosecond near-infrared pulses (1028 nm centre wavelength, 250 fs pulse
295 duration FWHM) from a regenerative laser amplifier (repetition rate tuneable from 0.61 MHz down to
296 single shot) in lithium niobate. Pairs of mutually delayed THz transients are prepared by transmitting the
297 THz pulses through a Michelson interferometer, in which the computer-controlled position of one end
298 mirror sets the delay time, τ . Crossed wire grid polarizers allow us to continuously tune the THz field
299 amplitude, for both pulses individually, without changing the waveform. To retrieve the far-field
300 waveforms that are incident in the STM junction, we mimic the aperture of the vacuum chamber on the
301 optical table.

302 **Single-molecule switch.** Sodium chloride (NaCl) is evaporated thermally onto a clean Cu(111) surface
303 under UHV conditions at ~ 275 K. Subsequently, at a sample temperature below 15 K, magnesium
304 phthalocyanine molecules are deposited to adsorb on chlorine sites of a NaCl surface such that the
305 molecular and substrate symmetry directions are rotated with respect to each other, resulting in two
306 degenerate, stable adsorption geometries⁴¹. As studied elsewhere, transient charging of the molecule by
307 lightwave-induced injection of a single electron into the LUMO induces switching events between the
308 two adsorption geometries with a certain probability⁴⁰. The onset of LUMO tunnelling, which depends on
309 the material composition of the substrate⁴¹, has been shown to remain the same for terahertz-induced and
310 DC electron tunnelling⁴⁰. Here, the differential conductance associated to LUMO tunnelling is peaked
311 around a bias voltage of 1.2 V and strongly Gaussian-broadened owing to Coulomb coupling between the
312 temporary excess charge in the molecule and the ions in the NaCl thin film – a phenomenon well known

313 from steady-state STM experiments⁴². Furthermore, it has been demonstrated that the lightwave-driven
314 switching probability is proportional to the rate of lightwave-triggered electron tunnelling into the
315 LUMO⁴⁰. At specific tip positions, the ultrafast atomic force associated with the near field can also be
316 used to trigger a coherent librational motion of the molecule, which can coherently modulate the
317 switching rate⁴⁰. By performing the experiments at a selected spatial location over the molecule, we
318 managed to minimize this influence⁴⁰, which is undesirable in the present context, to below the
319 uncertainty margin. Varying the THz field strength allows us to spectroscopically access the phonon-
320 broadened LUMO resonance and detect peak-field-dependent switching rates as shown in Fig. 2c and
321 when sampling near-field waveforms.

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

327 We monitor every switching event by a non-resonant detection current to directly retrieve the switching
328 probability. The detection current is induced by a small bias voltage on the order of 150 mV, far below
329 the voltage required for LUMO tunnelling and therefore too small to charge the molecule⁴⁰. Hence this
330 current stems from electrons tunnelling directly between tip and substrate, a process also denoted “non-
331 resonant cotunnelling”.

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

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

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

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

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

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

373 Extended Data Figure 2c shows the simulated field distribution about the tip upon plane-wave excitation.
374 In the top left corner of the panel, the incident plane waves propagate towards the junction with constant
375 amplitude, hardly influenced by the geometry. Closer towards the substrate, the wave fronts appear
376 transversally structured, which stems from an interference with the reflection off the flat metal substrate.
377 In proximity to the tip apex, pronounced field enhancement and phase retardation effects manifest.
378 Directly in the tunnelling gap, we find a field enhancement factor of $\sim 2 \times 10^5$ for a tip-sample distance of
379 1 nm (Extended Data Fig. 2d). According to classical antenna theory, the field enhancement is inversely
380 proportional to the gap size $E_{\text{NF}} \propto 1/d$ (ref. 45).

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

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

393 **Ab initio TDDFT simulations.** We performed the real-time TDDFT calculations with the Octopus
394 code^{46,47} employing the adiabatic local density approximation (LDA)⁴⁸ to describe exchange-correlation
395 effects. In order to obtain an efficient and accurate description of the relatively long-range interactions
396 between substrate, tip and molecule, the averaged density self-interaction correction was applied⁴⁹. To
397 ensure the stability of our time-propagation, we solved the time-dependent Kohn–Sham equations self-
398 consistently at every time step using the enforced time-reversal symmetry propagator⁵⁰. We employ
399 norm-conserving pseudo-potentials to describe the core-valence interactions. We constructed a
400 microscopic model system consisting of a sodium substrate-tip geometry with and without the confined
401 MgPc molecule according to Fig. 4a and b, respectively. The substrate was modelled as a finite slab of
402 256 atoms, and a tetrahedral structure of 55 atoms was used to represent the STM tip, located on top of a
403 phenyl H atom of the MgPc molecule. The use of Na instead of Cu and W considerably reduces the
404 computational cost, but we confirmed that it reproduces the proper physical description of a metallic STM
405 junction under a non-resonant, THz-range perturbation, giving access to the longer time-scale dynamics.
406 The MgPc geometry was optimized on a NaCl island to account for the presence of the distance spacer⁴⁰.
407 In the dynamical simulations the NaCl layers were replaced by vacuum space of the same height (9 Å).
408 Local observables (electric fields, charge and current) were averaged over the whole x - y plane and in a
409 3.7-Å region in the z -axis around the centre of the molecule.

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

415 is around 0.2 V/Å. A higher frequency than in the experiment was considered to run simulations in a
416 reasonable computation time at the affordable computational cost (320 cores). However, as vibrational
417 excitations are suppressed (ions are clamped in our simulations), and the plasmonic modes have energies³⁹
418 of the order of 1 eV, our approximated approach is accurate. The transient current under a (quasi) DC
419 external bias was obtained considering a static external field with a smoothed switch-on ramp of 3 fs
420 duration, modulated by a sine-squared envelope. This microscopic approach to obtain the DC response
421 from real-time dynamics has been proposed and applied previously⁵¹. The orbital current is calculated by
422 linear regression of the charge dynamics after the end of the initial ramp, subtracting the reference charge
423 dynamics of the junction without molecule.

424 **Methods References**

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446 **Figure 1 | Near-field waveform sampling by superposition.** When a THz waveform is coupled to a
447 nanotip tunnelling junction (**a**), its magnitude and shape change drastically in the near field such that the
448 transient voltage $V_{\text{NF}}(t)$ induced at atomistic distances is a priori unknown (**b**). When a weak test
449 waveform $V_{\text{NF}}(t)$ (**c**) and a delayed, comparatively strong gate waveform $V_{\text{gate}}(t-\tau)$ (**d**, labelled 1, 2, 3 for
450 different delay times τ) interfere in the near field, the test waveform is imprinted on the sum waveforms
451 $V_{\text{sum}}(t)$ (**e**, red curves labelled as in **d**) as an envelope for the sub-cycle waveform crests (blue curve).

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

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

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