

Probing the low-energy electron-scattering dynamics in liquids with high-harmonic spectroscopy

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High-harmonic spectroscopy (HHS) is a nonlinear all-optical technique with inherent attosecond temporal resolution, which has been applied successfully to a broad variety of systems in the gas phase and solid state. Here, we extend HHS to the liquid phase, and uncover the mechanism of high-harmonic generation (HHG) for this phase of matter. Studying HHG over a broad range of wavelengths and intensities, we show that the cut-off (E_c) is independent of the wavelength beyond a threshold intensity, and find that E_c is a characteristic property of the studied liquid. We explain these observations within an intuitive semi-classical model based on electron trajectories that are limited by scattering to a characteristic length, which is connected to the electron mean-free path. Our model is validated against rigorous multi-electron time-dependent density-functional-theory calculations in, both, supercells of liquid water with periodic boundary conditions, and large clusters of a variety of liquids. These simulations confirm our interpretation and thereby clarify the mechanism of HHG in liquids. Our results demonstrate a new, all-optical access to effective mean-free paths of slow electrons (≤ 10 eV) in liquids, in a regime that is inaccessible to accurate calculations, but is critical for the understanding of radiation damage to living tissue. Our work also establishes the possibility of resolving sub-femtosecond electron dynamics in liquids, which offers a novel, all-optical approach to attosecond spectroscopy of chemical processes in their native liquid environment.

I. INTRODUCTION

High-harmonic generation (HHG) is an extremely nonlinear process that occurs when a strong laser field interacts with gaseous, solid, or liquid targets. It results in an up-conversion of photon energies up to the tender X-ray regime [1], and has been well established as a highly versatile table-top source of attosecond pulses [2–8]. HHG has also led to a new branch of attosecond spectroscopy that relies on extracting dynamical information directly from measured spectra, known as high-harmonic spectroscopy (HHS). This technique has already enabled imaging of molecular orbitals [9–11], the reconstruction of charge migration [12] and time-dependent chirality [13], as well as tunneling-ionization dynamics [14]. While the majority of these applications are based on gas-phase HHG, solid-state HHG has recently attracted considerable attention because of its potentially higher efficiency and access to ultrafast dynamics and light-driven phase transitions in condensed matter [15–18]. A prerequisite for an accurate interpretation of the underlying dynamics from the measured high-harmonic spectra lies in the

formulation of a broadly applicable theoretical model.

In the gas phase, this understanding and modelling is often based on the semi-classical three-step model (TSM) [19], or its quantum-mechanical extension [20], which describes HHG as a set of electron trajectories initiated by a tunneling process. This approach is usually in good agreement with full *ab-initio* calculations, and allows interpretation of dynamical information in HHS [21, 22]. A hallmark of the model is that it correctly predicts the HHG cut-off and its quadratic dependence on, both, electric-field amplitude and wavelength, connected to the most energetic returning electron trajectory [23, 24]. For HHG in crystalline solids a similar trajectory picture, based on the material’s band structure, can in principle be applied in momentum space (after applying the Bloch theorem) [15, 16, 25–30]. The predicted cut-off energy was shown to scale linearly with both field amplitude and wavelength [15–17, 29, 31–34]. However, there still remains some debate about the scaling based on the active HHG mechanisms in different solid systems [18, 35–37]. Moreover, the direct comparison of crystalline and amorphous solids of the same composition (quartz vs. fused silica) has shown that the cut-off energy is much lower in the latter under the same driving fields [38]. Whereas this observation remains to be fully explained, it points to the importance of long-range order in condensed-phase HHG.

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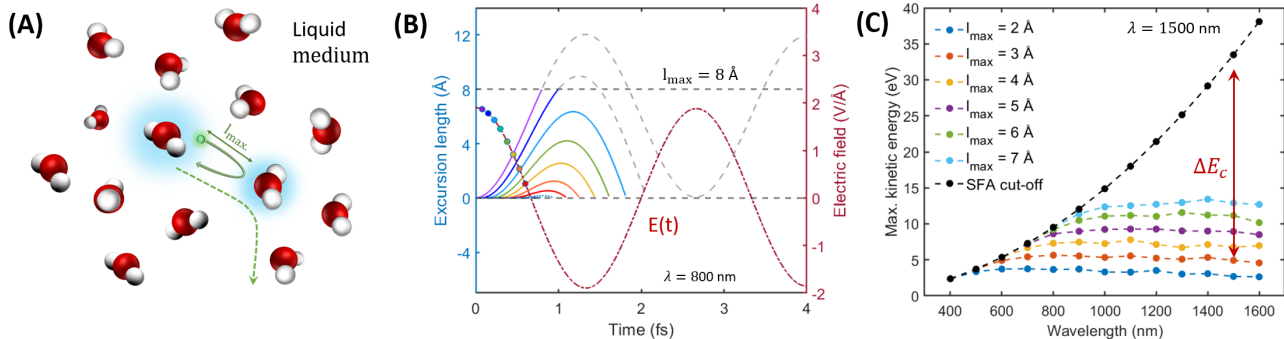


FIG. 1. **Effect of electron scattering on HHG spectra in liquids** (A) Schematic illustration of the extended trajectory-based semiclassical model. An electron (green) is ionized by the laser field, accelerated and either recombines directly with its parent ion (solid green arrows), or scatters off another molecule (dashed green arrows). (B) The returning electron trajectories from the standard TSM within an 800-nm driving laser field of 1.9 V/\AA . The dots on the electric field represent the ionization times of the electrons (the colour of dots corresponding to the colour of the respective trajectories). The grey dashed line denotes the limited excursion length (l_{max}) imposed by scattering. (C) Wavelength-scaling of E_c in the absence (standard TSM: black dashed line) and presence (l_{max} -limited: colored lines) of scattering for a laser intensity of $5 \times 10^{13} \text{ W/cm}^2$. The observable manifestation of scattering is a decrease in the cut-off by ΔE_c .

In contrast to gases and crystals, HHG in the liquid phase is far from being well understood. This is because it is challenging to: (i) experimentally measure HHG spectra from bulk liquids, (ii) numerically simulate strong-field physics in liquids, and (iii) there is still no intuitive model that describes non-perturbative light-driven dynamics in liquids. Liquids, therefore, present a unique case where neither gas (single isolated particle approach) nor solid-state (Bloch theorem and periodic boundary conditions) approaches are strictly applicable. This gap in knowledge limits potential applications to ultrafast spectroscopy that are especially appealing in liquid targets. Only very recently, HHG in bulk liquids have been demonstrated beyond the visible domain utilizing the flat-jet approach [39–41]. However, fundamental questions about the dominant HHG microscopic mechanisms, the cut-off scaling with wavelength or the macroscopic effects still remain unanswered. As most bio-chemical processes take place in a liquid environments, detailed experimental results and the development of theoretical tools capable of describing the HHG process are crucial for understanding the electron dynamics in liquids.

Here, we experimentally measure high-harmonic spectra from liquid water and alcohols over a broad range of laser wavelengths. We observe that the HHG cut-off energy (E_c) is wavelength independent, which is in strong contrast with the semi-classical TSM for gases [24], as well as some models for solid-state HHG [15, 16, 25, 26, 28–30, 32]. This implies that potentially new mechanisms are relevant in liquid HHG, and that the structural arrangement of the liquid (i.e. the lack of long-range order) might play a crucial role in the dynamics. We investigate this experimental result with a combination of newly developed *ab initio* techniques, and introduce a semi-classical model for HHG in liquids. Our proposed

model takes electron scattering into account and successfully reproduces the observed wavelength-independence of E_c . We identify a key parameter in HHG from the liquid phase - the effective mean-free path (λ_{MFP}) - which we extract from measurements using the extended semiclassical model. Our results shed light on fundamental strong-field-driven processes in liquids, that are distinct from what happens in either gas phase or solid-state environments, and form the basis of a first intuitive picture of HHG in liquids.

II. RESULTS

A. Effect of electron scattering on HHG

One noticeable difference between HHG in dilute gases and in condensed phases is the significance of electron scattering in the latter. We therefore start our analysis by formulating a semi-classical real-space trajectory picture similar to the TSM of gas-phase HHG, but include scattering from the beginning. Within this picture, harmonic photons are emitted as a result of electron trajectories that recombine with their parent ion. We assume that an electron may be photo-excited to the conduction band of the liquid at any time, t_{ion} during the laser cycle. Following this, Newtonian equations of motion can be analytically solved to obtain the electron trajectory along the laser polarization axis ($x(t)$, given in atomic units):

$$x(t) = \frac{qE_0}{m\omega^2} [\cos(\omega t) - \cos(\omega t_{\text{ion}}) + \omega(t - t_{\text{ion}}) \sin(\omega t_{\text{ion}})], \quad (1)$$

where E_0 is the laser field's peak amplitude, q and m are the electron charge and mass, and ω is its angular

frequency. Recombining trajectories arise by demanding that the electron returns to its initial position at time, t_{rec} , i.e. $x(t_{\text{rec}}) = 0$. This generates a set of short and long electron trajectories that are initiated at t_{ion} , recombine at t_{rec} , and have an emission energy of $\Omega = I_p + 0.5(dx/dt)^2$. The resulting cutoff in the absence of scattering is then obtained semi-analytically as $\Omega_{\text{cutoff}} = I_p + 3.17U_p$, where $U_p = E_0^2/4\omega^2$ is the classical ponderomotive energy. In the following, we consider only the trajectories for which the electrons return to their parent molecule, and ignore the recombination with other centers. We extend this model to include scattering processes of electrons with neighboring molecules: as a simple approximation, we assume that any trajectory that exceeds a characteristic length (denoted as l_{max}) will likely scatter and therefore not contribute significantly to the HHG emission (see Fig. 1A). That is, we neglect the contribution of scattered electrons to HHG.

This effectively translates to the following constraint - only recombining trajectories that uphold $|x(t_{\text{ion}} < t < t_{\text{rec}})| < l_{\text{max}}$ emit harmonics. The set of trajectories that fulfills these equations of motion are identical to those in the gas-phase case, except that trajectories extending beyond l_{max} are not included. As a consequence, this introduces a mechanism that modifies E_c and its scaling, and also naturally reduces E_c compared to the gas phase by ΔE_c .

Typical results for the model are presented in Fig. 1(C) where the cutoff energy follows the standard TSM prediction for short wavelengths (where both short and long trajectories do not surpass l_{max}), but rapidly saturates around 800 nm where the cutoff trajectories in the gas phase exceed a distance of few angstroms. We will show below that this simple model reproduces the main features of both measurements and *ab-initio* calculations. We note that the non-scaling of the cutoff with wavelength is reproduced by the semi-classical model for any choice of l_{max} , which only changes the maximal E_c (see Figure 1(B)). Moreover, this behavior does not depend on the laser intensity (see Supplementary Material (SM), Section S4.C and Fig. S6).

We emphasize that this simple picture likely does not capture the full physics of strong-field light-matter interactions in the liquid state. Nonetheless, the fact that the very peculiar cutoff behavior (compared to other phases of matter) is reproduced is encouraging. We also note that some of the approximations utilized here might not be accurate in the liquid phase (e.g. the SFA or neglecting multi-center recombination), but: (i) corrections accounting for these effects can conceptually be added, and (ii) the characteristic physical behaviour of the cut off is independent of these approximations, as demonstrated by the *ab-initio* results.

B. Experimental results

The experimental setup is shown in Fig. 2(A). It consists of a laser system delivering 30-40 fs laser pulses with adjustable central wavelength (800-1800 nm) and a high-vacuum chamber containing the liquid flat-jet system and a flat-field imaging spectrometer. Further details are given in the Methods section and in the SM, Section S1. We have measured high-harmonic spectra of water (H_2O) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) from the liquid and gas phases of each species at different wavelengths. A typical background-corrected HHG spectrum of water is shown in Fig. 2(B). The liquid- and gas-phase spectra are recorded back-to-back to minimize drifts in the experimental parameters. Figure 2(B) presents HHG spectra for H_2O with the top and bottom panels directly comparing the gas- and liquid-phase signals recorded with 800-nm and 1500-nm drivers, respectively. The liquid-phase harmonics are roughly ten times brighter than the gas-phase harmonics. Both spectra exhibit a distinct plateau, followed by a sharp cut-off region where the harmonic yield drops exponentially. Notably, the cut-off energy E_c is around H9 in the liquid spectrum and H17 in the gas spectrum. That is, the liquid phase shows a much-reduced cut-off compared to the gas phase. For generation in H_2O , the gas-to-liquid difference ΔE_c is about 10 eV at 800 nm and about 26 eV at 1500 nm. This observation is a first hint at different dominant mechanisms in each phase of matter, which prevents the emission of higher energy photons from the liquid.

We next explore the wavelength scaling of E_c . This basic property reveals information about the laser-driven electron dynamics in the liquid phase. Figure 2(C) and (D) shows measured high-harmonic spectra from water and ethanol at two different wavelengths, respectively. All spectra show the characteristic envelope with a plateau and a sharp cut-off region. This allows us to define the cut-off energy E_c as the intersection point of two lines that connect the plateau and cut-off intensities, respectively. The details of this procedure that is followed throughout this work are given in Section S3. For both liquids, all spectra share the same cut-off energy of the plateau, i.e. $E_c = 14.2$ eV and $E_c = 11.4$ eV in the case of water and ethanol, respectively. These results substantially differ from the gas-phase results, as well as the standard TSM, which both show that for the used laser intensities the cut-off should have extended by ~ 25 eV between the 800 nm and 1500 nm drivers.

Notably, E_c in ethanol is ~ 3 eV smaller than in water. We note that the difference in cut-off energies between these liquids is substantially larger than the difference in their band gaps (8 eV for H_2O and ~ 8.5 eV for ethanol [43, 44]). This is a crucial point, since in the gas phase, and within the standard TSM, the cut-off should only vary by this value. The larger variation is indicative of the fact that the liquid structure, and more precisely, the electron dynamics in the liquid-phase, are playing an additional and yet to be specified role.

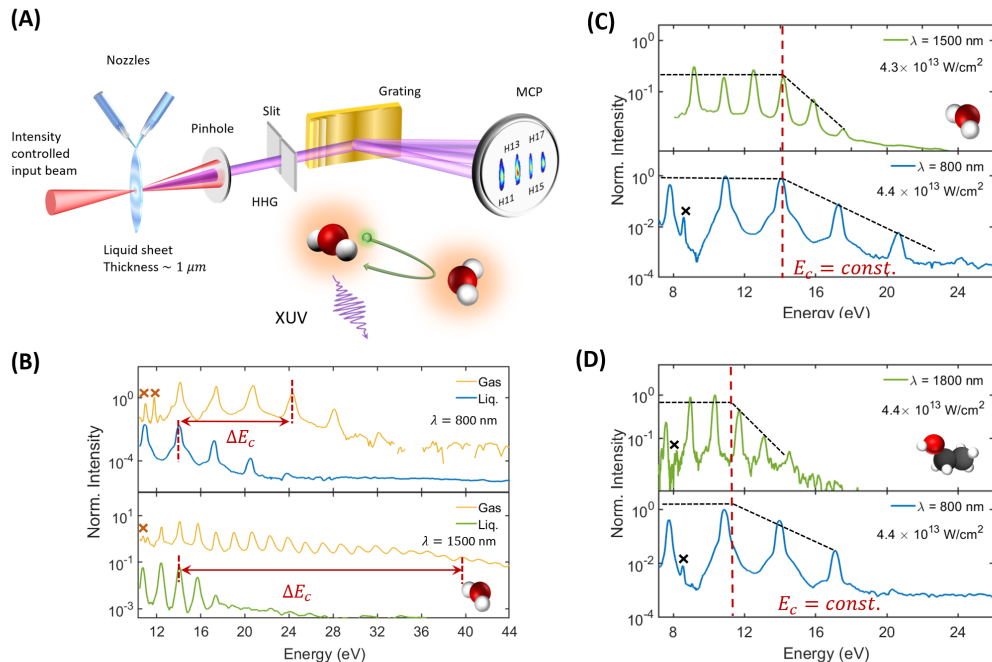


FIG. 2. **Wavelength scaling of HHG in liquids and gases** (A) Schematic of the experimental setup. Laser pulses with a central wavelength of 800 nm, 1500 nm or 1800 nm are focused on the flat liquid jet to generate high harmonics. The generated high harmonics pass through a slit into the XUV spectrometer that disperses and records the different harmonic orders. (B) High-harmonic spectra from liquid and gaseous water recorded under identical conditions using an 800-nm (top) or 1500-nm (bottom) driver. The difference in cut-off is indicated by the red arrows. The normalized liquid spectra are vertically scaled by a factor of 500(800 nm) and 1000(1500 nm) with respect to the gas spectra for better visualization. (C) High-harmonic spectra from liquid water recorded at different wavelengths, but very similar intensities. (D) High-harmonic spectra from liquid ethanol recorded at different wavelengths, but very similar intensities. In all panels, crosses mark the harmonics reflected in the second diffraction order of the grating.

We thus conclude two main points: (i) in the liquid-generated high-harmonic spectra the position of the cut-off depends on the nature of the liquid sample, and (ii) the cut-off energy is wavelength independent, at least in water and ethanol. In what follows, we will show that these results are reproduced by *ab-initio* calculations.

C. Numerical results: time-dependent density-functional theory

We now compare these experimental findings and the results of our simple model to two newly developed *ab initio* techniques for describing the strong light-matter response of liquids. Figure 3 presents simulated HHG spectra from liquid water that are based on a combination of well-established Car-Parrinello molecular dynamics (CPMD) [46] and time-dependent density-functional theory (TDDFT) [47] simulations in a periodic supercell including 64 water molecules at the experimental density of 1 g/cm^3 and temperature of 300 K (for details see Ref. [42] and the SM, Section S4.A). This is a real-

istic, currently tractable description of HHG in liquids. Overall, very good agreement with the experimental results is observed, and in particular, the cut-off energy and its wavelength independence are well reproduced in Figure 4. Note that since the DFT-GGA underestimates the liquid-water band gap, the calculated HHG cutoff is about 1.5 eV lower than the experimental value. This numerical approach qualitatively reproduces the experimentally observed weak dependence of the cut-off on the laser intensity (see discussion in SM, Section S4.A). This further supports that the above experimental findings are a signature for the microscopic mechanism in liquid and not the results of macroscopic effects, which are absent in our theoretical modeling. This result is complemented by a second set of *ab-initio* TDDFT calculations based on molecular clusters which employ some additional approximations (for details, see ref. [52]). The advantage of this approach is that it allows for faster calculations while still leading to accurate results; thus, it can be employed for a more detailed numerical study. Figure 3(B) shows simulation results of HHG in liquid water with the cluster approach for many wavelengths at a fixed laser intensity.

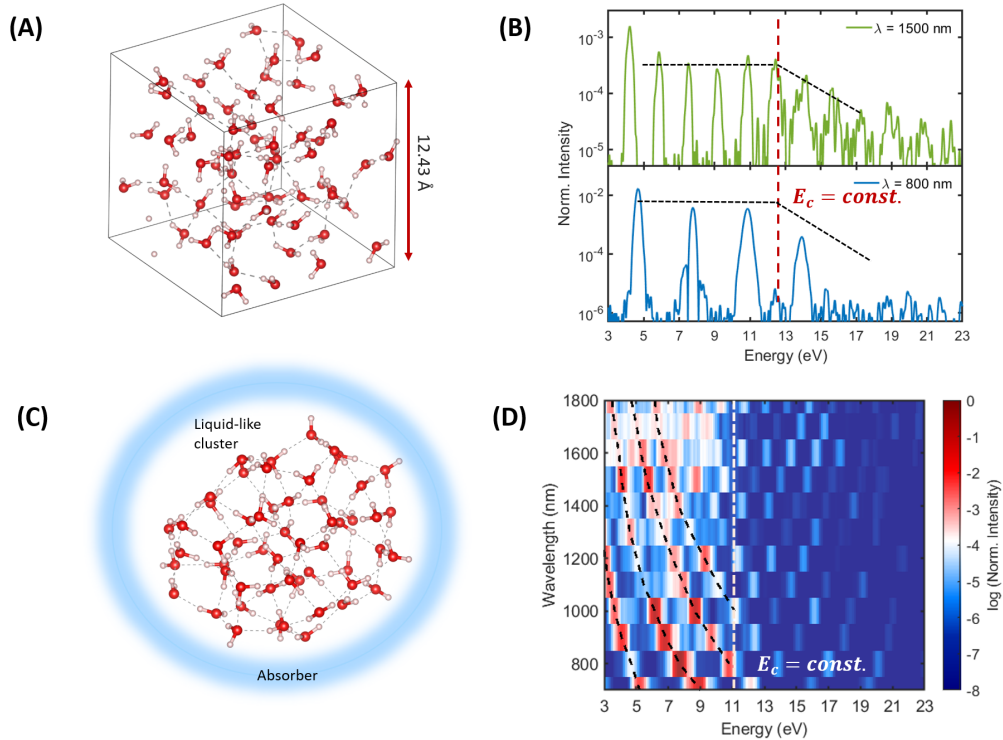


FIG. 3. **TDDFT calculations in the supercell approach** (A) A schematic representation of liquid water in supercell approach. There are 64 water molecules in a cubic cell at the experimental density of 1 gr/cm^3 ; periodic boundary conditions are implemented in 3D where each lattice vector is of length $\sim 12.43 \text{ \AA}$. (B) HHG spectra calculated for liquid water using two different wavelengths. The peak intensity for all wavelengths is the same and it is equal to approximately 20 TW/cm^2 . These HHG spectra are averaged over 5000-5500 water molecules in the liquid phase (for details see the SI and Ref. [42]). **TDDFT calculations in the cluster approach** (C) Illustration of the computational approach with a cluster radius of $\sim 15.5 \text{ \AA}$. (D) Wavelength scaling of high-harmonic spectra calculated for a constant peak intensity.

Clearly, the same trend is observed and the cut-off is independent of the wavelength, at least in the range of 500 nm - 1800 nm. In the SM, Section S4.B, we show that the cut-off with the cluster approach is similarly weakly dependent on the laser intensity (above a saturation intensity of $5 \cdot 10^{13} \text{ W/cm}^2$), and that the wavelength independence of the cut-off is maintained for other laser intensities, as well. With the cluster approach, we also perform calculations for two additional liquids (ammonia, NH_3 , which is polar, and methane, CH_4 , which is non-polar). In the SM, Section S4.B, we show that HHG calculations in liquid NH_3 and liquid CH_4 also predict the same wavelength independence of E_c . These results, in combination with our measurements, lead to the conclusion that this characteristic non-scaling of E_c is a fundamental general and unique property of the liquid-phase HHG, and applies both for polar and non-polar liquids. These accurate quantum-dynamical simulations reproduce and complement our experimental findings, which validates the broad applicability of our conclusions.

III. DISCUSSION AND CONCLUSIONS

We have so far demonstrated the wavelength-independence of E_c , both experimentally and theoretically, (Figs. 2 and 3) and we have shown that a scattering-limited trajectory model reproduces this behavior (Fig. 1). Importantly, a main conclusion arising from our results is that if E_c is limited by the electron mean free path λ_{MFP} in the liquid, then E_c should scale with the density of the liquid. Figure 4 demonstrates that this is the case, both experimentally (A) and theoretically (C).

Very recently, some of us have reported the first measurements of the temperature of liquid flat-jets [45]. The temperatures, measured by Raman thermometry under conditions identical to those of the present HHG experiments, range from $\sim 300 \text{ K}$ at the top, to $\sim 255 \text{ K}$ at the bottom of the first sheet, translating to a density variation of close to 5% (Fig. 4(B)) in the case of ethanol. Over this range of conditions, E_c is found to decrease by $\sim 2 \text{ eV}$ (panel (A)). The same trend is also observed in the calculations performed on liquid water (panel (B)). Having

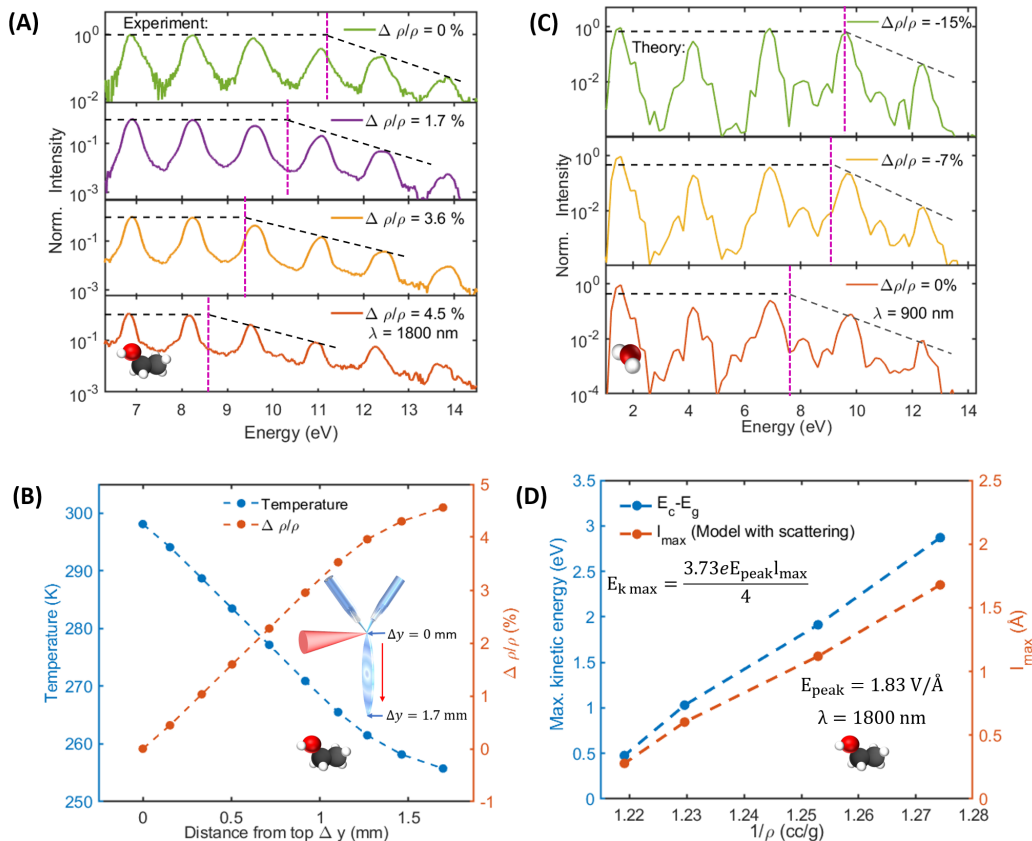


FIG. 4. **Scaling of the cut off with the density of the liquid** (A) Measured high-harmonic spectra (1800 nm driver, $6 \times 10^{13} \text{ W/cm}^2$) as a function of vertical position on the liquid flat-jet, corresponding to the indicated change in density. The change in density has been determined from an absolute temperature measurement carried out by Raman thermometry [45], as shown in (B). (C) Spectra calculated with the *ab-initio* cluster approach (900 nm, $4 \times 10^{13} \text{ W/cm}^2$) for varying densities ($\Delta\rho/\rho = -15\%$, -7% , 0% , 7%). The harmonics above the cut-off show a systematic decrease in yield with increasing density. (D) Maximal observed kinetic energy as a function of the inverse density for ethanol and the corresponding l_{\max} obtained from the formula shown in the inset (derived in SM, Section S4.D). The vacuum electric field is corrected using the 1800-nm refractive index in ethanol, to obtain the peak electric field (E_{peak}) inside the liquid.

measured E_c over a range of densities, we can now verify how the maximal energy $E_{k,\max}$, gained by the electron from the driving laser field, scales with the density. Experimentally, we use $E_{k,\max} = E_c - E_g$, where E_g is the band gap of the liquid. We find that $E_{k,\max}$ scales linearly with the inverse density (blue symbols in Fig. 4(D)). This type of scaling precisely corresponds to the prediction of our simple trajectory-limited model (Fig. 1), because $\lambda_{\text{MFP}} = 1/(n\sigma) \propto 1/(\rho\sigma)$.

This conclusion is further supported by converting the measured E_c to the corresponding maximal excursion length l_{\max} . As we show in the SM, Section S4.D, we find that $E_{k,\max} = 3.73/4 * e * E * l_{\max}$. A direct consequence of this relation is that it allows us to retrieve l_{\max} from the experimental spectra, provided that they were recorded under conditions where the wavelength-independence of the cut-off is observed, which is the case here (see Fig. 2D). The orange symbols in Fig. 4D show

that l_{\max} also scales linearly with the inverse density.

We therefore conclude that all experimental and theoretical evidence available at present agrees on the fact that E_c is proportional to the maximal excursion length of the laser-driven electrons in the liquid phase. This suggests that it should be possible to accurately determine effective electron mean-free paths (MFPs) from liquid-phase HHG spectra.

Electron MFPs play a very important role in describing electron-driven processes in the liquid phase, but they are notoriously difficult to measure and calculate, at least at low energies. The interest in developing new methods for accessing these quantities is therefore considerable and relevant for many physical processes. Here, we do not attempt to determine the MFPs with high precision because this would require a more sophisticated scattering model, including a large number of different scattering channels (see Ref. [53] and references therein).

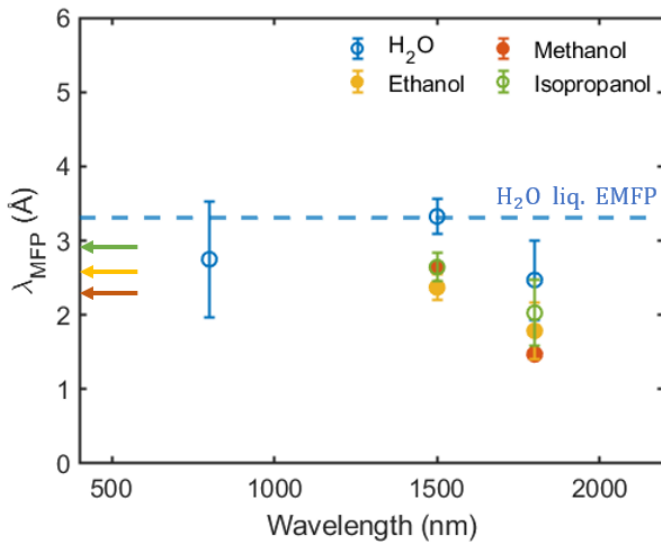


FIG. 5. **Comparison of the determined electron mean-free paths with literature data.** Mean-free paths for electron scattering in the liquid phase determined from the experimentally observed cut-off energies (E_c) as a function of laser wavelength. The dashed blue line indicates the elastic mean-free path for liquid water [48] at $E_k = 4.5$ eV. The arrows indicate the value of the mean-free paths obtained from the integral elastic scattering cross sections of the corresponding alcohols in the gas phase [49, 50] at E_k of ~ 3 -4.5 eV, using the number densities obtained from the densities of different liquids at 20° C [51].

Instead, we aim at retrieving an effective MFP, which is best thought of as containing all types of scattering processes. Since the elastic scattering cross sections are by far dominant at the very low kinetic energies (~ 10 eV) of interest here [48, 53–55], we compare our results to the elastic MFPs in Fig. 5. In this comparison, we use $\lambda_{\text{MFP}} = l_{\text{max}}$, taking into account that the electron travels up to the maximal excursion length before getting scattered. In the SM (Fig. S10), we show that this simple approximation is physically meaningful because replacing the “sharp” truncation of the trajectories (at the travel distance l_{max}) with an exponential distribution of path lengths (inherent to the definition of λ_{MFP}) leaves E_c unchanged. Figure 5 compares the λ_{MFP} values obtained from the HHG spectra (symbols) with the available literature values. In the case of liquid water, we are comparing to the most recent MFPs (blue dashed line), which were determined from a Monte-Carlo simulation of experimental liquid-microjet data using the most accurate *ab-initio* differential scattering cross sections available to date [48]. In the case of the alcohols, liquid-phase MFPs have to our knowledge not been reported in the literature so far. We are therefore comparing our results to MFPs determined from the corresponding experimental gas-phase elastic scattering cross sections and the known number densities of the alcohols. The agreement is very good in all cases, confirming the possibility to retrieve

electron MFPs from liquid-phase HHS. To summarize, we explored here the microscopic mechanisms responsible for liquid HHG with a combination of experimental and theoretical methods. Our measurements in water and ethanol show that contrary to crystals and gases, the cut-off energy in liquid HHG is mostly independent of the laser wavelength. Microscopic quantum mechanical calculations based on both supercells and clusters agree with this result, and show that it extends to other liquids and laser conditions. We proposed an extended semi-classical model for the electron dynamics in the liquid to explain this result. The model incorporates effects of ultrafast scattering of electrons off neighboring molecules, which are shown to reduce the HHG cut-off compared to the gas phase case through the spatial limitation of electron trajectories. The model reproduces well the wavelength independence of the HHG cut-off and highlights the importance of the electron mean-free path in liquids, indicating that this quantity is imprinted onto the high-harmonic spectra and can be retrieved. We also expect that our results would be highly relevant for HHG from amorphous solids [38, 56]. Our work paves the way to a deeper understanding of the strong-field dynamics in disordered condensed phases, and to resolving attosecond dynamics in liquids.

METHODS

The experimental set-up consists a 1 kHz Ti:Sapphire laser delivering ~ 30 fs pulses at 800 nm. Driving wavelengths of 1500 nm and 1800 nm are obtained by optical parametric amplification (OPA) of the 800 nm pulses, respectively. The driver beams are focused with a spherical mirror on a sub-micron-thin liquid flat-jet target, further described in Refs. [39, 40]. The beam intensities are calculated from the harmonic cut-off energy of the gas-phase measurements, using the semi-classical TSM[19]. The emerging high harmonics are analysed with a custom-built XUV spectrometer consisting of an aberration-free flat-field grating (SHIMADZU) and a multi-channel plate (MCP) coupled with a phosphor screen. The phosphor-screen image is recorded by a CCD camera. Each spectrum is typically integrated for 10 - 20 ms and measured 20 times. These spectra are averaged prior to all subsequent analysis. Further details of the experimental and theoretical methods are described in the SM, Section S1.

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AUTHOR CONTRIBUTIONS

A.M., Z.Y. and V.S. performed the experimental measurements and data analysis. O.N. carried out the cluster calculations and the numerical extended semiclassical model for HHG in liquids. Z. N. carried out the supercell calculations. N. T.-D. developed the analytical analysis of the HHG cutoff from the extended semiclassical model. A.R. and H.J.W. supervised the work. All the authors participated in the discussion of the results and contributed to the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

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Supporting Information for Probing low-energy electron-scattering dynamics in liquids with high-harmonic spectroscopy

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S1. EXPERIMENTAL DETAILS

A. Optical beamline

The experiments were performed with a 1 kHz regeneratively-amplified Ti:Sapphire laser (Coherent). From the laser output, 1.2 mJ beam was split and directed to a dedicated grating compressor delivering about 960 μJ , ~ 30 fs pulses with a central wavelength of 800 nm. The linear and vertically (s) polarized driving beam was focused on a liquid flat-jet target with a pair of metallic mirrors (protected Ag) in a Z-shaped configuration, where the first mirror was flat and the second mirror was spherical with $R = 800$ mm. The whole set was mounted on a common base plate on top of a manual translational stage to allow fine tuning of the overlap between the laser focus and the flat jet.

For experiments with mid-IR wavelengths (1500 nm and 1800 nm), a commercial optical parametric amplifier (OPA, HE-TOPAS from Light Conversion) pumped with 6.5 mJ, 30 fs pulses at 800 nm was used. The signal or idler beam was separated from the residual wavelengths exiting the OPA using a pair of dielectric mirrors for the particular wavelength and focused with the same set of two metallic mirrors.

B. Flat jet

The flat jet was created by two colliding cylindrical jets with about ~ 54 μm inner diameter. The samples were pumped via an HPLC pump (JASCO) into the interaction region with a flow rate ranging from 3 ml/min to 5 ml/min. The established flat jet was about 1 μm thick [1]. Due to evaporation, the liquid jet was surrounded by a region with high gas density, as compared to the

backing pressure in the target chamber ($\sim 5 \cdot 10^{-4}$ mbar), allowing a simultaneous probing of liquid and gas phases. All liquid samples have been used without further purification: pure Milli Q water with an electric resistivity of 18 M Ω and 99.8 % pure alcohols (ethanol, methanol, iso-propanol) from Sigma Aldrich.

S2. INTENSITY SCALING OF GAS- AND LIQUID-PHASE HHG SPECTRA

Figure S1 presents experimentally measured HHG spectra emitted from liquid water at 800 nm driving wavelength for different laser intensities in the range of $1.4 \cdot 10^{13}$ W/cm² to $5.8 \cdot 10^{13}$ W/cm². At each intensity, we compare the gas- (Fig. S1A) and liquid- (Fig. S1B) phase spectra. For the gas phase there is a systematic linear increase of the cutoff with laser intensity (red dashed line), in accordance with the standard TSM. In contrast, the liquid HHG cut-off energy remains roughly constant (blue dashed line). This effectively demonstrates that in the given intensity range, the cut-off energy of the liquid spectra is independent (or weakly dependent) on the peak laser intensity. We have also verified that this is the case for liquid ethanol.

A. Scaling of the highest harmonic order vs. scaling of the plateau's cutoff

In relating the present results to the previous literature, it is important to distinguish the scaling of the highest emitted harmonic order (E_{max}) from the scaling of the plateau's cutoff (denoted E_c , and discussed in the main text). Previous literature on condensed-phase HHG has mainly studied and discussed the scaling of E_{max} . Most prominently, this is the case for Ghimire et al. for the solid state [2] and for Luu et al. for the liquid phase [3]. In contrast, the overwhelming majority of the literature on gas-phase HHG has studied and discussed the scaling of E_c , influenced by the definition provided

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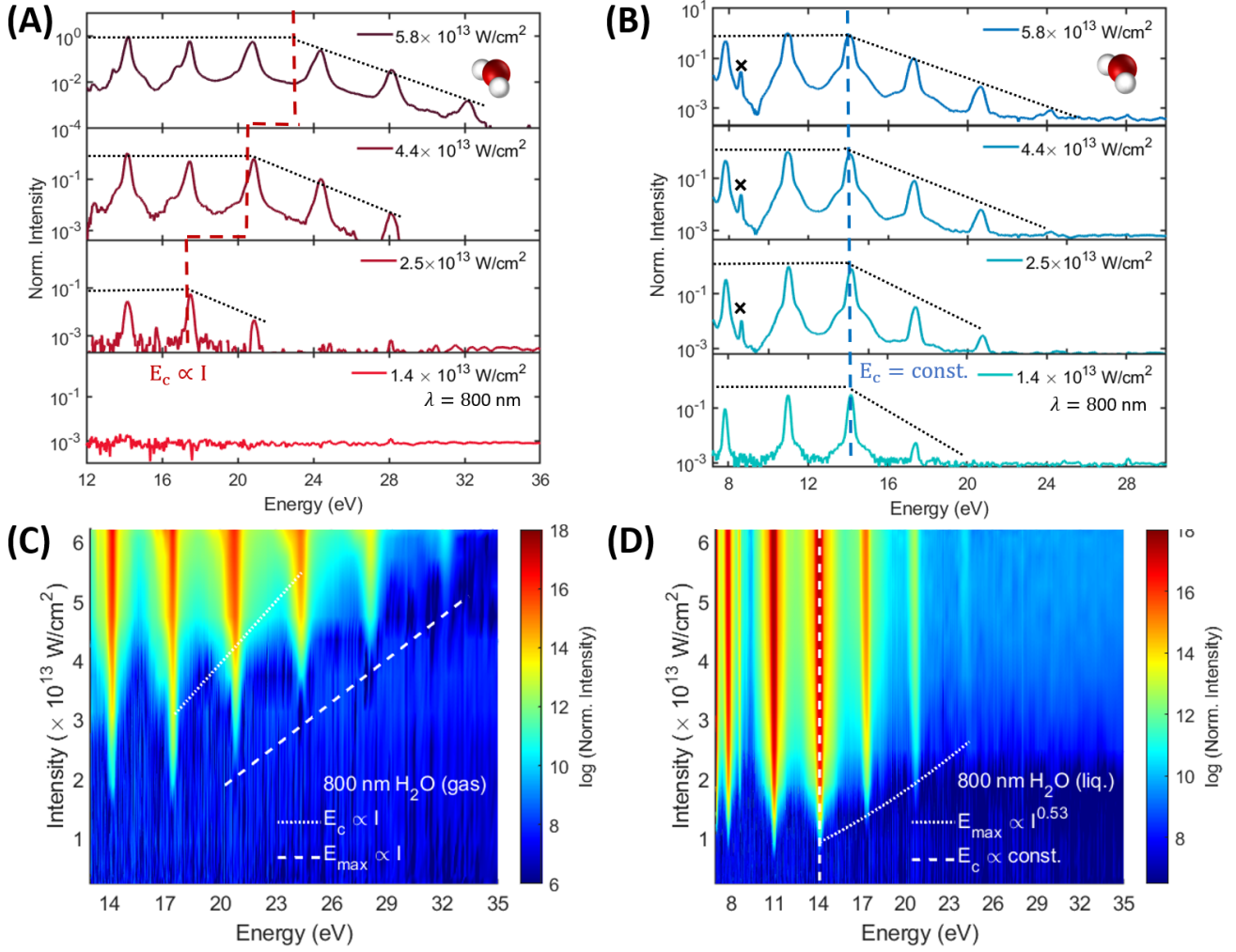


FIG. S1. For 800 nm driver, a comparisons between liquid (A) and gas (B) phase high-harmonic spectra of H₂O is given for three intensities. As expected, the gas phase cut-off energy depends on intensity (red dotted line) but the liquid phase is intensity independent (blue dotted line). For 800 nm driver, a comparison between gas (C) and liquid (D) phase high-harmonic spectra of H₂O is given for a range of intensities.

by Lewenstein et al. [4]. Here, we show that the scaling of these two quantities is actually different in the liquid phase and thereby show that the present conclusion regarding the scalings of E_c are consistent, or at least in no contradiction, with previous literature, in particular with Luu et al. [3].

Figure S1C and D show the data in a form that highlights the scalings of both E_{\max} and E_c . Panel C shows that, in the gas phase, both E_{\max} and E_c scale linearly with the intensity. Panel D, in contrast, shows that the scalings of the two quantities are noticeably different. A non-linear least-squares fitting of E_{\max} to the functional form $E_{\max} \propto I^y$ returns $y = 0.53$, consistent with Luu et al. [3]. The independence of E_c on I is visible, both in Fig. S1B and in Fig. S1D. This validates the conclusions reached in the main text and clarifies their relation with previous work.

We also performed ab-initio calculations to test the intensity dependence of the cutoff with both the supercell (Fig. S3) and the cluster (Fig. S5) approach for liquid HHG. Both types of calculations show that the cutoff is independent of the laser driving intensity, beyond a certain threshold. In each case the cutoff increases with the laser intensity until reaching a saturation point, where the increase stops. For the supercell approach, this saturation is found at $\sim 0.25 \cdot 10^{14}$ W/cm², while for the cluster approach it is observed at $\sim 0.5 \cdot 10^{14}$ W/cm². Variations between the two methods are a result of slightly different electronic structures (band gaps, in particular) obtained with the two approaches. Notably, the ranges of laser intensities for which the cutoff is intensity-independent correspond well with the experimental measurements.

Lastly, we also point out that the observed weak de-

pendence of the HHG cutoff with respect to the laser intensity is also captured by our proposed extended semi-classical model. Figure S6 presents the calculated HHG cutoff vs. the peak laser intensity with the extended semi-classical model, assuming 800 nm driving, and intermolecular distances similar to those in liquid water. Initially, the HHG cutoff increases quadratically with the laser intensity just as in the standard TSM (because the trajectories are very short and do not extend beyond l_{max}). However, this dependence is reduced to a weak linear scaling in the range of intensities $> 0.5 \cdot 10^{14}$ W/cm². In fact, over the intensity range of $0.5 \cdot 10^{14}$ W/cm² to 10^{14} W/cm², the HHG cutoff only increases by ~ 2 eV. This result substantially differs from the gas phase, where the standard TSM predicts that the cutoff should increase by ~ 9 eV in that region. Notably, a change of ~ 2 eV in the cutoff energy at 800 nm driving would only move the HHG cutoff by approximately one harmonic order, which might be difficult to detect experimentally. Thus, we overall conclude that in our examined conditions, the liquid-HHG cutoff is weakly dependent on the laser driving intensity, an effect that is described remarkably well by our suggested semi-classical picture that includes scattering. We note that potential improvements to our extended semi-classical model (e.g. relaxing some of the utilized approximations) might also improve its correspondence to the measured and ab-initio calculated results.

S3. DETERMINATION OF HARMONIC CUT-OFF ENERGY FROM EXPERIMENTAL DATA

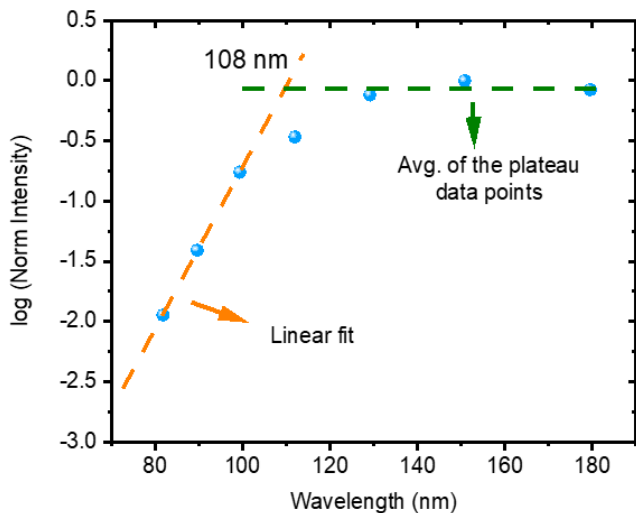


FIG. S2. Plot of harmonic signal as a function of harmonic wavelength. The cut-off is determined by the intersection of the green and orange lines.

In order to accurately determine the cut-off from the experimental spectra we use the following method. The

signal at each harmonic wavelength from the experimental spectra is acquired. It is known that the harmonic signal beyond the plateau region shows as exponential decay, which results in a linear decline in the logarithmic scale. Fig. S2 depicts this clearly, where the plateau region has a constant harmonic yield followed by a linear decay in the harmonic signal. The green line indicates the average signal of the plateau harmonics and the orange line indicates a linear fit to the intensities in the cut-off region. The intersection of the green and orange lines denotes the cut-off wavelength, which is converted to E_c , the cut-off energy of the plateau.

S4. THEORETICAL DETAILS

A. *Ab initio* supercell calculations

1. Molecular dynamics simulations

In order to study theoretically the interaction of strong-field pulse with liquid water, the first step is simulating the structural and dynamical properties of liquid water. In this regard, we use Car-Parrinello molecular dynamics (CPMD) simulations in the canonical ensemble at the temperature of 300 K. The simulated system, as displayed in the main text, is a periodic cubic supercell, including 64 H₂O molecules in the experimental liquid water density of 1 gr/cm³. Our computed radial distribution function between oxygen atoms (shown in Ref. [5]), which is averaged over a time length of approximately 20 ps, is in a good consistent with the experimental neutron scattering and x-ray diffraction measurements; it confirms the accuracy of our liquid water molecular dynamics simulation. Our CPMD simulations are performed using Quantum Espresso package [6]. We use norm-conserving GGA-revPBE [7] pseudopotentials for oxygen and hydrogen atoms and Grimme-D2 dispersion correction to describe the non-local correlation effects. For more details please see Ref. [5].

2. Ultrafast dynamics simulations

In the next step, to study the interaction of ultrashort intense pulse with liquid target, we use real-time time-dependent density functional theory implemented in Octopus package [8–10]. Note that the ultrashort laser pulse stimulates the system in the time-scale of femtosecond while our CPMD simulation reproduce the macroscopic characteristics of liquid water in the time-scale of picosecond. So in order to obtain the converged response, we need to consider a sufficient number of different configurations of the liquid supercell system, denoted as 'subsystems'. The time interval between consecutive subsystems are in the order of picosecond, and the number of required subsystems for convergence depend on the target system as well as pulse characteristics (wavelength

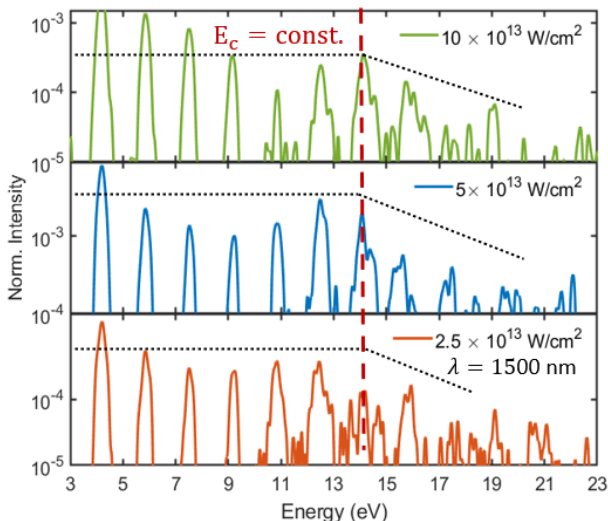


FIG. S3. High-harmonic spectra obtained from calculations with the supercell approach using a driving wavelength of 1500 nm.

and intensity).

In the supercell simulations, we consider the dynamics of nuclear based on Ehrenfest-TDDFT approach [11] during the interaction of ultrashort intense pulses with the liquid system. However, the effect of ionic current is negligible and the calculated HHG arises totally from electron dynamics.

The exchange-correlation term in TDDFT calculations is described by the same GGA-*revPBE* pseudopotentials as those used in CPMD calculations. But, vdW interactions are not included, as they lead to no difference in the spectra. We consider a grid spacing of 0.3 bohr thorough TDDFT calculations, and a dense k-point grid of $5 \times 5 \times 5$. Also, we use *aetrs* algorithm to approximate the evolution operator and the time step of 0.2 a.u. within our TDDFT calculations.

3. Pulse characteristics

In order to evaluate the impact of pulse wavelength and its intensity on HHG spectra, we consider the pulse characteristics corresponding to our experimental conditions. To see the impact of driving wavelength on HHG cutoff energy, we consider two different wavelengths of 800 and 1500 nm under the constant intensity of about 20 TW/cm² (shown in Fig. 3B of the main text). Additionally, to check the intensity scaling of HHG cutoff, the pulse intensity enhances from 25 to 100 TW/cm², the pulse wavelength is constant and equal to 1500 nm (shown in Fig. S3). In all cases, the pulse duration at full width at half-maximum (FWHM) is equal to 18 fs with a sine-squared envelope shape for the vector potential.

B. Cluster approach ab-initio calculations

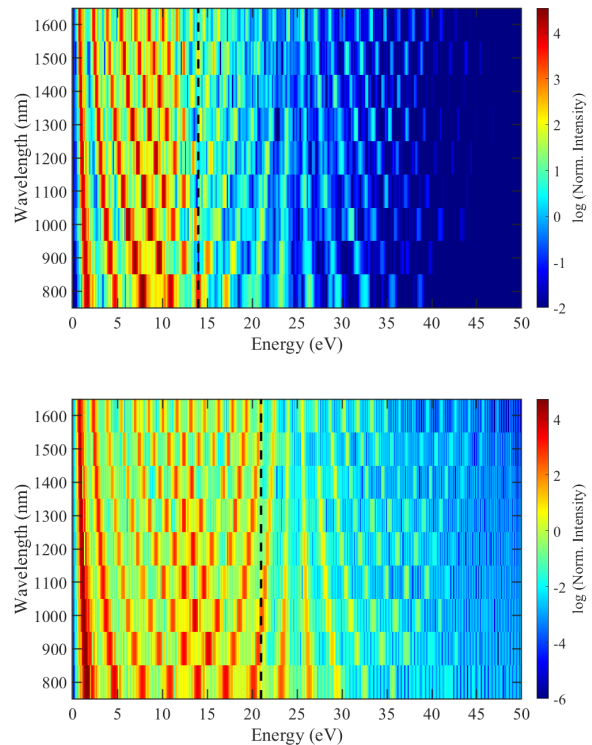


FIG. S4. High-harmonic spectra obtained from calculations on ammonia (NH_3) clusters (top) and methane (CH_4) clusters (bottom) over a broad range of driving wavelengths with a peak intensity of 50 TW/cm².

The numerical approach based on clusters that is utilized in the main text is thoroughly described in ref. [12]. We provide here some additional technical details for the calculations presented in the main text. All calculations were performed using the real-space grid-based code, OCTOPUS [8–10]. Cluster geometries for liquid H_2O were taken from ref. [13] using 43-molecule large clusters for the cut-off scaling calculations, and larger 54-molecule clusters for the calculations with varying liquid density that are more sensitive. Cluster geometries for NH_3 and CH_4 were taken from refs. [14] and [15], respectively, with 48-molecule and 40-molecule sizes, respectively. For each cluster, the ground state was obtained by DFT within the PBE [16] approximation for the XC functional with an added van-der-Waals correction term [17], with a real-space cartesian grid of spacing of 0.4 Bohr and spherical grid boundaries with a radius that extended 15 Bohr beyond the farthest atom from the cluster center. In the next step, the HHG response was calculated by propagating the KS states following the prescription in ref. [12] (by suppressing contributions from the surface states, employing orientation averaging, and utilizing the independent particle approximation (the XC potential is

frozen to its ground-state form)). The laser pulse was taken to have a trapezoidal envelope in all calculations with a two-cycle long turn-on and turn-off, and a four-cycle-long flat top. The dipole response was filtered with a super-Gaussian prior to obtaining the HHG spectra.

Figure S4 show high-harmonic spectra obtained with this approach for NH_3 clusters (top) and CH_4 clusters (bottom). Both panels show a cut-off energy E_c that is clearly independent of the wavelength. Ammonia was chosen as an example of a different polar molecule that also forms hydrogen bonds (like water and alcohols, studied in the main text) and methane was chosen as an example of an apolar molecule. The results of Fig. S4 thus show that the wavelength independence of E_c is not specific to the liquids studied in the main text, but appears to be a general property of liquid-phase HHG.

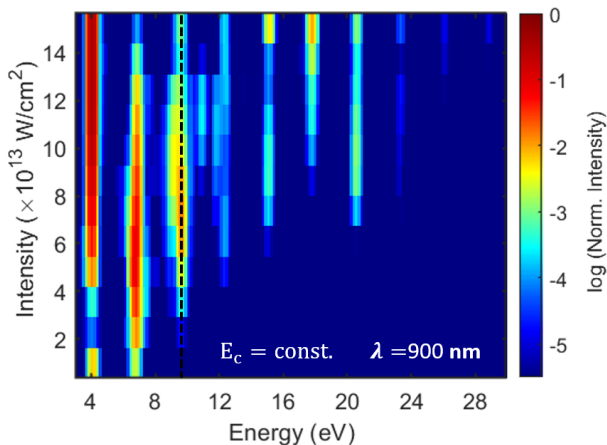


FIG. S5. High-harmonic spectra obtained from calculations on water clusters using a driving wavelength of 900 nm.

To complement the data shown in the main text (Figs. 3C, 3D, 4C), we show here in Fig. S5 the scaling of the high-harmonic spectra with the peak intensity of the driving field with a central wavelength of 900 nm. The figure nicely shows the saturation of the cut-off beyond a threshold intensity.

C. Extended semi-classical calculations

Based on our suggested extended semi-classical model (main text, Section II.A), we performed semi-analytical calculations for the HHG cutoff vs. the driving laser wavelength and intensity. We also performed calculations with varying l_{max} parameters. In all cases, the Newton equations of motion for the electrons were solved analytically for a given time of ionization, and then represented numerically on a temporal grid to scan for re-collisions. The solutions were numerically filtered for each re-colliding trajectory to test whether that particular trajectory extruded beyond l_{max} or not, while the

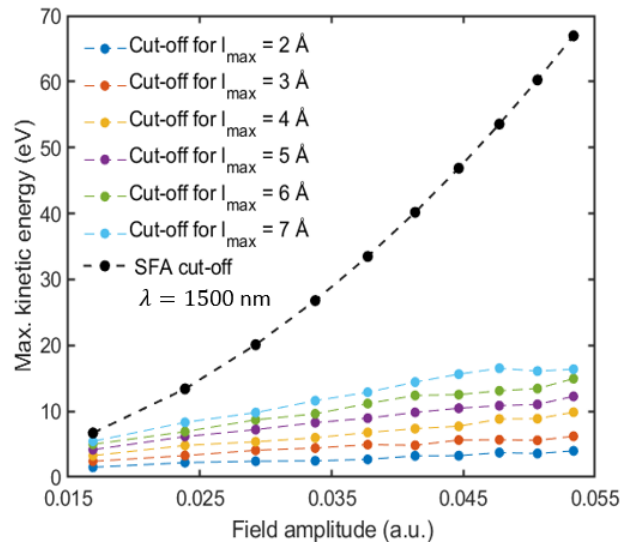


FIG. S6. Scaling of the maximal electron kinetic energy with the peak electric field of the driving pulse.

standard TSM was not filtered with this condition. In each case the cutoff was given by the most energetic re-colliding trajectory with the added band gap of the liquid. The calculations in Fig. S6 confirm the linear scaling of the maximal kinetic energy with the peak electric-field amplitude of the driving pulse. The onset of saturation is observed at the highest field amplitudes for $l_{max} = 7 \text{ \AA}$.

D. Semi-classical description of HHG and cutoff scaling including scattering

In this section, we aim at deriving an approximate fully analytical picture that describes the cutoff energy of HHG, as described by our extended semi-analytical semi-classical three-step model. We examine what is the analytical connection between the HHG cutoff and the maximum allowed excursion length of the electron trajectories in the extended model.

Our starting point is the full semi-classical picture discussed in the main text. We consider the classical motion of an electron in an electric field $E(t) = E \cos(\omega t)$, where ω is the frequency of the laser. The magnetic field, as well as the electric field due to the parent ion are neglected and the dipole approximation is employed. The electron is ionized at a time t_i , and we consider the dynamics following this time.

$$x(t) = \frac{qE}{m\omega^2} [\cos(\omega t_i) - \cos(\omega t) - \sin(\omega t_i) \omega(t - t_i)], \quad (1)$$

$$v(t) = \frac{qE}{m\omega} [\sin(\omega t) - \sin(\omega t_i)], \quad (2)$$

where we imposed as initial condition that the trajectories start at $x(t_i) = 0$, with a vanishing velocity ($v(t_i) = 0$).

The time at which the electron returns to its parent ion, referred here as the return time t_r , is obtained by imposing that $x(t_r) = 0$. This gives a first relation, that defines trajectories returning to the parent ion:

$$[\cos(\omega t_i) - \cos(\omega t_r)] = [\sin(\omega t_i)]\omega(t_r - t_i). \quad (3)$$

From the return time, we can obtain the kinetic energy for a trajectory starting at t_i

$$\Delta E_K(t_i) = 2U_p \left[\sin(\omega t_r) - \sin(\omega t_i) \right]^2. \quad (4)$$

The solution of the Eq. (3) can be performed numerically, see Fig. S7, from which we obtain the well known gas-phase result for the maximum kinetic energy of $\approx 3.17U_p$, corresponding to $\omega t_i \approx 0.305$.

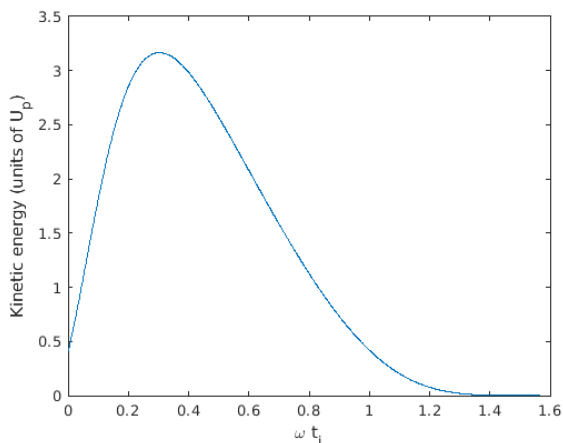


FIG. S7. Evolution of the return kinetic energy versus the ionization phase, obtained from Eq. (4), solving numerically Eq. (3) for each value of t_i .

Let us now consider the case that not all trajectories are allowed, as formulated in our extended model for the liquid. We first need to determine for a given trajectory, determined uniquely by t_i and Eq. (3), what is the maximum excursion.

The maximum excursion is reached when $\partial_t x(t) = v(t) = 0$. This gives us the condition defining the time of maximal excursion t^* :

$$\frac{qE}{m\omega} [\sin(\omega t^*) - \sin(\omega t_i)] = 0 \quad (5)$$

which has a simple analytical solution $\omega t^* = \pi - \omega t_i$.

We therefore have an exact expression for the excursion distance l_{exc} for any given ionization time

$$l_{exc}(t_i) = |x(t^*)| = \frac{eE}{m\omega^2} [2 \cos(\omega t_i) - \sin(\omega t_i)(\pi - 2\omega t_i)], \quad (6)$$

with $e = |q|$ is the elementary charge. Solving this equation numerically for the most energetic trajectory

($\omega t_i = 0.306$), we find that without limiting the trajectories, the cutoff energy corresponds to an excursion of $\approx 1.145 \frac{eE}{m\omega^2}$, which verifies the analytic analysis.

We next consider that the maximal excursion is limited to l_{max} . We can distinguish two cases. As long as $1.145 \frac{eE}{m\omega^2}$ is smaller than l_{max} , the kinetic energy gained is given by the usual formula $\Delta E_K \approx 3.17U_p$. Above this threshold, the value of the kinetic energy gain will be modified, as the most energetic trajectory is forbidden, and the cutoff will be reduced. Below, we assume that we are in this regime.

The task is therefore to find the most energetic trajectory that returns to the parent ion, and whose excursion is smaller or equal to l_{max} .

This gives us the condition

$$l_{exc} = \frac{eE}{m\omega^2} [2 \cos(\omega t_i) - \sin(\omega t_i)(\pi - 2\omega t_i)] \leq l_{max}. \quad (7)$$

The function $l_{exc}(t_i)$ is a function that decreases monotonously from 2 to 0 over the interval of interest of the ionization time $[0 : \pi/2]$. Therefore a value t_i^* exists such that the condition (7) is satisfied, for all $t_i > t_i^*$ (and smaller than $\pi/2$). Because we are in a regime where not all the trajectories are allowed, this time corresponds to a “short trajectory”, meaning that the ionization phase is larger than 0.306, which is the time corresponding to the most energetic trajectory without scattering. Said differently, we only select the short trajectories that have an excursion smaller than l_{max} . Now, we also know that the return kinetic energy decreases monotonously for the short trajectories (see Fig. S7). Therefore, the critical time t_i^* corresponds to the highest kinetic energy in our scattering model.

This ionization time that corresponds to the most energetic trajectory with an excursion smaller or equal to l_{max} is given by the relation

$$[2 \cos(\omega t_i^*) - \sin(\omega t_i^*)(\pi - 2\omega t_i^*)] = L_{red}, \quad (8)$$

where we define the dimensionless quantity $L_{red} = \frac{m\omega^2 l_{max}}{eE}$.

We therefore have two defining equations, Eq. (8) and Eq. (3), where the first one determines the ionization time as a function of the reduced maximum excursion L_{red} , and the second one that determines the corresponding return time.

We have solved numerically these two equations: for each value of L_{red} , we can find the numerical solution of Eq. (8) and then use this value to numerically solve Eq. (3). The result of the kinetic energy (in units of U_p) as a function of L_{red} is shown in Fig. S8. For not too large values of L_{red} , this is well approximated by a linear function. In this regime, which is the one relevant for our experiment, we find that

$$\Delta E_K(\omega t_i) \approx 3.73U_p L_{red} = \frac{3.73}{4} eE l_{max} \quad (9)$$

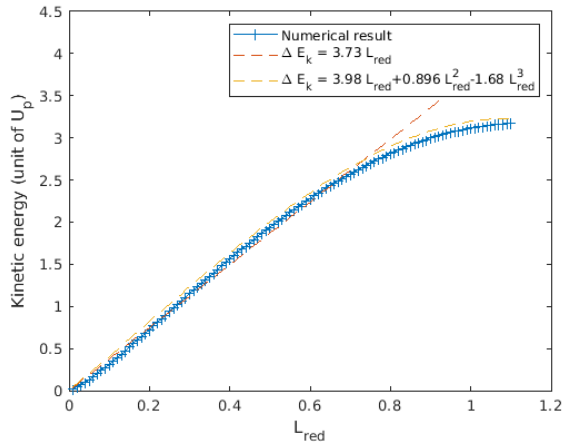


FIG. S8. Evolution of the return kinetic energy versus L_{red} . The linear and cubic fits are also shown.

From this result, we clearly see the role of introducing a mean-free path in our model. The cutoff becomes independent of the wavelength and is linear with the electric field. The comparison between the full numerical result and the linear fit is shown for different laser parameters in Fig. S9, showing that for our range of parameters, the approximate linear scaling law matches very well the exact numerical result of our model.

S5. INTENSITY DEPENDENCE OF LIQUID-HHG CUTOFF

In the main text we concluded that the liquid-HHG cutoff was independent of the driving wavelength. However, since the HHG measurements for different wavelengths slightly vary in the driving peak laser intensity (because the threshold intensity of plasma generation depends on the laser wavelength), this conclusion is only valid if the liquid-HHG cutoff also weakly depends on the driver peak intensity in these conditions. We here show that this is indeed the case with both measurements and calculations, which validate that the HHG spectra from liquids is independent of the driving wavelength.

S6. COMPARATIVE STUDY OF CUT-OFF ENERGY WITH DIFFERENT TRAJECTORY-TRUNCATION METHODS

To study the dependence of the cut-off energy on the implementation of the electron mean free paths, we compare the cut-off energies obtained from two different truncation methods. A system with an ionization energy of 10 eV is subjected to a Gaussian pulse with $1.5\text{V}/\text{\AA}$ peak electric field, a pulse duration of 65 fs and 1500 nm wavelength. The electrons are assumed to be released with

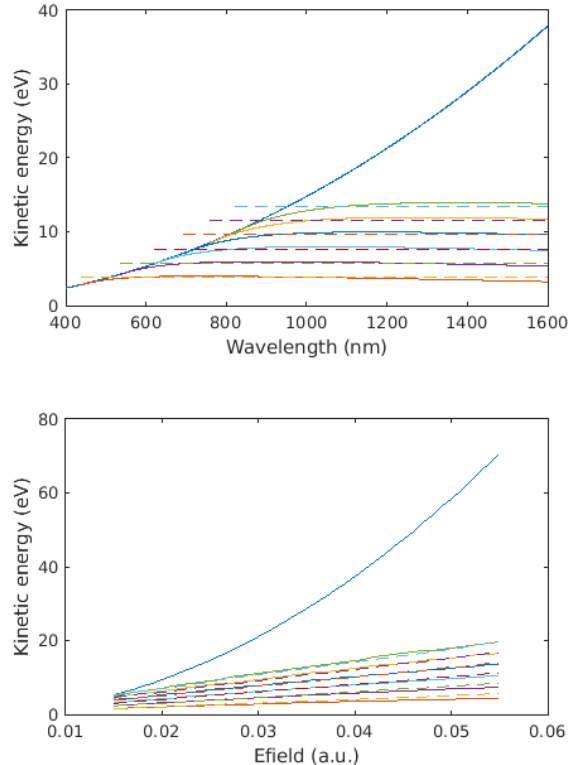


FIG. S9. Evolution of the return kinetic energy versus electric field (left panel) and wavelength (right panel). The parabola corresponds to the result without scattering, whereas the solid lines correspond to the result including scattering, for values of $l_{\text{max}} \in \{2, 4, 6, 8, 10, 12, 14\}$ Bohr. The dashed lines correspond to the same results, but obtained using the simpler formula $\Delta E_K = 3.73 U_p L_{\text{red}}$.

zero kinetic energy at 10 equidistant temporal points between 0.15 fs and 1.15 fs, where the peak electric field is assumed to occur at $t = 0$ fs. The energy of the returning trajectories is stored and sorted as a function of energy with a bin width of 0.82 eV (corresponding to the photon energy at 1500 nm wavelength). Fig. S10 shows the variation of harmonic yield (i.e. the number of returning trajectories) as a function of the electron energy. There are three different cases considered here. The no bound (blue dots) case indicates the normal semiclassical model without any trajectory truncation. As expected this model shows that all harmonics are equally probable until the classical cut-off energy at ~ 30 eV. The orange dots indicate the second case where we assume a "hard-cut off", where all trajectories beyond a distance of 7\AA (λ_{MFP}) are discarded. This reduces the cut-off energy from 30 eV to ~ 20 eV. However, in reality trajectories extending beyond the λ_{MFP} are expected to return but with exponentially decaying probability. This is indeed observed in the third case (green dots) where we

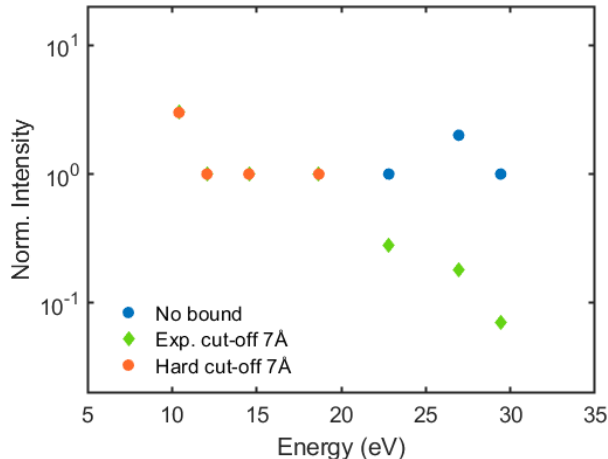


FIG. S10. The harmonic yield as a function of the harmonic energy is plotted for three different path-length truncation methods for a one dimensional classical trajectory calculation. blue dots represent the harmonic yields where no truncation is implemented. The orange dots indicate the harmonic yields for the case where trajectories extending beyond 7 \AA are rejected. The green dots represent the case where each returning trajectory extending beyond 7 \AA is weighted by an exponential function $\exp(-l_{max}/\lambda_{MFP})$, where l_{max} is the maximum excursion length.

weight each returning trajectory extending beyond λ_{MFP} by $\exp(-l_{max}/\lambda_{MFP})$, where l_{max} is the maximum electron displacement. As a result, although the maximum electron energy extends till the classical cut-off, the yield of harmonics beyond λ_{MFP} falls exponentially, likely below the detection limit.

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