Supporting Information

Field-Induced Tunneling Ionization and Terahertz-Driven Electron Dynamics in Liquid Water

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Materials and Methods

Water Sample
A liquid water jet of approximately 50 µm thickness without external windows serves as the sample in the nonlinear THz experiments, which are performed in a transmission geometry. The jet provides a fresh water sample for each THz pulse pair, avoiding cumulative heating effects in the sample. The gravity-driven jet is guided by two parallel wires.\(^1\)\(^2\) By adjusting the height of the water reservoir above the water jet and by varying the position of the excitation spot, the thickness of the water layer can be changed between 20 and 100 µm. In the experiments, the exact thickness is determined by measuring the delay of a THz pulse transmitted through the jet relative to the traveling time without jet. The thickness is derived with the help of the refractive index data of ref 3.

All measurements were performed with ultrapure water (ROTIPURAN Ultra, Carl Roth) at a temperature of 296 K (23°C). To ensure the water jet stability for several days, 0.6% of soap [sulfo-amber-acid–bi(2'ethylexylester) sodium salt] was added.\(^2\) Different concentrations and other types of soap did not influence the measured nonlinear signals, which are entirely due to interaction of the THz pulses with water.

Two-Dimensional Terahertz (2D-THz) Spectroscopy
A schematic of our experimental setup for 2D-THz spectroscopy is presented in Figure S1.\(^4\)\(^5\) The THz pulses are generated by optical rectification of ultrashort pulses from a Ti:sapphire oscillator-amplifier system (Spectra-Physics MaiTai and Spitfire). The near-infrared pump pulses have a duration of 35 fs, a pulse energy of 2.5 mJ, a center wavelength of 800 nm, and a repetition rate of 1 kHz. The main part of these pulses is used for generating THz pulses by optical rectification in a 1.3 mol% MgO-doped stoichiometric LiNbO\(_3\) crystal using tilted wave fronts to achieve phase matching.\(^6\)\(^7\) The THz pulses have a center frequency of 0.7 THz, a pulse length of 1 ps, and are focused by an off-axis parabolic mirror (\(f=2.5\) cm) to achieve electric field amplitudes on the sample of up to 2 MV/cm. The spot diameter of the THz pulses on the sample is approximately 0.7 mm.

The output of the THz generator is split into two pulses by the gold-coated diamond beam splitter BS2. After one of the two pulses is delayed using a variable translation stage, the two pulses are recombined with a second beam splitter (BS3) and interact in a collinear geometry.
Figure S1. Schematic of the experimental setup. BS means beam splitter, BS1 reflects 5% of the 800 nm output from the amplifier to be used as read-out pulses for electrooptic sampling. BS2 and BS3 are gold-coated diamond beam splitters for the THz range to generate and recombine the THz pulses A and B, and BS4 is a pellicle beam splitter to combine the THz and the read-out pulses. The box lettered “THz gen.” represents the setup for THz generation using a LiNbO₃ crystal and a grating to produce a tilted wave front for phase matching. QW means quarter-wave plate, WP is a Wollaston polarizer, and PD1 and PD2 are balanced photodiodes. With the sample. The individual pulses have electric-field amplitudes of 500 kV/cm (pulse A) and 300 kV/cm (pulse B). For amplitude-dependent measurements both pulse amplitudes are adjusted by a pair of wire-grid polarizers inserted directly after the THz generation.

After transmission through the water jet, the THz transients are measured with electrooptic sampling. The electric field leads to a change of the refractive indices of the electrooptic crystal, which is measured by a weak 40 fs read-out pulse centered at 800 nm, using a quarter-wave plate, a polarizer and a pair of balanced photodiodes. The read-out pulse is derived from the output of the Ti:sapphire laser system with the beam splitter BS1. To map the time dependence of the electric field, the arrival time of the 800 nm pulse on the electrooptic crystal is varied by a computerized translation stage.
A 10 µm thick (110) ZnTe crystal serves for electrooptic sampling. To prevent signal distortions by reflections from the back surface of the crystal, it is mounted on a 500-µm thick (100) ZnTe crystal, which for this orientation does not show an electrooptic signal. Since ZnTe is cubic, there is no reflection at the interface between the differently oriented crystals. In this way a time range up to 10 ps is covered without interference by reflected THz and/or 800 nm pulses. The 10 µm thick electrooptic crystal ensures a high bandwidth of electrooptic sampling so that the frequency response is determined only by the pulse length of the read-out pulse. Under these conditions, the THz electric field is directly proportional to the voltage from the balanced photodiodes. The space between THz generation and electrooptic sampling is purged with dry nitrogen gas to prevent absorption and dispersion from water vapor.

The 2D THz measurements are performed by keeping pulse B fixed in time (this position is taken to be the real time \( t = 0 \)), whereas the position of pulse A is varied (the time difference between pulses A and B is the delay time \( \tau \)). Using a chopper in the path of pulse B, we measure the fields transmitted through the sample, \( E_{AB}(t, \tau) \) (both pulses A and B are incident on the sample) and \( E_A(t, \tau) \) (only pulse A), depending on whether the chopper transmits or blocks pulse B. In a separate measurement \( E_B(t) \) is determined (since pulse B is fixed in time, \( E_B(t) \) does not depend on \( \tau \)). From these measurements we determine the nonlinear signal \( E_{NL}(t, \tau) = E_{AB}(t, \tau) - E_A(t, \tau) - E_B(t) \). A 2D Fourier transform of \( E_{NL}(t, \tau) \) yields the nonlinear signal in the frequency domain, which allows the separation of the total nonlinear signal into different nonlinearities, among them the A-pump–B-probe signal (pulse A acts as the pump pulse, pulse B as the probe pulse), the B-pump–A-probe signal, and photon-echo signals.\(^5\)

By applying a frequency filter and a Fourier back-transform on one of these signals one can isolate the nonlinearity underlying the signal. In our data set, there exists only the A-pump–B-probe signal. The B-pump-A-probe signal, third-order photon-echo signals, and higher-order signals are negligible. The absence of the B-pump–A-probe signal is a consequence of the threshold behavior of the nonlinear signal, i.e., the electric-field amplitude of pulse B is smaller than the threshold.
Experimental Results

Pump-Probe Experiments with 800 nm Pump Pulses

Complementary experiments with femtosecond 800 nm pump pulses were performed to compare the properties of hydrated electrons generated this way with the behavior observed in the 2D-THz experiments. After excitation at 800 nm, nonlinear absorption changes were measured (i) with femtosecond probe pulses at 800 nm, and (ii) with THz probe pulses.

Results of the 800 nm pump / 800 nm probe experiments are presented in Figure S2a,b. The transient absorption increase plotted in Figure S2a displays a delayed onset with a rise time of approximately 0.5 ps, an initial partial decay on a few-picosecond time scale, and a long-lived absorption increase persisting up to delay times beyond 100 ps (not shown). The delayed onset and the fast decay reflect the formation of and energy dissipation by solvated electrons, in good agreement with work in the literature.8-10. The long-lived signal allows for estimating a concentration of solvated electrons $c_e = 81 \mu M$, which is in a range similar to the results reported in ref 10 for 800 nm excitation. In Figure S2b, the electron concentration $c_e$ is plotted as a function of $W_{800}$, the energy of the 800 nm pump pulses (symbols). The error bars correspond to the experimental noise observed for positive delay times in Figure S2a. Within the experimental accuracy, the data points follow the 7th power of $W_{800}$ (solid line), pointing to a predominant seven-photon absorption process for the generation of hydrated electrons. This corresponds to the absorption of a total energy of $7 \times 1.5 \text{ eV} = 10.5 \text{ eV}$, close to the ionization potential of water of 11 eV.

For measurements with 800 nm pump and THz probe pulses, the setup shown in Figure S1 was modified so that instead of a THz pulse an 800 nm pump pulse travels along the path of pulse A. The 800 nm pump has a pulse energy of 0.94 mJ or 1.32 mJ and a spot diameter of 0.4 mm (FWHM) on the water jet, resulting in a peak intensity of 5.3 or 7.5 TW/cm². The spot diameter of the THz probe beam was 0.6 mm (FWHM). Transient THz spectra after 800 nm excitation are presented in Figure 3f,g of the article and compared to the calculated nonlinear THz response. Figure S2c-e summarizes pump-probe data measured with a pump energy $W_{800} = 0.94 \text{ mJ}$, generating a concentration of solvated electrons of $c_e = 24 \mu M$. In Figure S2c, the transmitted THz probe field $E_{\text{pr}}(t)$ without 800-nm pump is plotted, while Figure S2d shows the nonlinear signal $E_{\text{NL}}(t,\tau)$, i.e., the difference between THz transients with and without pump, as a function of real time $t$ and delay time $\tau$. A Fourier transform along real time $t$ gives the
spectrally-resolved absorption change \( \Delta A(v, \tau) = - \ln(|E_B(v) + E_{NL}(v, \tau)|^2) - \ln(|E_B(v)|^2) \), which is shown in Figure S2e for a pump-probe delay of \( \tau = 3.65 \) ps (same data as in Figure 3f).

**Figure S2.** Hydrated electron generation by 800-nm pump pulses. (a) Transient absorption change \( \Delta A_{800}(\tau) = \Delta \alpha_{\text{abs}}(800 \text{ nm})d \) for a photo-generated electron concentration \( c_e = 81 \mu \text{M} \) as a function of the pump-probe delay \( \tau \) measured with probe pulses centered at 800 nm (symbols). The red curve is a multi-exponential fit with a rise time \( \tau_{\text{rise}} = 500 \) fs and a time constant of 700 fs for the first partial decay. (b) Electron concentration \( c_e \) as a function of the energy \( W_{800} \) of the 800 nm pump pulses. (c-e) Results from 800-nm pump–THz probe measurement. (c) Transmitted THz electric field without pump. (d) Nonlinear signal, i.e., difference between transmitted THz fields with and without pump for an electron concentration of \( c_e = 24 \mu \text{M} \). The temporal position of the pump pulse is shown by the diagonal line. (e) Differential THz absorption spectrum at a pump-probe delay \( \tau = 3.65 \) ps. The absorption change \( \Delta A(v, \tau) \) is plotted as a function of the THz probe frequency \( v \). (f) Comparison of our THz probe spectrum with that of ref 10.
Results from experiments with 800 nm pump and THz probe pulses have also been reported in ref 10. There are two major differences between the two data sets: (i) The spectra of the THz pulses (Figure S2f) and, thus, the observed nonlinear response are different. Our THz pulses cover a spectral range from 0.3 to 1.5 THz while the pulses of ref 10 extend to some 5 THz, i.e., average over a wider spectral window. As is evident from Figure 3c-e of the article, one expects a different net absorption change in the two cases. (ii) Our data analysis focuses on the nonlinear absorption change, which is proportional to the imaginary part of the transient refractive index. In contrast, Figure 1 of ref 10 displays the nonlinear signal \( E_{NL}(t,\tau) \) at a fixed real time \( t = 0 \), i.e., a single temporal position within the THz probe field. The latter quantity reflects changes of both absorption and the real part of the refractive index of the sample.

A comment should be made on the comparison of the experimental and calculated THz absorption changes presented in Figure 3f,g of the article. The highly nonlinear (7th power) dependence of the generated electron concentration \( c_e \) on the 800 nm pump energy \( W_{800} \) results in a narrowing of the lateral profile of \( c_e \) over the pump spot. Probing this profile with the THz pulse implies an averaging over the diameter of the pumped volume and, thus, a rescaling of the amplitude of the observed absorption changes. We have accounted for this effect by calculating scaling factors for the theoretical response (dashed lines in Figure 3f,g) with the help of Gaussian profiles of the 800 nm pump and THz probe pulses and the dependence of \( c_e \) on \( W_{800} \).

THz Kerr Effect and Anisotropic vs Isotropic Nonlinear Absorption in THz pump / 800 nm Probe Experiments

The THz Kerr effect in water was studied to benchmark our results with literature data. THz pulses with an amplitude of 1.9 MV/cm excite the water jet sample of 50 µm thickness. The resulting absorption changes are measured in a polarization-resolved way with femtosecond 800 nm probe pulses. To this end, a 800-nm probe pulse with a linear polarization rotated 45 degrees relative to the linear THz polarization was sent through the water sample, split into its parallel and perpendicular polarization components with a polarizer, and detected simultaneously by two photodiodes. A special electronic circuit allows for measuring in parallel the difference signal with a high signal-to-noise ratio (SNR) and the individual signals from the photodiodes with a somewhat smaller SNR. For measurements of the THz-induced Kerr rotation we added a \( \lambda/4 \) plate to the 800-nm beam path in front of the polarizer.
Results of the Kerr experiment are presented in Figure S3. Panel (a) shows the incoming and the transmitted THz electric field. The frequency-dependent absorption and dispersion in the 50-µm thick water sample leads to a limited modification of the time-dependent electric field, mainly by reducing the high-frequency components. Panel (b) shows the absolute square of the effective THz field $|E_{\text{eff}}(\tau)|^2$ acting on the water sample (dashed line) together with the measured Kerr rotation $\Delta \Phi_{\text{Kerr}}(\tau) = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ at 800 nm (symbols), which has a negative sign. Here, $I_\parallel$ and $I_\perp$ are the photodiode signals for the two polarization directions. Due to the $\lambda/4$ plate

Figure S3. THz-induced Kerr rotation. (a) Incident (black) and transmitted THz pulse (red) with an amplitude of 1.9 MV/cm. (b) Symbols: transient Kerr rotation at a probe wavelength of 800 nm. Dashed line: effective THz intensity $|E_{\text{eff}}(\tau)|^2$ experienced by the probe pulse. The latter includes the temporal modification of the THz pulse as it propagates along $z$ in the water sample measured in the frame of reference of the 800 nm probe. (c) Same analysis as in panel B for the experimental data from ref 11. For a better comparison we shifted the latter curves along the delay time.
before the polarizer the rotation angle $\Delta \Phi_{\text{Kerr}}(\tau) \propto [\Delta n_\parallel(\tau) - \Delta n_\perp(\tau)]$ is proportional to the difference of the refractive-index changes for parallel and perpendicular polarizations.

Panel (c) shows data taken from ref 11 for comparison. They display a similar $\Delta \Phi_{\text{Kerr}}(\tau)$ of negative sign for $\tau < 2$ ps. The higher sample thickness of 200 µm used in ref 11 results in a substantially stronger reshaping of the THz field and, thus, a somewhat stretched time evolution of $\Delta \Phi_{\text{Kerr}}(\tau)$ compared to our measurement. Moreover, the maximum $\Delta \Phi_{\text{Kerr}}(\tau)$ of ref 11 is roughly ten times smaller than ours. This reduction agrees well with the ratio of the peak THz field amplitudes squared $(0.51 \text{ MVcm}^{-1} / 1.9 \text{ MVcm}^{-1})^2 = 0.072$.

Applying the analysis of ref 11 to our data set, one estimates a maximum change of refractive index $\Delta n \approx 3 \times 10^{-7}$, i.e., roughly ten times larger than in ref 11. Such changes are orders of magnitude smaller than the 10% refractive index changes observed in the 2D-THz experiments (cf. Figure 3b of the article). We conclude that the Kerr effect makes a negligible contribution to the 2D-THz response.

In addition to the Kerr signal $\Delta \Phi_{\text{Kerr}}(\tau)$ we performed measurements without the $\lambda/4$ plate before the polarizer. The quantities $I_{\parallel,0} + I_{\|,pu}, \Delta I_\parallel = I_{\|,pu} - I_{\|,0}, I_{\perp,0} + I_{\perp,pu}, \text{ and } \Delta I_\perp = I_{\perp,pu} - I_{\perp,0}$ were recorded (the subscript pu stands for a water sample excited with the 1.9-MV/cm THz pulse and subscript 0 for the unexcited sample). This information allows for deriving simultaneously the rotation-free absorption change $\Delta A_{\text{iso}} = (\Delta I_\parallel + 2 \Delta I_\perp)/(I_\parallel + 2 I_\perp)$ and the anisotropic absorption change $\Delta A_{\text{aniso}} = (\Delta I_\perp - \Delta I_\parallel)/(I_\parallel + I_\perp)$. Such quantities are plotted in Figure S4(a,b). Since $\Delta A_{\text{aniso}}(\tau)$ is two orders of magnitude smaller than $\Delta A_{\text{iso}}(\tau)$, the THz-induced dichroism observed at a probe wavelength of 800 nm is of minor importance. Therefore we neglected any anisotropic properties of the hydrated electrons in the analysis of the 2D-THz data.

The amplitude $\Delta A_{\text{iso}}(\tau)$ at late delay times is similar to those observed in Figure S2a. We conclude that a 1.9-MV/cm THz pulse generates a concentration of hydrated electrons around $c_e \approx 50 \mu$M, a value about 10 times larger than in the 2D-THz experiments. The onset of the absorption changes in Figure S4 is different from Figure S2a because of the different time structure of the THz and the 800 nm pump pulses. Because of the very small $\Delta A_{\text{iso}}(\tau)$ for $c_e \approx 5 \mu$M generated in the 2D-THz experiments with a peak field of $E_{A,P} = 500$ kV/cm, we measured this value only for two delays and found $\Delta A_{\text{iso}}(175\text{ps}) = (5\pm1) \times 10^{-4}$ and $\Delta A_{\text{iso}}(325\text{ps}) = (6\pm1) \times 10^{-4}$.
Figure S4. THz-induced isotropic vs anisotropic nonlinear absorption. (a) Isotropic absorption change $\Delta A_{\text{iso}}(\tau)$ at 800 nm caused by the THz pulse shown in Figure S3a. The measurements were performed under the same conditions as for the transient Kerr rotation but without the $\lambda/4$ plate before the polarizer in front of the photodiodes. (b) THz-induced dichroism, i.e., the anisotropic contribution to the transient absorption change $\Delta A_{\text{aniso}}(\tau)$.

Other Possible Nonlinear THz Response Mechanisms of Water

Two other mechanisms could in principle contribute to the nonlinear THz response. First, the THz-induced increase in sample transmission may be assigned to a nonlinear decrease of the weak THz absorption of water in the frequency range covered by the THz pulses. The following estimate allows for safely ruling out this interpretation: The incoming photon flux of the THz pump pulse $A$ with a peak field $E_{A,p} = 500 \text{ kV/cm}$ has a value of approximately $5 \times 10^{17}$ photons/cm$^2$. With the help of the absorption coefficient $\alpha_{\text{abs}} = (4\pi\nu/c_0)n_{\text{m}}(\nu)$ and the thickness $d = 5 \times 10^{-3} \text{ cm}$ of the water jet, one derives a flux of $2.8 \times 10^{17}$ photons/cm$^2$ absorbed in the sample. On the other hand, the area density of water molecules in the relevant sample volume is $1.7 \times 10^{20}$ molecules/cm$^2$, i.e., less than two in thousand water molecules are excited. This fraction is orders of magnitude too small to explain the change of $n(\nu)$ by some 10%. Second, the
observed effects may be the result of a temperature increase of the water after absorption of the THz pulse. The calculated heat jump generated by a single THz pulse with a peak field of $E_{A,P} = 500\, \text{kV/cm}$ has a value of only $\Delta T = 0.01\, \text{K}$ and, thus, can be safely neglected.

**Theoretical Methods and Results**

**Molecular Dynamics (MD) Simulations**

Fluctuating intermolecular electric fields in liquid water were evaluated with the help of atomistic MD simulations. The simulations were performed with AMBER 18 (ref 15) employing the TIP4P-FB$^{16}$ water model because of its excellent performance, e.g., in reproducing the experimental oxygen-oxygen radial distribution function (Figure S5a). Simulations were performed with the PMEMD program and the GPU accelerated PMEMD.CUDA program (Tesla K80).$^{17,18}$ Equilibration of a cubic box of 216 water molecules was performed by initial minimization of the system (50000 optimization steps). Subsequent MD (1.3 ns, NPT ensemble, 0.5 fs time step) was performed to obtain convergent density (pressure 1.0 bar, 4 ps pressure relaxation time, Langevin dynamics with 5 ps$^{-1}$ collision frequency for temperature regulation, 298 K). In all MD simulations periodic boundary conditions were imposed with electrostatic interactions evaluated with the particle mesh Ewald method, using a cut-off for long range interactions of 7 Å. MD simulations (800 ps) were subsequently performed in the NVT ensemble with time steps of 0.5 fs.

**Figure S5.** (a) Simulated oxygen-oxygen radial distribution of liquid water. (b, c) Molecular 1b$_1$ and 3a$_1$ orbitals of H$_2$O (HOMO and HOMO-1 orbitals; HF/cc-pVDZ level of theory). (d, e) Projection axes of the electric field amplitude at molecular orbital centers.
Electric field amplitudes experienced by the central water molecule were evaluated for a 200 ps segment of the MD trajectory (Figure S6a-d). They were calculated at the midpoint of the hydrogen-hydrogen axis, at the approximate center of the 1b₁ molecular orbital (HOMO, highest occupied molecular orbital), and at the approximate center of the 3a₁ molecular orbital (HOMO-1 orbital) of the H₂O molecule. Respective electric field amplitudes were subsequently projected on the H…H axis, on the 1b₁ molecular orbital axis and on the bisector axis of the H-O-H angle (3a₁ molecular orbital axis). Relative electric field fluctuation amplitudes at the position of the 3a₁ molecular orbital (Figure 1b) were obtained by subtracting the mean value of the electric field.

We find fluctuation amplitudes on the order of 50-100 MV/cm, due to ultrafast sub-100 fs librational motion. Spikes of particular high electric field amplitudes at the position of the 3a₁ molecular orbital occur every 60 to 100 ps during periods of transiently under-coordinated water configurations with ~3 hydrogen bonds during large angular jump events triggering a reorganization of the hydrogen bond network. Such events are geometrically characterized as dimeric water structures with a particular short O…O distance that sample the low end of the radial distribution function g(r) (Figure S7b).

**Figure S6.** Fluctuating electric field in liquid water. (a-d) Fluctuating electric field plotted as a function of time and evaluated at the midpoint of the hydrogen-hydrogen (H…H) axis, at the approximate center of the 1b₁ molecular orbital and at the approximate center of the 3a₁ molecular orbital of the H₂O molecule (cf. Figure S5d,e) followed by projection of the electric field amplitude on the (a) H…H axis, (c) the 1b₁ molecular orbital axis, and (b, d) the bisector axis of the H-O-H angle. (e-h) Corresponding histograms of the electric field trajectory.
The time correlation function of the fluctuating electric field (Figure S7a) displays an initial decay on a 20-fs time scale, followed by slower sub-picosecond decay components. This result is in good agreement with previous theoretical work\textsuperscript{19} and photon-echo peak shift data for solvated electrons.\textsuperscript{20} The initial decay defines the highest fluctuation frequencies of the electric force the water environment exerts on charges embedded in it. This interaction leads to decoherence of quantum-coherent excitations such as electron wavepackets, and to charge recombination as is discussed in the next section.

**Field-Induced Electron Tunneling and Charge Separation in Liquid Water**

The spatio-temporal evolution of the electron wavefunction $\psi(x,t)$ in tunneling from the highest occupied molecular orbitals into continuum states of the water environment is a key process of the electron dynamics observed in the experiments. For analyzing the relevant physical mechanisms, we calculated the coherent evolution of $\psi(x,t)$ of an electron in a one-dimensional (rectangular) model potential exposed to a time-dependent Gaussian electric field. We have chosen the parameters of the potential, the p-like initial electron state, and the applied external electric field such that the situation mimics a water molecule subject to the strongest electric-field spike shown in Figure 1b of the article. In the calculations, we determined the time-evolution operator by diagonalizing the (time-dependent) Hamilton operator in each time step.
Results of the simulation are shown in Figure S8. In panel (a) we show the model potential at $t = 0$, i.e., at the maximum electric field $E(t = 0) = 250$ MV/cm together with the electron density $|\phi_2(x)|^2$ of the initial state (blue curve), i.e., the first excited state (P orbital) with an energy of 11 eV below the ionization continuum. Panel (b) shows the electric field (black line) together with the emitted electron wavepacket emerging at a distance $x = 5$ nm from the potential well as a function of real time $t$ (red line). In panel (c), the time-dependent density $|\psi(x,t)|^2$ of the coherently evolving electron wavefunction $\psi(x,t)$ is plotted on a length scale up to $x = 2.5$ nm for different times $t$ between 0 and 1 fs (logarithmic ordinate scale).

The wavepacket dynamics shown in Figure S8 exhibits the following properties of the tunneling process: (i) the released electron wave packet has a duration of approximately 2 fs (FWHM), much shorter than the driving electric field of a 10-fs duration. This behavior is due to the highly nonlinear dependence of the tunneling probability on the driving field (Figure S8d), i.e., the high field amplitudes in a narrow time interval around $t=0$ are most relevant. (ii) In space, the wavepacket strongly broadens during propagation within the first few femtoseconds and reaches nanometer dimensions, which are much larger than the spatial extension of 0.15 nm of the initial bound wavefunction. (iii) The wavepacket is a coherent superposition of propagating states in the ionization continuum of the unperturbed potential delocalized on a length scale corresponding to many water molecules.

The electron tunneling probability $P_T$ per water molecule calculated as a function of the peak value $E_{\text{peak}}$ of the Gaussian driving field [panel (b)] by spatially integrating the electron density $|\psi(x,t)|^2$ outside the binding potential, i.e., for $x \geq 0.25$ nm and a fixed time $t = 1$ fs, and normalizing it to the total electron density, i.e., the integral of $|\psi(x,t)|^2$ from $x = 0$ to infinity. At $t = 1$ fs, there is a clear spatial separation of the electron density outside the binding potential from the potential barrier. As shown in Figure S8d, the tunneling probability $P_T$ rises from several $10^{-12}$ to several $10^{-5}$, i.e., by 7 orders of magnitude, upon an increase of $E_{\text{peak}}$ from 150 MV/cm to 450 MV/cm. For an extrapolation of this result to the fluctuating electric field in liquid water, we average the tunneling probability $P_T$ over the ~65 electric field peaks occurring in the 200 ps interval of our MD trajectory (Figure S6d). This procedure gives an average tunneling probability of $P_{T,av} = 3.4 \times 10^{-7}$.

So far, we have considered the quantum-coherent spatio-temporal evolution of the electron wavepacket. As long as this wavefunction retains its coherence, it would essentially
revert to its original form because after the end of the electric field the attractive Coulomb interaction between electron and parent ion prevails. In other words, there would be no ionization eventually. In liquid water, however, the Coulomb interaction of the electron with the fluctuating electric field induces decoherence, a necessary condition for making charge separation irreversible. The decoherence rate $\gamma_{\text{decoh}}$ can be estimated with the following expression derived in ref 21:

$$\frac{\gamma_{\text{decoh}}}{\gamma_{\text{fluc}}} = \frac{4\pi^2 m_e kT}{h^2} \Delta x^2 = \left[\frac{\Delta x}{l_t}\right]^2$$

Here, $\gamma_{\text{fluc}} \approx 5 \times 10^{13} \text{ s}^{-1}$ is the fluctuation rate of the electric field in water (cf. fast decay of the correlation function in Figure S7a), $\Delta x$ the spatial separation of the two parts of the electron wavefunction (on the parent ion and outside of it), and $l_t = \hbar/[2\pi(m_e k T)^{1/2}] \approx 1.75 \text{ nm}$ the thermal deBroglie wavelength of an electron at a temperature $T = 300 \text{ K}$ ($h$: Planck’s constant, $k$: Boltzmann's constant). For a spatial separation $\Delta x \approx 4 \text{ nm}$ the electron reaches after 2-3 fs, one estimates $\gamma_{\text{decoh}} \approx 4\gamma_{\text{fluc}} = 2.6 \times 10^{14} \text{ s}^{-1}$, corresponding to a decoherence time on the order of 4 fs. This number is very similar to decoherence times of the solvated electron calculated from quantum-classical MD simulations.\textsuperscript{22} Decoherence suppresses propagation of the electron wavepacket and effectively localizes it at the distance $\Delta x$.

In a water environment in thermal equilibrium, i.e., without an external THz field, the relevant energy determining the chemical equilibrium constant in the law of mass action of this locally charge-separated state is approximately 1 eV higher than that of the neutral ground state, as estimated from the charge separation free energy of water ($2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$, ref 23). The charge separated state decays predominantly via recombination with its ionized parent molecule. This radiationless decay is induced by the fluctuating forces from the water environment coupling the two electronic states, a process analogous to the radiationless relaxation of the solvated electron from its excited state to the ground state. In ref 22, the latter process has been analyzed with the help of quantum-classical molecular dynamics simulations. This treatment gives an excited state lifetime on the order of 100 fs, while experiments with a 10 fs time resolution give a value of 50 fs.\textsuperscript{24}

The equilibrium concentration of water molecules in the short-lived charge-separated state is estimated as follows: The generation rate $G$ of the charge separated species per molecule given by $G = R_{\text{peak}} P_{T,av} = 1.1 \times 10^5 \text{ s}^{-1}$ with $R_{\text{peak}} = 65/200 \text{ ps}^{-1} = 3.33 \times 10^{11} \text{ s}^{-1}$, the rate at which
electric field peaks occur in the MD trajectory (Figure S6d). Taking a decay time of the charge-separated state of $\tau_{CS} = 50$ fs, one derives an equilibrium concentration of charge separated species $c_{CS} = c_{H2O} \times G \times \tau_{CS} = 3 \times 10^{-7}$ M ($c_{H2O} = 56$ M, bulk water concentration). This number is close to the concentration of $H_3O^+$ and $OH^-$ ions of $10^{-7}$ M at pH=7. Because of this very small concentration, a spectroscopic observation of the charge-separated species is very difficult.

The application of the external THz field induces a spatial separation of the electron from the parent ion, suppresses recombination, and leads to the formation of spatially separated solvated electrons. The maximum concentration of solvated electrons that can be generated this way is given by $c_{e,max} = \eta \times c_{H2O} \times G \times \Delta t_{THz}$ where $\eta$ is the quantum yield of charge separation and $\Delta t_{THz}$ the duration of the THz pulse. For $\eta = 1$ and a THz pulse duration $\Delta t_{THz} = 2$ ps, one estimates $c_{e,max} \approx 12 \mu$M, a value in the range of the concentration of solvated electrons observed in the experiments. In view of the limitations of the tunneling model and the MD simulations, we would like to emphasize that such estimates serve for illustrating the order of magnitude of the relevant concentrations rather than giving a quantitative description.

**Figure S8.** (a-c) Spatio-temporal aspects of field-induced electron tunneling (for details see text). (d) Electron tunneling probability $P_T$ as a function of the peak electric field of a 10-fs Gaussian driving pulse (cf. panel (b)).
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