

Ultrafast longitudinal and transverse dielectric response of collective polar modes in liquids

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(Received 21 March 2025; accepted 12 June 2025; published 24 June 2025)

Electrons solvated in polar liquids are a prototypical many-body system, in which electric interactions on different length scales have a strong impact on quantum states and elementary excitations. Impulsively excited polarons in liquid water and alcohols display coupled coherent motions of electrons and their solvation shells at terahertz (THz) frequencies, affecting both the longitudinal and transverse dielectric function. To address the barely characterized connection between the longitudinal and transverse dielectric response in experiment, an ultrafast pump-probe scheme is employed. Two femtosecond near-infrared pump pulses in sequence generate solvated electrons by ionization of isopropanol solvent molecules. The resulting changes of the dielectric function are mapped in time-resolved measurements by a broadband THz probe pulse, which is detected in a phase-resolved way. Longitudinal polaron oscillations modulate both the longitudinal and transverse dielectric function with a frequency set by the partial electron concentration generated in the separate excitation steps. On top, the transverse response includes steplike components, which are governed by the total electron concentration and well described by Clausius-Mossotti theory. The different longitudinal and transverse response is caused by the different character and spatial range of the underlying electric interactions.

DOI: [10.1103/45x5-vztx](https://doi.org/10.1103/45x5-vztx)

I. INTRODUCTION

Many-body ensembles of charged particles, such as plasma, liquids and solids containing free electrons or ions, display complex nonequilibrium dynamics, which are governed by Coulomb interactions between electric charges and dipole moments. The long-range character of Coulomb forces results in a length scale of interaction, which is typically much larger than the spatial separation of particles. As a consequence, there is spatial dispersion in such interactions, generating a nonlocal spatial relation between the electric displacement $\mathbf{D}(\mathbf{r}, t)$ and the electric field $\mathbf{E}(\mathbf{r}, t)$ in the ensemble [1–3]. This behavior strongly modifies optical properties of materials, leading, e.g., to negative refraction of light or anomalous skin effects in metals [4–6]. The linear and nonlinear optical response of such systems has been described with the help of transverse and longitudinal dielectric functions and/or susceptibilities, in general depending on wave vector and frequency. In liquids and solutions, many-body effects are scarcely understood and, in particular, the longitudinal dielectric response has essentially remained unaddressed in experiment [7–9].

Free electrons in polar liquids are a prototypical system in this context [10–14]. After their generation in delocalized con-

tinuum states by, e.g., multiphoton ionization, they undergo an ultrafast solvation process, localizing them in a potential minimum connected with a void or cavity of subnanometer size in the liquid structure [15–18]. Basic physical properties of the solvated electron are accounted for by the quantum-mechanical cavity model, which describes the electron in an effective potential defined by the polar environment [10]. This approach provides the energy levels and wavefunctions of the electron, the optical transition dipole between the s -like ground and p -like excited states, and the depth of the localization potential.

Beyond this single-particle picture, long-range Coulomb interactions in the liquid couple the electron and a large subset of dipolar solvent molecules on a nanometer length scale, a range much longer than the subnanometer distances between neighboring molecules. As a result, many-body excitations of the electron and the solvent cloud are expected to arise, in analogy to polarons in solids [19,20]. The first evidence for a polaronic response of electrons in polar liquids originates from recent studies of the ultrafast dielectric response of water and alcohols in the terahertz (THz) frequency range [21–24].

In such experiments, a femtosecond near-infrared pump pulse [pulse A in Fig. 1(a)] generates electrons by multiphoton ionization of solvent molecules. The resulting changes of the dielectric function are mapped by a THz electric-field transient [pulse THz in Fig. 1(a)] transmitted through the sample and detected in amplitude and phase [21,25]. Electron generation and subpicosecond localization change both the real part $\text{Re}[n(\nu)]$ and imaginary part $\text{Im}[n(\nu)]$ of the refractive index $n(\nu) = \sqrt{\epsilon(\nu)}$ [$\epsilon(\nu)$: dielectric function; ν : frequency]. In the alcohol isopropanol (IPA), the change of $\text{Im}[n(\nu)]$ leads to an absorption change, in time following a steplike kinetics with

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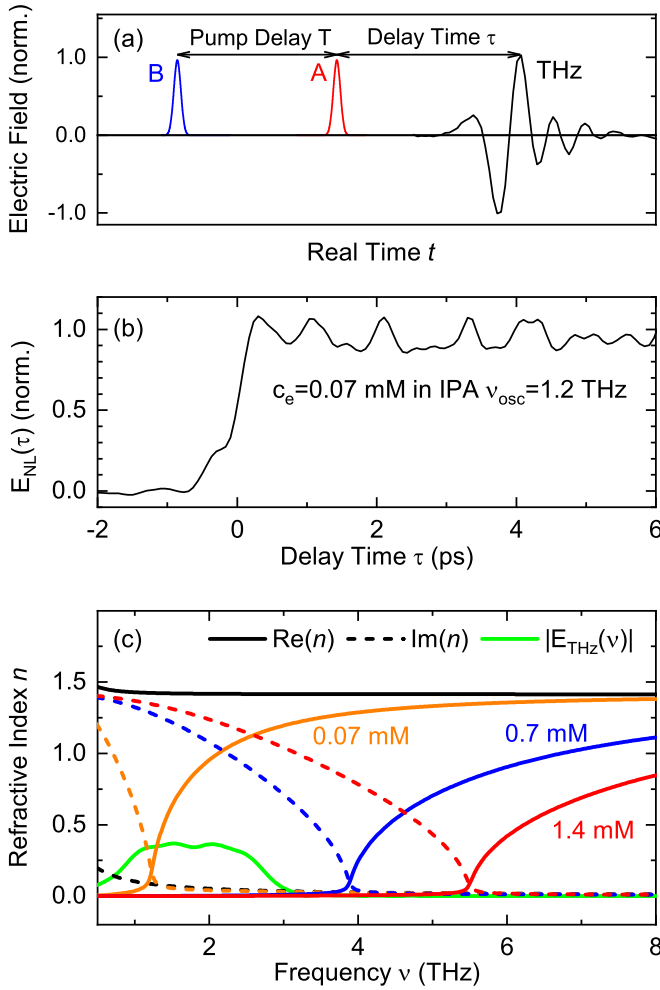


FIG. 1. (a) Experimental pulse sequence consisting of two femtosecond excitation pulses A and B centered at 800 nm and a THz probe pulse. The sequence is plotted as a function of real time t . The delay T between the excitation pulses and the delay time τ of the THz pulse are measured relative to the maximum of pump pulse A at $T = \tau = 0$. (b) Transient absorption change of liquid isopropanol (IPA) containing electrons at a concentration $c_e = 0.07$ mM as a function of delay time τ between pulse A and the THz probe pulse (two-pulse experiment without pulse B). The nonlinear signal $E_{NL}^A(t_0, \tau) = E^A(t_0, \tau) - E^T(t_0)$ taken at a fixed real time t_0 is the difference of the THz electric field transmitted through the sample with $[E^A(t_0, \tau)]$ and without $[E^T(t_0)]$ excitation. The frequency of the oscillatory component is $\nu_{osc} = 1.2$ THz. (c) Refractive index of neat isopropanol (IPA, black lines) and IPA containing solvated electrons at the respective electron concentration (colored lines) as a function of THz frequency. Solid and dashed lines give the real and imaginary parts of the refractive index. The presence of electrons introduces a zero crossing of $\text{Re}[\epsilon(\nu)] = \text{Re}[n(\nu)]^2 - \text{Im}[n(\nu)]^2 = 0$ at ν_0 , defining the polaron frequency. Green line: spectrum $|E(\nu)|$ of the THz pulses.

a subpicosecond rise time [Fig. 1(b)] [22]. On top, there is an impulsively excited oscillatory change of THz absorption with a frequency set by the generated electron concentration and a damping time well beyond 100 ps.

The elementary excitation underlying the oscillations is a longitudinal vibration of the solvent cloud around the solvated

electron, in space covering a spherical volume of a radius set by the screening length of the radial electric field from the electron. This longitudinal excitation modulates the transverse dielectric function as well and, thus, polaron oscillations manifest in the transverse electric field of the transmitted THz probe pulse [23]. Beyond this linear response, the oscillatory component displays a pronounced optical nonlinearity, which, e.g., manifests in oscillations at the third harmonic of the fundamental frequency [22,24].

The modified transverse THz dielectric function in presence of solvated electrons is well accounted for by a macroscopic Clausius-Mossotti picture [26]. The resulting changes are illustrated in Fig. 1(c), displaying the real part (solid lines) and imaginary part (dashed lines) of the refractive index $n(\nu)$ of IPA. The presence of electrons introduces a zero crossing $\text{Re}[\epsilon(\nu)] = \text{Re}[n(\nu)]^2 - \text{Im}[n(\nu)]^2 = 0$ at a frequency position ν_0 depending on the electron concentration. The frequency of the oscillatory change of THz absorption is identical to ν_0 .

The connection and interplay of the longitudinal and transverse dielectric response need further clarification in order to understand the complex dynamic many-body scenario in the polar liquid. In particular, the role of electrons in their initial continuum versus final localized states and the solvent response induced by them need to be elucidated. To address such issues, an extended experimental approach is required.

In this article, we demonstrate that the ultrafast THz response of polar liquids provides detailed insight in the character and dynamics of their longitudinal and transverse dielectric properties. Our study of polaron excitations in the alcohol IPA goes beyond previous experiments by employing a three-pulse sequence with two near-infrared excitation pulses A and B and a broadband THz probe pulse [Fig. 1(a)]. Each of the two pump pulses generates free electrons and the THz probe pulse monitors both the steplike and oscillatory changes of the dielectric function. We demonstrate that the polaron oscillation frequency is set by the partial electron concentration generated in each excitation step, while the steplike changes of the dielectric function are determined by the total electron concentration. This surprising result allows for a distinction of the transverse and longitudinal dielectric response and the particular spatial range of the underlying Coulomb interactions.

II. EXPERIMENTAL METHODS

In the experiments, a liquid IPA jet of a thickness of $s = 75 \mu\text{m}$ interacts with a sequence of two near-infrared pump pulses and a THz probe pulse. The pump pulses centered at 800 nm are derived from the output of an amplified Ti:sapphire laser system, have an energy of up to 360 μJ each and a pulse duration of 30 fs. Solvated electrons are generated by five- to six-photon ionization of IPA molecules by the pump pulses [21], which are focused onto the sample jet with a lens of a 300 mm focal length (spot size 300 μm).

The THz probe pulse is generated by difference frequency mixing within the spectrum of an 800 nm driving pulse, using a (110) ZnTe crystal (thickness 500 μm). The THz probe spectrum covers a range from 0.5 to 3 THz [green line in Fig. 1(c)]. The probe pulse is focused onto the sample by an

off-axis parabolic mirror of a 25.4 mm focal length. The THz spot size of 250 μm is close to the diameter of the focused pump beam. The electric field of the THz pulse transmitted through the sample jet is detected in amplitude and phase by electro-optic sampling in a ZnTe crystal [(110) oriented, thickness 10 μm on a (001)-oriented ZnTe substrate]. Pulses from the oscillator of the Ti:sapphire laser system with a 10 fs duration serve as sampling pulses in this detection scheme.

Measurements were performed with the three-pulse sequence shown in Fig. 1(a) and with two-pulse sequences consisting of either pulse A or B and the THz probe pulse. The respective data sets were recorded in sequence by applying mechanical choppers to the individual pump and probe beams. The electric field of the nonlinear THz signal in the three-pulse experiment is given by $E_{\text{NL}}^{AB}(t, \tau, T) = E^{AB}(t, \tau, T) - E^T(t)$, where $E^{AB}(t, \tau, T)$ is the transmitted probe field measured with both pump pulses A and B present and $E^T(t)$ is the probe field transmitted through the unexcited sample. Correspondingly, the nonlinear signals in the two-pulse measurements are $E_{\text{NL}}^A(t, \tau) = E^A(t, \tau) - E^T(t)$ and $E_{\text{NL}}^B(t, \tau + T) = E^B(t, \tau + T) - E^T(t)$. Details on data analysis are given in Appendix A.

The electron concentration generated by the excitation pulses was determined in independent measurements with identical pumping conditions and a femtosecond 800 nm probe pulse. The latter monitors the near-infrared absorption of the solvated electrons, which originates from the dipole-allowed transition from the electron ground to first-excited states. The electron concentration is derived from the measured absorption increase, the sample thickness, and the known molar extinction coefficient of electrons solvated in IPA [14]. We use the symbol c_e for the total electron concentration in the sample. In the experiments with a single excitation pulse A or B, $c_e = c_{A,B}$, where $c_{A,B}$ is the concentration generated by pulse A or pulse B. For excitation with both pulses A and B, the total electron concentration is $c_e = c_A + c_B$.

III. RESULTS

Time-resolved data were recorded with the different pulse sequences and results from an individual set of measurements are summarized in Fig. 2. The data were analyzed with the methods described in Appendix A. In panels (a) and (b), the THz electric fields E^A and E^B transmitted through the sample after interaction with the single excitation pulse A or B is plotted as a function of real time t (abscissa) and delay time τ (ordinate), while panel (c) shows the transmitted THz field E^{AB} recorded in a measurement with both pump pulses A and B. The pulses A and B have a similar energy of some 250 μJ , each generating an electron concentration $c_e \approx 0.7$ mM. The nonlinear signal fields E_{NL}^A , E_{NL}^B , and E_{NL}^{AB} are shown in panels (d)–(f). As a function of delay time τ , one observes pronounced changes of the electric-field amplitudes, while changes of the phase of the THz fields manifest as minor shifts of the striplike patterns along the real-time axis t . Such phase behavior has been analyzed in detail in Ref. [27] and will not be reconsidered in the following. Panel (g) displays the sum of the nonlinear signals E_{NL}^A and E_{NL}^B recorded with a single pump pulse each [cf. panels (d) and (e)]. Subtraction

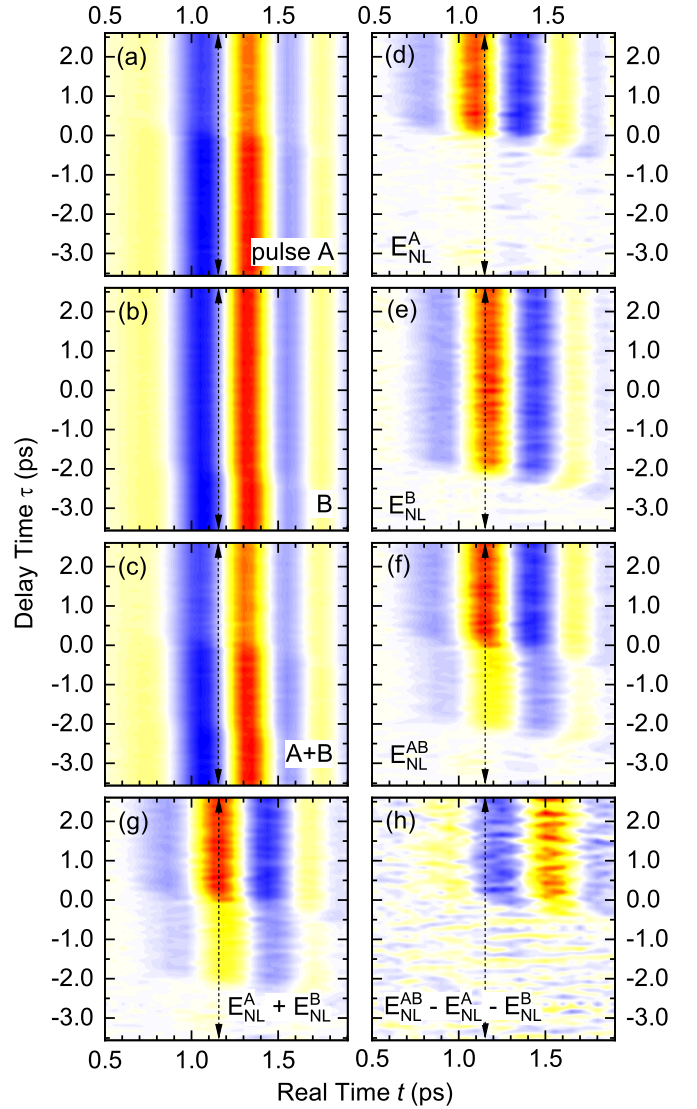


FIG. 2. (a)–(c) 2D-contour plots of the THz pulse transmitted through the IPA jet as a function of real time t and delay time τ for (a) $E^A(t, \tau)$ only pumping with pulse A, (b) $E^B(t, \tau + T)$ only pumping with pulse B, and (c) $E^{AB}(t, \tau, T)$ pumping with both pulses separated by $T = 2.1$ ps. A single pump pulse generates an electron concentration of $c_e = 0.7$ mM. (d)–(f) Nonlinear signals $E_{\text{NL}}^A(t, \tau)$, $E_{\text{NL}}^B(t, \tau + T)$, and $E_{\text{NL}}^{AB}(t, \tau, T)$ corresponding to panels (a)–(c), respectively. The signals are gained by subtracting the THz pulse transmitted through the unpumped sample. (g) Sum of panels (d) and (e). (h) Nonlinear signal $E_{\text{NL}}^{3\text{-pulse}} = E_{\text{NL}}^{AB}(t, \tau, T) - E_{\text{NL}}^A(t, \tau) - E_{\text{NL}}^B(t, \tau + T)$. The dashed double arrows indicate the temporal cuts shown in Figs. 3 and 4(a). All contour plots range from the respective minimum (blue) to maximum value (red) of the electric field with (a)–(c) ± 125 kV/cm, (d) and (e) ± 32 kV/cm, (f) and (g) ± 54 kV/cm, and (h) ± 7 kV/cm.

of this sum from the signal E_{NL}^{AB} recorded with two pump pulses gives the contour $E_{\text{NL}}^{3\text{-pulse}}$ shown in panel (h). The latter demonstrates that the amplitude changes observed after two-pulse excitation are slightly smaller than the sum of the changes observed with a single pump pulse. The modulation of the signal along the delay time τ is within the experimental

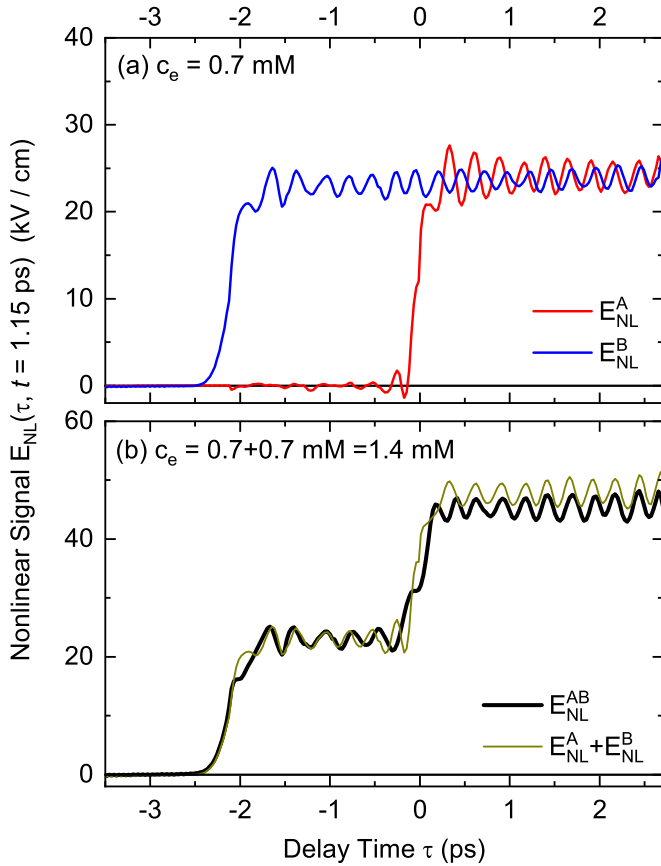


FIG. 3. Temporal cuts of the nonlinear signals at $t = 1.15$ ps along the dashed double arrows shown in Fig. 2. (a) Both single-pump-pulse signals $E_{\text{NL}}^A(\tau)$ (red) and $E_{\text{NL}}^B(\tau)$ (blue) show a steplike contribution which is superimposed by polaron oscillations of a frequency $\nu_{\text{osc}} \approx 3.9$ THz. (b) Experiment with both pump pulses $E_{\text{NL}}^{\text{AB}}(\tau)$ (thick line) compared with the sum $E_{\text{NL}}^A(\tau) + E_{\text{NL}}^B(\tau)$ (thin curve). Outside of the vicinity of the steps the oscillations of both curves are almost perfectly in phase. For $\tau > 0$ the amplitude of the steplike contribution $E_{\text{NL}}^{\text{AB}}(\tau)$ is 5% smaller than that of the sum.

noise and absent when averaging over several data sets [see Fig. 8(e) in Appendix A].

To bring out the amplitude changes in a more direct way, we averaged a total of seven individual data sets and generated cuts of the signal along delay time τ at a fixed real time $t = 1.15$ ps (Fig. 3). At this real time, the THz electric field is negative [Figs. 2(a)–2(c)] and the nonlinear signal positive [Figs. 2(d)–2(f)], the latter corresponding to a reduced electric-field amplitude and, thus, an absorption increase. Figure 3(a) displays the data generated with a single pump pulse A or B, while results of the experiment with both pump pulses are shown in Fig. 3(b). All transients exhibit a steplike change of the electric-field amplitudes upon generation of free electrons by the respective pump pulse, which is superimposed by pronounced oscillations. The oscillatory response displays a negligible damping in the delay range covered in Fig. 3 and persists for delay times longer than 100 ps (not shown).

In Fig. 3(b), the oscillation frequency remains essentially unchanged after excitation by the second pump pulse, which doubles the electron concentration in the sample. This fact is

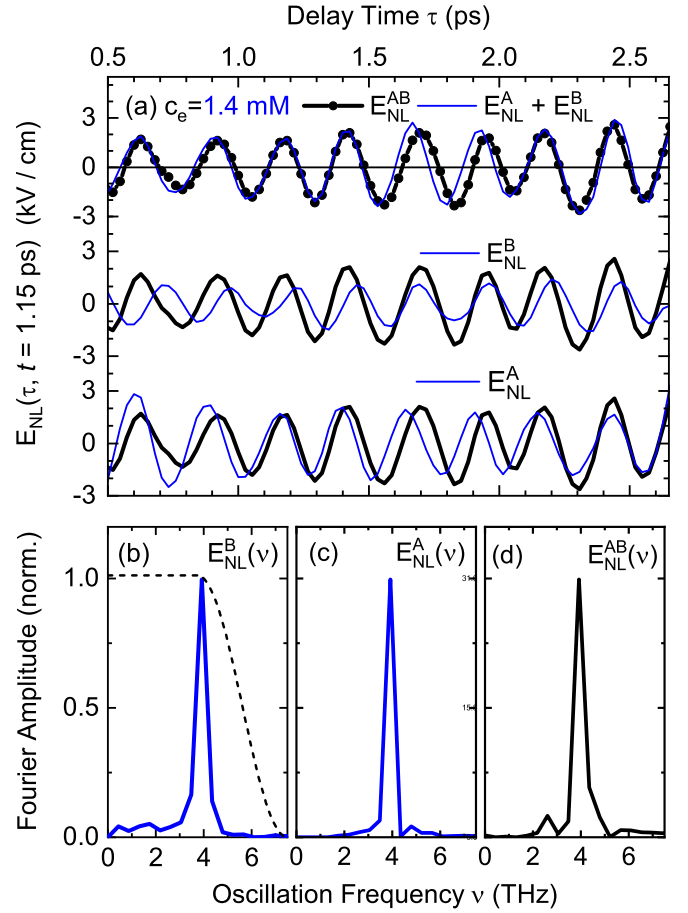


FIG. 4. (a) Purely oscillatory nonlinear THz signals, which are derived from the transients in Fig. 3 by subtracting the steplike components. Thick black lines give $E_{\text{NL}}^{\text{AB}}(\tau)$ as a function of delay time τ , while thin blue lines represent the sum $E_{\text{NL}}^A(\tau) + E_{\text{NL}}^B(\tau)$ (upper time trace), $E_{\text{NL}}^B(\tau)$ (middle trace), and $E_{\text{NL}}^A(\tau)$ (bottom trace). (b)–(d) Fourier spectra of the transients shown in panel (a). The Fourier amplitudes $|E_{\text{NL}}^A(\nu)|$, $|E_{\text{NL}}^B(\nu)|$, and $|E_{\text{NL}}^{\text{AB}}(\nu)|$ are plotted as a function of frequency ν . The maximum is located at $\nu = 3.9$ THz in all spectra. The dashed line in panel (b) shows the profile of the 2D-Fourier filter defined in Eq. (A12).

evident from the comparison of the transient recorded with both pump pulses (black line) to the sum of the two transients measured with pump pulse A and B only (green line). Such behavior represents a key result of the present study and demonstrates that the oscillation frequency is determined by the electron concentrations c_A and c_B generated in the separate excitation steps, but not by the total electron concentration $c_e = c_A + c_B$ in the sample. It should be noted that in all experiments with a single pump pulse $c_e = c_A$ or $c_e = c_B$, and the oscillation frequency is set by the zero crossing of $\text{Re}[\epsilon(\nu)]$ at ν_0 [Fig. 1(c)] induced by the respective electron concentration.

The steplike components were subtracted from the total nonlinear signals in Fig. 3 for an in-depth comparison of the oscillatory response observed with the different pumping schemes. The resulting oscillatory transients are plotted in Fig. 4(a), where we focus on the delay range $\tau > 0.5$ ps after the second step in the overall nonlinear signal (cf. Fig. 3).

Consecutive data points are separated by a delay step of 25 fs, as shown for the transient E_{NL}^{AB} . This delay step corresponds to a sampling frequency of 40 THz or a Nyquist frequency of 20 THz. The phase shift between the oscillatory components of E_{NL}^A and E_{NL}^B is minor and displays small fluctuations from cycle to cycle, which reflect the experimental uncertainty. The oscillations observed in the experiment with both pump pulses $E_{NL}^{AB}(\tau)$ (thick black lines) match almost perfectly those of the sum $E_{NL}^A(\tau) + E_{NL}^B(\tau)$ (thin blue line, upper trace). Quantitatively, the standard deviation of this comparison is three times smaller than those comparing $E_{NL}^{AB}(\tau)$ with the individual single-pulse signals $E_{NL}^B(\tau)$ (blue line, middle trace) and $E_{NL}^A(\tau)$ (blue line, lower trace). The Fourier spectra of the different oscillatory time traces in Figs. 4(b)–4(d) display a very similar envelope and all peak at 3.9 THz, thus confirming identical oscillation frequencies after excitation by one and two pump pulses.

Additional measurements were performed at higher pump fluences, resulting in total electron concentrations of $c_e = 2.8$ mM and 4.6 mM after two-pulse excitation. Results from the two individual data sets were again processed with the methods described in Appendix A. Figure 5(a) shows the oscillatory signals $E_{NL}^{AB}(\tau)$ (points, thick black lines) and $E_{NL}^A + E_{NL}^B$ (red lines) for $c_e = 2.8$ mM, measured with a sampling frequency of some 30 THz. Transients recorded at $c_e = 4.6$ mM are presented in Fig. 5(b) and exhibit stronger phase noise because of the limited sampling rate of 24 THz. Figure 5(c) displays the Fourier spectra $E_{NL}^{AB}(\nu)$ for the three different electron concentrations studied. The oscillation frequency has a value of 3.9 THz, 5.5 THz, and 6.6 THz for $c_e = 1.4$ mM, 2.8 mM, and 4.6 mM, respectively. The spectrum for $c_e = 4.6$ mM displays substantial noise originating from the phase noise in the corresponding time traces [panel (b)].

IV. DISCUSSION

The pump-probe approach applied in the present experiments maps transient changes of the macroscopic dielectric function in the THz frequency range upon generation of electrons by multiphoton ionization of IPA solvent molecules. The electric fields of the near-infrared pump and THz probe pulses are of a transverse character and, thus, the measured signals represent changes of the transverse dielectric function in a spatially inhomogeneous ensemble of electrons and solvent molecules. This transverse response displays two time-dependent components, steplike changes of THz absorption and underdamped oscillatory contributions with a frequency set by the generated concentration of electrons. In the following, we discuss the two signal components separately.

A. Steplike response and transverse dielectric function

The steplike absorption increase shown in Figs. 2 and 3 represents a change of the imaginary part of the THz dielectric function. The absorption change exhibits a femtosecond rise, which follows the increase of electron concentration in a quasi-instantaneous way, and persists for the lifetime of the solvated electrons up to the microsecond time range [14]. The

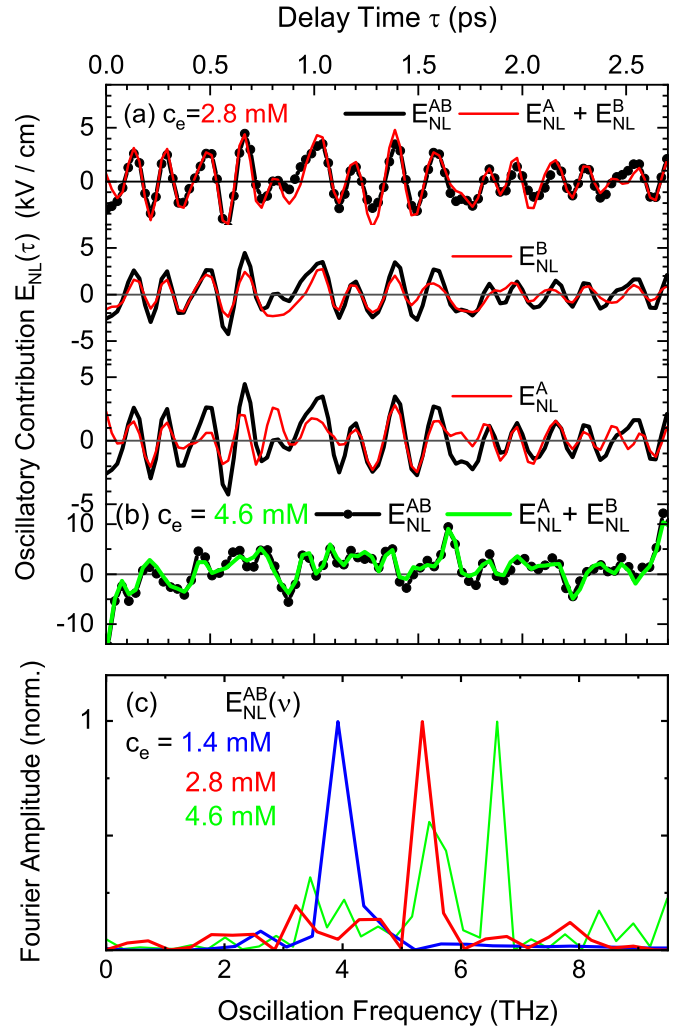


FIG. 5. Oscillatory nonlinear THz signals measured for total electron concentrations of (a) $c_e = 2.8$ mM and (b) 4.6 mM after two-pulse excitation. The red curves in panel (a) are in the same representation as the blue curves in Fig. 4(a). Thick black lines give $E_{NL}^{AB}(\tau)$ as a function of delay time τ for the two concentrations. (c) Fourier spectra of the transients $E_{NL}^{AB}(\tau)$ shown in Fig. 4(a) (blue) and panels (a), (b). The Fourier amplitudes $|E_{NL}^{AB}(\nu)|$ are plotted as a function of frequency ν . The maximum is located at $\nu = 5.5$ THz (red) and 6.6 THz (green) for $c_e = 2.8$ mM and 4.6 mM, respectively.

total transverse dielectric function is accounted for by the Clausius-Mossotti relation including a term proportional to the electron concentration c_e and electron polarizability α_{el} :

$$3 \frac{\epsilon(\nu, c_e) - 1}{\epsilon(\nu, c_e) + 2} = 3 \frac{\epsilon_{neat}(\nu) - 1}{\epsilon_{neat}(\nu) + 2} + c_e N_A \alpha_{el}(\nu), \quad (1)$$

$$\text{with } \alpha_{el} = - \frac{e^2}{\epsilon_0 m [(2\pi\nu)^2 + i\gamma(2\pi\nu)]}, \quad (2)$$

with Avogadro's constant N_A , the vacuum permittivity ϵ_0 , the electronic mass m , and a damping constant γ , set to zero in the following. The quantity $\epsilon(\nu, c_e) = \text{Re}[\epsilon(\nu, c_e)] + i\text{Im}[\epsilon(\nu, c_e)]$ is the complex transverse dielectric function of the liquid containing electrons of a concentration c_e , while $\epsilon_{neat}(\nu)$ represents the dielectric function of neat IPA. The interaction of the THz field with photogenerated electrons

in both continuum and localized states has a nonresonant character, leading to a practically identical electron polarizability given by Eq. (2). In other words, the subpicosecond transition of the photogenerated electrons from the continuum into their localized ground state remains invisible in the time-resolved absorption changes.

The real and imaginary parts of the complex refractive index, $\text{Re}[n(c_e, \nu)]$ and $\text{Im}[n(c_e, \nu)]$ with $n(c_e, \nu) = \sqrt{\epsilon(c_e, \nu)}$ were derived from the Clausius-Mossotti relation [Eq. (1)] and are plotted in Fig. 1(c) for different electron concentrations c_e . The presence of electrons introduces a zero crossing $\text{Re}[\epsilon(\nu)] = \text{Re}[n(\nu)]^2 - \text{Im}[n(\nu)]^2 = 0$ at a frequency position ν_0 determined by c_e (colored lines). In contrast, $\text{Re}[\epsilon_{\text{neat}}(\nu)]$ of the neat solvent is spectrally flat in this range. For the low electron concentration $c_e = 0.07$ mM [Fig. 1(b)], the frequency ν_0 is located within the spectrum of the THz pulses [green line, cf. Fig. 1(c)]. In contrast, the pulse spectrum is well below ν_0 for the higher concentrations studied here. Below the respective zero crossing $\text{Re}[\epsilon(c_e, \nu_0)] = 0$, one finds a pronounced increase of $\text{Im}[n(c_e, \nu)] = c/(4\pi\nu)\bar{\alpha}(c_e, \nu)$ [with $\bar{\alpha}(c_e, \nu)$: absorption coefficient; c : velocity of light] giving rise to the absorption increase observed in the time-resolved experiments.

The THz transients E_{NL}^A and E_{NL}^B recorded with a single pump pulse A or B display a single-step absorption increase with an amplitude determined by the increase of $\text{Im}[n(c_e, \nu_0)]$ compared to neat IPA (Fig. 2). In the experiments with both pump pulses, the initial step induced by pulse B is followed by a second step generated by pulse A, which interacts with the sample containing the electrons generated by the preceding pulse B. The increase in electron concentration by pulse A enhances $\text{Im}[n(c_e, \nu_0)]$ again, i.e., the total absorption change after interaction with pulse A combines such two steps. The total amplitude of this signal E_{NL}^{AB} is slightly smaller than that of the sum $E_{\text{NL}}^A + E_{\text{NL}}^B$, due to the sublinear increase of $\text{Im}[n(c_e, \nu_0)]$ with electron concentration c_e . A comparison of the three $\text{Im}[n(c_e, \nu_0)]$ curves plotted in Fig. 1(c) for $c_e = 0.07, 0.7$, and 1.4 mM illustrates this sublinear relationship.

A quantitative analysis of the absorption changes requires a modeling of THz pulse propagation in the sample and an integration of the transmitted THz electric fields along real time t . The experimentally observed changes of the THz pulse transmitted through the IPA sample (Fig. 2) have a broadband spectral character, i.e., upon pumping we observe essentially an amplitude reduction for all real times t and a small phase shift of the entire THz pulse. Please note that the step amplitudes taken at a fixed real time (i.e., $t = 1.15$ ps in Fig. 3) are different from spectrally averaged quantities and, thus, do not reflect absolute values of absorption (or transmission) changes.

To relate the experimental amplitude changes to the transverse dielectric function [Eq. (1)] we calculate the propagation of a THz pulse through an IPA sample as a function of the excited electron concentration c_e , using the theoretical concept described in Ref. [27]. The calculated spectra of the transmitted THz pulses are integrated and normalized to the integrated spectrum of the THz pulse transmitted through the unpumped IPA sample. This ratio defines the THz electric-field transmission of a sample with an electron

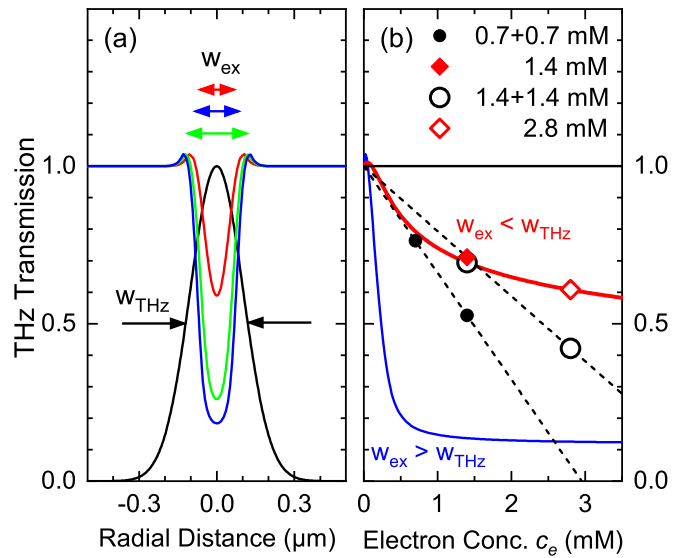


FIG. 6. (a) Calculated spatially resolved THz transmission ratios, i.e., the THz amplitude of a region containing electrons divided by that in neat IPA for peak concentrations of $c_e = 0.2$ mM (red), 0.4 mM (green), and 0.6 mM (blue). The black curve shows the beam profile of the THz pulse as a function of its radial distance. (b) Solid lines: calculated transmission ratios as a function of the peak concentration c_e for $w_{\text{ex}} > w_{\text{THz}}$ (blue) and the volume mismatch occurring in the experiment (red) discussed in more detail in Appendix B. Circles and dashed lines: experimentally observed transmission ratios for one single-pulse excitation or the sum of two single-pulse excitations [cf. Fig. 2(g)] with peak concentrations as indicated. Diamonds: experimental values in the case of double-pulse excitation.

concentration c_e . In Fig. 6(b), the electric-field transmission calculated for a complete spatial overlap of the THz beam with the excited sample volume is plotted as a function of c_e (blue line).

In the experiment, the spot sizes of the near-infrared pump pulses and the THz probe pulse on the sample are similar. However, the highly nonlinear character of electron generation by five- to six-photon ionization leads to (i) a cross section of the electron-containing volume, which is substantially smaller than the volume probed by the THz pulse, and (ii) a strong radial variation of electron concentration over the (Gaussian) profile of the pump beam [27]. This mismatch in volume is illustrated in Fig. 6(a), where the THz electric-field transmission calculated for different concentrations c_e of generated electrons is plotted versus the radial distance from the center of the THz beam (colored lines). There is a pronounced variation of transmission over the THz beam profile (black line), which originates from the radial electron density variation. The overall transmission of the THz pulse is given by the frequency-dependent radial average of such profiles. The method for this averaging has been described in detail in the Supplemental Material of Ref. [27]. The red curve in Fig. 6(b) shows the overall transmission, which exhibits a clearly sublinear decrease with increasing electron concentration c_e . This behavior is in contrast to the linear dashed lines, representing the sum of two

single-pulse excitations. More details of this analysis are given in Appendix B.

The symbols in Fig. 6(b) show the experimentally observed transmission ratios. The circles represent transmission ratios for excitation with a single pump pulse and the sum of two single-pulse excitations [cf. Fig. 2(g)], each generating electron concentrations c_e as indicated. The diamonds show the experimental values for double-pulse excitation for a total concentration as indicated. Experimentally, we find a good agreement of generating $c_e = 1.4$ mM with a single pulse (open circle) and $c_e = 0.7 + 0.7$ mM using two excitation pulses (solid diamond). There is an excellent agreement of the experimental results with the calculated transmission (red curve), underlining the validity of the Clausius-Mossotti approach [Eq. (1)] for describing the transverse dielectric function.

B. Oscillatory response and longitudinal dielectric function

The experiments reveal pronounced oscillatory changes of the transverse dielectric function, on top of the steplike absorption increase. Such oscillations represent a quasiparticle excitation, which is launched during the initial femtosecond phase of electron motion in the liquid, i.e., on a time scale much shorter than the subpicosecond electron localization. At such early times, this excitation has both transverse and longitudinal components and screening of electric interactions in the many-body ensemble is weak. The oscillation frequency is accounted for by the Clausius-Mossotti relation (1) for the transverse dielectric function. Upon electron localization, the coherent many-body excitation develops a purely longitudinal character, in analogy to polarons in plasma and solids. The longitudinal polaron oscillations periodically modulate the charge density in a solvent cloud around a solvated electron, affecting both the transverse and longitudinal response. The radial electric field from the solvated, i.e., localized electron, is fully screened by the solvent cloud with a radius set by the screening length.

For a description of the longitudinal dielectric response, we introduce a polaron picture based on a linear dynamical screening of Coulomb interactions in a dielectric continuum [23] and consider the wave vector and frequency-dependent longitudinal dielectric function $\epsilon_L(q, \nu)$. This approach is similar to polaron theories developed in solid state physics [19,28–30]. The model is based on a Gaussian electron wave packet $\psi(\mathbf{r}) = (\eta/\pi)^{3/2} \exp[-\eta(\mathbf{r} - \mathbf{r}_0)^2]$, which has a time-dependent width $\eta(t)$ centered around the time-dependent position $\mathbf{r}_0(t)$ to account for the localization kinetics of the photogenerated electrons. Its longitudinal dielectric displacement field $\mathbf{D}_e(\mathbf{r}, t)$ is given by [31]

$$\mathbf{D}_e(\mathbf{r}, t) = -e\nabla \left[\int \left(\frac{2\eta(t)}{\pi} \right)^{3/2} \frac{\exp(-2\eta(t)|\mathbf{r} - \mathbf{r}'|^2)}{4\pi|\mathbf{r}_0(t) - \mathbf{r}'|} d^3\mathbf{r}' \right]. \quad (3)$$

This displacement field is related to the longitudinal electric field through

$$\mathbf{E}_L[\mathbf{q}, \nu, c_{A,B}] = \frac{\mathbf{D}_e(\mathbf{q}, \nu)}{\epsilon_0} \frac{1}{\epsilon_L[\mathbf{q}, \nu, c_{A,B}]}. \quad (4)$$

$\mathbf{E}_L[\mathbf{q}, \nu, c_{A,B}]$ and $\mathbf{D}_e(\mathbf{q}, \nu)$ are the four-dimensional Fourier transforms of $\mathbf{E}_L[\mathbf{r}, t, c_{A,B}]$ and $\mathbf{D}_e(\mathbf{r}, t)$. The expression for $\mathbf{E}_L[\mathbf{q}, \nu, c_{A,B}]$ contains both the electric field from the electron and the longitudinal response of the surrounding liquid medium during the solvation process. The solvent response induces both the deceleration of electron motion in the medium via frictional forces and the concomitant reduction of the wavepacket size down to its final (minimal) value, i.e., the transition $\eta(t) \rightarrow \eta_{se}$. In the final quasiequilibrium ground state of the solvated electron, the longitudinal electric field is static and given by the (radial) gradient of the potential of an electron wavepacket at rest $d\mathbf{r}_0/dt = 0$ with a width $\eta = \eta_{se}$.

To analyze this time-dependent, self-consistent problem, we return to real space $\mathbf{r}$ and time domain t , and decompose the total electric field $\mathbf{E}_{tot}(\mathbf{r}, t)$ and the total current density $\mathbf{j}_{tot}(\mathbf{r}, t)$ into their longitudinal and transverse components:

$$\mathbf{E}_{tot}(\mathbf{r}, t) = \mathbf{E}_L(\mathbf{r}, t) + \mathbf{E}_T(\mathbf{r}, t), \quad (5)$$

$$\mathbf{j}_{tot}(\mathbf{r}, t) = \mathbf{j}_L(\mathbf{r}, t) + \mathbf{j}_T(\mathbf{r}, t). \quad (6)$$

The longitudinal current density describes the redistribution of charge in the electron-localization process and is directed along the gradient of the time-dependent charge density $\rho(\mathbf{r}, t)$:

$$\mathbf{j}_L(\mathbf{r}, t) = \frac{\mathbf{j}_{tot}(\mathbf{r}, t) \cdot \nabla \rho(\mathbf{r}, t)}{|\nabla \rho(\mathbf{r}, t)|^2} \nabla \rho(\mathbf{r}, t), \quad (7)$$

$$\begin{aligned} \mathbf{j}_L(\mathbf{r}, t) &= 0 \quad \text{for} \quad \nabla \rho(\mathbf{r}, t) = 0 \\ 0 &\leq |\mathbf{j}_L(\mathbf{r}, t)| \leq |\mathbf{j}_{tot}(\mathbf{r}, t)|, \end{aligned} \quad (8)$$

$$0 \leq |\mathbf{j}_T(\mathbf{r}, t)| \leq |\mathbf{j}_{tot}(\mathbf{r}, t)|. \quad (9)$$

The longitudinal current density is related to the longitudinal electric field via

$$\mathbf{E}_L(\mathbf{r}, t) = -\frac{1}{\epsilon_0} \int_{-\infty}^t \mathbf{j}_L(\mathbf{r}, s) ds. \quad (10)$$

The longitudinal current density fulfills the continuity equation

$$\nabla \cdot \mathbf{j}_L(\mathbf{r}, t) = -\partial_t \rho(\mathbf{r}, t). \quad (11)$$

As a result, both longitudinal quantities $\mathbf{j}_L(\mathbf{r}, t)$ and $\mathbf{E}_L(\mathbf{r}, t)$ are either time dependent or identically vanish. The spatiotemporal dynamics of $\rho(\mathbf{r}, t)$ is determined by the localization process of the electron wavepacket and, after localization, by the polaron oscillations. After the decay of the latter, the charge density becomes quasistatic and the longitudinal current density vanishes.

We now insert the total current density $\mathbf{j}_{tot}(\mathbf{r}, t)$ into the Maxwell equation for $\nabla \times \mathbf{B}$ in the regime of linear response, i.e., a negligible influence of the magnetic field on the current and charge densities. This gives

$$\frac{1}{\mu_0} \nabla \times \mathbf{B} = \epsilon_0 \frac{\partial \mathbf{E}_T}{\partial t} + \mathbf{j}_T + \left(\epsilon_0 \frac{\partial \mathbf{E}_L}{\partial t} + \mathbf{j}_L \right) \quad (12)$$

$$= \frac{\partial \mathbf{D}_{tot}}{\partial t} = \frac{\partial \mathbf{D}_T}{\partial t} \quad (13)$$

$$\mathbf{D}_L(\mathbf{r}, t) = 0. \quad (14)$$

Here, $\mathbf{D}_L(\mathbf{r}, t)$ is the total longitudinal dielectric displacement including the contributions of the electron and the solvent. We recall that, in this limit, the longitudinal quantities are fully orthogonal to the transverse ones.

There is no magnetic field generated by $\mathbf{j}_L(\mathbf{r}, t)$ because it is exactly compensated for by the time derivative of the longitudinal electric field. In the Maxwell equation (12), the term in the bracket on the r.h.s. identically vanishes as does the total longitudinal displacement in Eq. (14) everywhere in space and at all times. The latter corresponds to $\epsilon_L(\mathbf{q}, \nu) = 0$. Thus, the longitudinal dielectric function describes all longitudinal elementary excitations. In our experiments, appreciable magnetic fields occur exclusively during the 800 nm excitation pulses, while the magnetic fields of the THz probe pulses are negligibly small. As a result, the longitudinal “world” is decoupled from the transverse one for all times after the excitation process as illustrated in Fig. 7.

After photogeneration, the Coulomb interaction of the released electron with the liquid environment induces a re-orientation of dipolar solvent molecules, eventually resulting in the formation of the self-consistent localization potential [red curve in Fig. 7(a)]. This process is connected with a transfer of kinetic energy to the liquid environment via frictional forces described by $\text{Im}[1/\epsilon_L(q, \nu, c_{A,B})]$ [Eq. (4)]. In parallel, the solvent reorientation on the subpicosecond time scale of electron localization leads to a buildup of screening of long-range Coulomb interactions [orange line in Fig. 7(b)]. As a consequence, screening is weak immediately after electron generation [black line in panel (b)], but becomes strong when the electron has reached its quasistatic localized ground state [orange and/or red curves in panel (b)]. In the latter, the length scale of screening is set by the Debye screening length L_D . For an electron concentration $c_{A,B} = 1.0$ mM and a sample at ambient temperature ($T = 300$ K), one estimates a value of $L_D \approx 2.3$ nm in the THz frequency range shown in Fig. 1(c). A spherical volume of a radius L_D around the localized electron contains some 400 IPA molecules, which screen the electron’s electric field. An appreciable longitudinal electric field [Eq. (4)] from the electron and its polaron oscillations exists only within this “Debye” solvent cloud, which appears electrically neutral from the outside and does not contribute to the macroscopic longitudinal field.

The ultrafast loss of electron kinetic energy is connected with the impulsive excitation of transverse and longitudinal degrees of freedom. This mechanism kicks off the observed polaron oscillations [blue curve in Fig. 7(b)] with a frequency fulfilling the condition $\epsilon_L[q, \nu, c_{A,B}] = 0$ after electron localization. It is important to note that the polaron frequency ν_0 is set by the partial concentrations $c_{A,B}$, in line with the experimental results. Pre-existing fully solvated electrons [red curves in Figs. 7(d)–7(f)] are irrelevant because of their electrically inert character in the Debye solvent cloud. After localization, the longitudinal dynamics consist in coherent polaron oscillations of the electron wavepacket size $\eta(\tau)$ and the surrounding solvent cloud of a radius L_D . In the energy-loss function, this spatial range is encoded in the q dependence of $\epsilon_L[q, \nu, c_{A,B}]$. The inverse of the polaron frequency ν_0 essentially determines the time scale of the buildup of screening. Since the damping of longitudinal elementary excitations is extremely weak and frequency dependent, one gets an

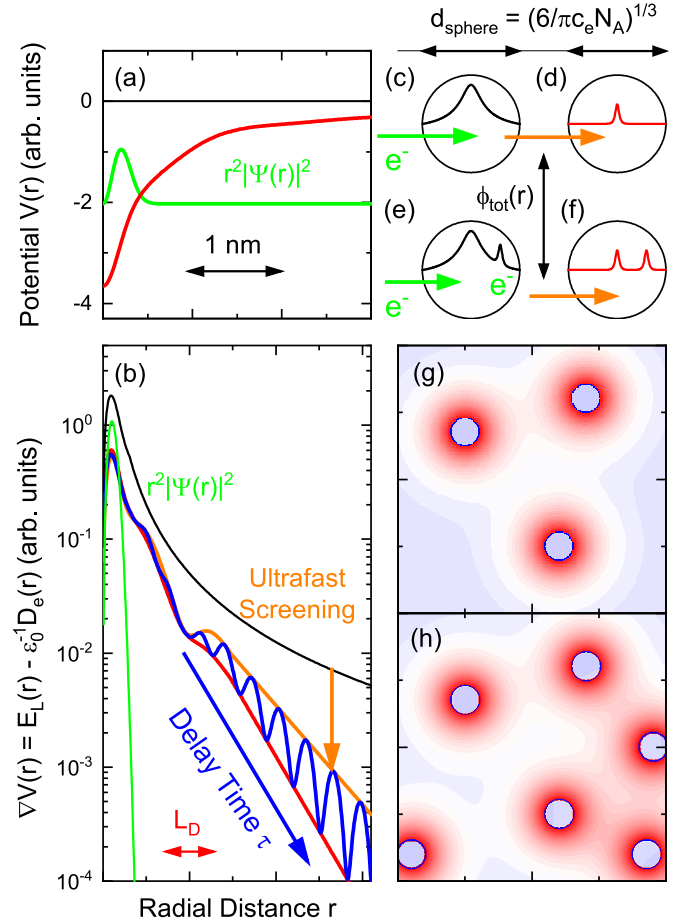


FIG. 7. Cartoon of the ultrafast electron solvation (screening) inducing polaron oscillations in one- and two-pulse excitation schemes. (a) Self-induced potential $V(r)$ of a solvated electron (red line) together with the radial electron density $r^2|\Psi(r)|^2$ (green line) as a function of the radial distance r from its center. (b) Gradient of the potential $\nabla V(r) = E_L(r) - \epsilon_0^{-1}D_e(r)$ having purely radial field components in different phases after electron generation. Black line: initially unscreened potential observed directly after electron injection. Orange: ultrafast screening leads to an exponential decay of $\nabla V(r)$ with the Debye screening length L_D exhibiting an “overshoot” (red) causing polaron oscillations (blue) as a function of τ . (c), (d) One- and (e), (f) two-pulse excitation schemes in a sphere of IPA [diameter $d_{\text{sphere}} = (6/\pi c_e N_A)^{1/3}$] containing just one electron after one-pulse excitation. The total electric potential $\phi_{\text{tot}}(r)$ (i.e., solvation shell plus electron) is plotted in each sphere having the respective compensating positive charge homogeneously distributed on its surface. Ultrafast screening (orange arrow) leads to concentration of the polaron oscillation to a volume of $\approx L_D^3$ being orders of magnitude smaller than $L_D^3 \ll (c_e N_A)^{-1}$. Consequently, the screening of the second injected electron and its polaron oscillation (e), (f) is not affected by the (already) shrunk first polaron. (g), (h) Schematic ensemble of electrons and their solvation shells after (g) the first and (h) the second pump pulse. For the electron concentrations in the experiments, the distance between two solvation sites is much larger than shown here.

overshoot of screening which eventually oscillates between two extremal values.

As illustrated in Figs. 7(b)–7(h), ultrafast screening (orange arrows) limits the polaron oscillations in space to a

volume of $\approx L_D^3$ which is typically orders of magnitude smaller than the inverse photoexcited electron concentration $L_D^3 \ll (c_e N_A)^{-1}$. In other words, the screening of the second injected electron [panels (e) and (f)] and its polaron oscillation frequency are not affected by the (already) shrunk first polaron. An illustrating sketch of the ensemble of electrons and their solvation shells after the first and the second pump pulse is shown in panels (g) and (h), respectively.

A quantitative analysis of our experimental results based on this theoretical picture requires knowledge of the longitudinal dielectric function $\epsilon_L[q, \nu, c_{A,B}]$. For describing the spatiotemporal dynamics of the electrons, the q dependence is of particular relevance. So far, the longitudinal dielectric functions of polar liquids are scarcely known [7,8] and there is no quantitative information for IPA, the solvent used in our experiments. An appropriate theoretical treatment at the molecular level requires a quantum-mechanical description of the localized electrons in combination with the long-range electrostatics of several thousands of disordered solvent molecules in collective motion. Such theory is currently not available. Even classical molecular dynamics simulations of such large ensembles of dipolar molecules are highly complex and do not exist. For such lack of information, the present discussion is limited to the key physical mechanisms, without providing a quantitative comparison between theory and experiment.

V. CONCLUSIONS

In conclusion, the present study reveals the interplay of transverse and longitudinal excitations during and after the solvation process of electrons in a polar liquid. Femtosecond multiphoton ionization generates electrons in spatially extended continuum states. As a result, the transverse dielectric function of the liquid in the THz frequency range is strongly modified. A change of the imaginary part manifests in an absorption change, in time following a steplike behavior with a rise time set by the femtosecond pulse duration. The change of the real part affects the phase of a propagating THz pulse.

The presence of electrons introduces a zero crossing of the real part of the transverse dielectric function as described by the Clausius Mossotti relation. The zero crossing sets the frequency of a new elementary excitation of an electron coupled to the dipolar solvent molecules surrounding it. On this resonance, ultrafast electron transport and relaxation impulsively excite underdamped coherent oscillations, which persist for more than 100 ps. Upon electron localization, the coherent excitation acquires a purely longitudinal polaron character, characterized by longitudinal oscillations of the electrons and their surrounding solvent clouds. The radius of the latter is set by the electrostatic screening length. Such vibrating objects are essentially decoupled from the macroscopic dielectric response and have no impact on polaron oscillations launched in a subsequent excitation process.

Our study demonstrates the potential of nonlinear THz spectroscopy for unraveling the complex interplay of the transient transverse and longitudinal many-body response of polar liquids. Moreover, polaronic excitations are established as a most sensitive probe of the many-body dielectric function of liquids. All current analysis of such behavior is based on

macroscopic electrodynamic quantities with a missing link to dynamics at the molecular level. In particular, there is no adequate microscopic picture of the longitudinal and transverse dielectric response on the distinct length scales relevant here, namely the multianometer extension of electron wavepackets in continuum states, the nanometer size of the solvent cloud involved in polaron oscillations, and the subnanometer radius of the electron localization potential. Even for classical molecular dynamics calculations the vastly different length scales, the large number of polarizable solvent molecules embedding a finite number of electrons, and their complex trajectories define major challenges. Our results represent a benchmark for developing such theoretical treatments.

ACKNOWLEDGMENTS

This research has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Program (Grant Agreement No. 833365, principal investigator T.E.).

DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

APPENDIX A: DATA ANALYSIS

The experiments employ two 800 nm pump pulses and a single THz probe pulse, as discussed in Sec. II. The different two- and three-pulse sequences are generated by implementing three mechanical choppers in the experiment. The THz electric field transmitted through the sample is detected with and without pumping.

For the reduction of noise and improvement of the data quality, we applied the following analysis to this data.

(i) We correct for noise arising from small experimental drifts in amplitude and timing along the experimental time axes τ and T . In the measurements, the transmitted THz fields $E^T(\nu, \tau, T)$ (no pump), $E^{A,B}(\nu, \tau, T)$ (pump A or B), and $E^{AB}(\nu, \tau, T)$ (both pump pulses A and B) depend on τ and T , because small drifts of the amplitude and timing of the THz probe pulse occur over periods of many laboratory hours and have to be correctly referenced in the analysis. To evaluate these τ - and T -dependent experimental spectra, it is helpful to define τ - and T -dependent complex transmission spectra with the help of the Fourier transforms along real time t , i.e., $E^T(\nu, \tau, T)$, $E^A(\nu, \tau, T)$, $E^B(\nu, \tau, T)$, and $E^{AB}(\nu, \tau, T)$:

$$T^A(\nu, \tau, T) = \frac{E^A(\nu, \tau, T)}{E^T(\nu, \tau, T)}, \quad (A1)$$

$$T^B(\nu, \tau, T) = \frac{E^B(\nu, \tau, T)}{E^T(\nu, \tau, T)}, \quad (A2)$$

$$T^{AB}(\nu, \tau, T) = \frac{E^{AB}(\nu, \tau, T)}{E^T(\nu, \tau, T)}. \quad (A3)$$

The correctly referenced signals are gained by multiplying these complex transmission spectra with the spectrum of an averaged THz probe pulse:

$$E_{\text{ave}}^T(\nu) = \frac{1}{m} \sum_{k=1}^m E^T(\nu, \tau_k, T_{\text{fixed}}), \quad (\text{A4})$$

$$E_{\text{ave}}^A(\nu, \tau, T) = T^A(\nu, \tau, T) E_{\text{ave}}^T(\nu), \quad (\text{A5})$$

$$E_{\text{ave}}^B(\nu, \tau, T) = T^B(\nu, \tau, T) E_{\text{ave}}^T(\nu), \quad (\text{A6})$$

$$E_{\text{ave}}^{AB}(\nu, \tau, T) = T^{AB}(\nu, \tau, T) E_{\text{ave}}^T(\nu). \quad (\text{A7})$$

Subsequently, the correctly referenced nonlinear signals are obtained by subtracting $E_{\text{ave}}^T(\nu)$:

$$E_{\text{NL}}^A(t, \tau, T) = E_{\text{ave}}^A(t, \tau, T) - E_{\text{ave}}^T(t), \quad (\text{A8})$$

$$E_{\text{NL}}^B(t, \tau, T) = E_{\text{ave}}^B(t, \tau, T) - E_{\text{ave}}^T(t), \quad (\text{A9})$$

$$E_{\text{NL}}^{AB}(t, \tau, T) = E_{\text{ave}}^{AB}(t, \tau, T) - E_{\text{ave}}^T(t), \quad (\text{A10})$$

$$E_{\text{NL}}^{3\text{-pulse}}(t, \tau, T) = E_{\text{NL}}^{AB}(t, \tau, T) - E_{\text{NL}}^A(t, \tau, T) - E_{\text{NL}}^B(t, \tau, T). \quad (\text{A11})$$

(ii) We apply a 2D-Fourier filter to the data to suppress high-frequency noise. Therefore, we perform a 2D-Fourier transform along τ and t for fixed delay times T_{fixed} resulting in the 2D spectra $E_{\text{NL}}^A(\nu, \nu_t, T)$, $E_{\text{NL}}^B(\nu, \nu_t, T)$, and $E_{\text{NL}}^{AB}(\nu, \nu_t, T)$, the latter of these shown in Fig. 8(a). Such spectra are multiplied with a 2D filter function given by

$$F(\nu, \nu_t, \nu_c) = \Theta(\nu_c - \sqrt{\nu_t^2 + \nu^2}) + \Theta(\sqrt{\nu_t^2 + \nu^2} - \nu_c) \\ \times \Theta(2\nu_c - \sqrt{\nu_t^2 + \nu^2}) \sin^2\left(\frac{\pi\sqrt{\nu_t^2 + \nu^2}}{2\nu_c}\right), \quad (\text{A12})$$

which is plotted as a contour 2D-plot in Fig. 8(b) having the radial profile already shown as dashed line in Fig. 4(b). Choosing $\nu_c = \nu_{\text{osc}}$, the experimentally observed polaron oscillation amplitude is not reduced, but higher-frequency noise is effectively suppressed as exemplarily shown in Figs. 8(c) and 8(d). An inverse 2D Fourier transform returns the filtered data to the 2D time domain. For a single 2D scan, the result of such 2D-Fourier filtering for various nonlinear signals is shown in Fig. 2.

(iii) A key step in analyzing the data is to extract the polaron oscillations from the 2D signals in Eqs. (A8)–(A11), consisting of oscillatory and steplike components. The step signal and baseline fluctuations of a single 2D scan are isolated by connecting the center points between neighboring pairs of oscillation minima and maxima by straight lines. This procedure gives the overall stepfunction $\text{Step}_{\text{ave}}(t, \tau, T)$ when averaged over all recorded data sets. The purely oscillatory signal as a function of t and τ is extracted by subtraction of step signals of individual 2D scans from Eqs. (A8)–(A11).

To increase the signal-to-noise ratio, it is helpful to average the extracted oscillatory signals over several 2D scans. This procedure requires special attention due to slightly varying polaron oscillations frequencies, and thus phases, in

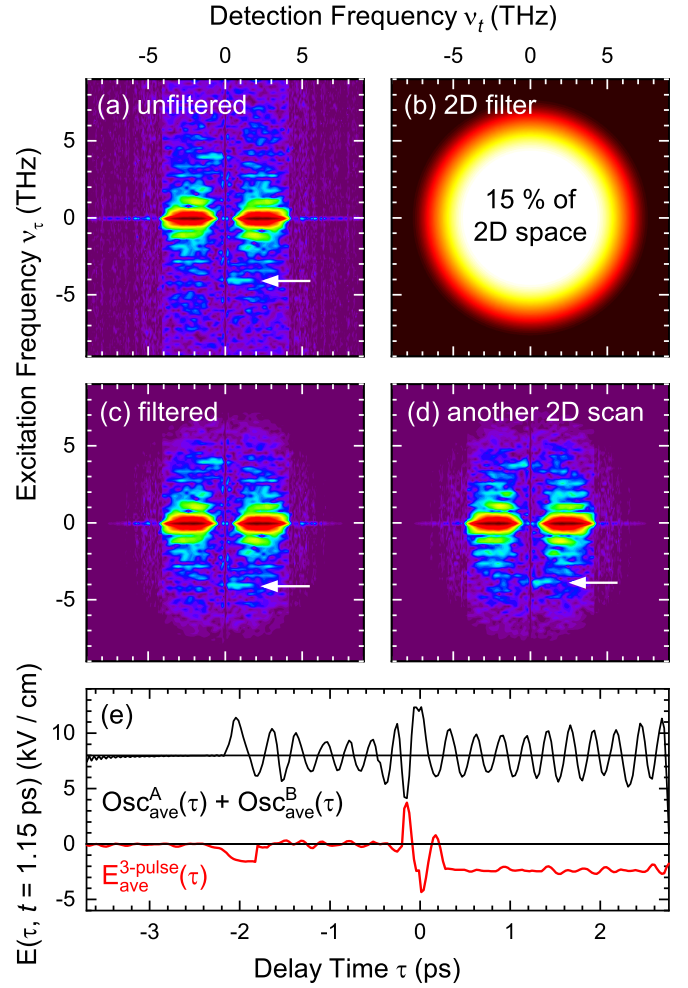


FIG. 8. (a) Inner part of an unfiltered 2D (amplitude) spectrum of a single 2D scan ($c_e = 0.7 + 0.7$ mM). The entire 2D spectrum spans ± 10 THz for ν_t and ± 19 THz for ν_τ . The polaron oscillations at $\nu_\tau \approx 4$ THz (white arrow) occur predominantly for detection frequencies $\nu_t < 1.5$ THz. To suppress high-frequency noise we apply the 2D filter defined in (A12) shown as contour plot in panel (b) with a radial profile shown as dashed line in Fig. 4(b). (c), (d) Filtered 2D spectra of two subsequently measured 2D scans. (e) The purely oscillatory signal $\text{Osc}_{\text{ave}}^A(\tau) + \text{Osc}_{\text{ave}}^B(\tau)$ (black curve) averaged over seven 2D scans according to (A13) at $t = 1.15$ ps [cf. dashed arrows in Figs. 2(g) and 2(h)] is directly compared with the three-pulse nonlinear signal $E_{\text{ave}}^{3\text{-pulse}}(\tau, t = 1.15 \text{ ps})$ (red curve) averaged over seven 2D scans, too. In contrast to the black curve, the oscillation (outside the generation steps) of the three-pulse signal (red curve) disappears when averaging several 2D scans.

concomitant scans, i.e., the polaron oscillations in the 2D-frequency plane vary slightly around $\nu_\tau \approx 4$ THz [white arrows in Figs. 8(c) and 8(d)] and occur predominantly for detection frequencies $\nu_t < 1.5$ THz. To overcome this issue, we average the amplitudes and phases of the oscillatory signals separately. Therefore, we calculate a “complex continuation” of all oscillatory signals by performing a Fourier transform along τ , multiplying each resulting signal with $2\Theta(\nu_\tau)$, and finally performing an inverse Fourier transform, resulting in the “complex-complemented” signal $\text{Sig}(t, \tau, T)$. This signal is easily decomposed into its amplitude

$|\text{Sig}(t, \tau, T)|$ and phase $\arg[\text{Sig}(t, \tau, T)]$, which then are averaged over all recorded data sets, giving $|\text{Sig}_{\text{ave}}(t, \tau, T)|$ and $\arg[\text{Sig}_{\text{ave}}(t, \tau, T)]$. Thus, the averaged oscillatory signal is given by

$$\text{Osc}_{\text{ave}}(t, \tau, T) = |\text{Sig}_{\text{ave}}(t, \tau, T)| \times \cos(\arg[\text{Sig}_{\text{ave}}(t, \tau, T)]). \quad (\text{A13})$$

Finally, the full 2D signals Eqs. (A8)–(A11) averaged over all concomitant data sets are given by $\text{Step}_{\text{ave}}(t, \tau, T) + \text{Osc}_{\text{ave}}(t, \tau, T)$ and are the basis of experimental data presented in Figs. 3, 4, and 8(e).

In Fig. 8(e) we show most directly that for the purely oscillatory signal $\text{Osc}_{\text{ave}}^{\text{A}}(\tau) + \text{Osc}_{\text{ave}}^{\text{B}}(\tau)$ (black curve) averaging over seven 2D scans makes the oscillations increasingly clear. In contrast, for the three-pulse nonlinear signal $E_{\text{NL}}^{\text{3-pulse}}(\tau, t = 1.15 \text{ ps})$ (red curve) averaging over seven 2D scans makes (outside the generation steps) any oscillatory features disappear.

APPENDIX B: SPECTRAL BEHAVIOR OF NONLINEAR THZ SIGNALS AND THz TRANSMISSION INCLUDING VOLUME MISMATCH

The nonlinear 2D spectra shown in Fig. 8 demonstrate most directly that the oscillatory response located at $\nu_{\tau} \approx 4 \text{ THz}$ occurs predominantly at low detection frequencies $\nu_t < 1.5 \text{ THz}$, whereas the steplike response has its maximum around $\nu_{\tau} = 0$ and extends from $\nu_t \approx 1 \text{ THz}$ up to $\nu_t \approx 4 \text{ THz}$ (the steps in combination with a finite range of measured delay times τ is responsible for the sinc-function-like pattern along the excitation frequency ν_{τ}).

Due to the chirp of the THz probe pulse transmitted through the IPA sample [Fig. 1(a)], the polaron oscillations are most clearly observed within the first negative half cycle of the THz pulse at real time $t = 1.15 \text{ ps}$. This half cycle contains most of the low-frequency components $\nu_t < 1.5 \text{ THz}$ of the THz probe pulse. Reading the oscillatory response directly in the 2D-time domain has the advantage that one “simultaneously” achieves the best possible time resolution along delay time τ because no additional frequency filtering along ν_t is involved.

The generation of free electrons by five- to six-photon ionization of solvent molecules results in a cross section w_{ex} of the electron-containing sample volume, which is substantially smaller than the spot size of the focused 800 nm excitation beam with a Gaussian intensity profile. More specifically, the radial profile of electron concentration c_e exhibits a Gaussian shape with $w_{\text{ex}} \approx \sqrt{m} \cdot d_{800}$, where $m = 5$ to 6 and d_{800} is the spot size of the pump beam. As the spot size of the THz probe beam $w_{\text{THz}} \approx d_{800}$, there is a mismatch between the excited and the probed sample volume, which has to be taken into account for a proper treatment of the THz transmission of the sample.

Considering the volume mismatch due to the lateral THz beam profile, i.e., $w_{\text{THz}} > w_{\text{ex}}$ we performed a radial frequency-dependent averaging which is based on pin-hole reference experiments. Such data and the calculation of the corrected overall THz transmission have been discussed in detail in the Supplemental Material of Ref. [27]. For the

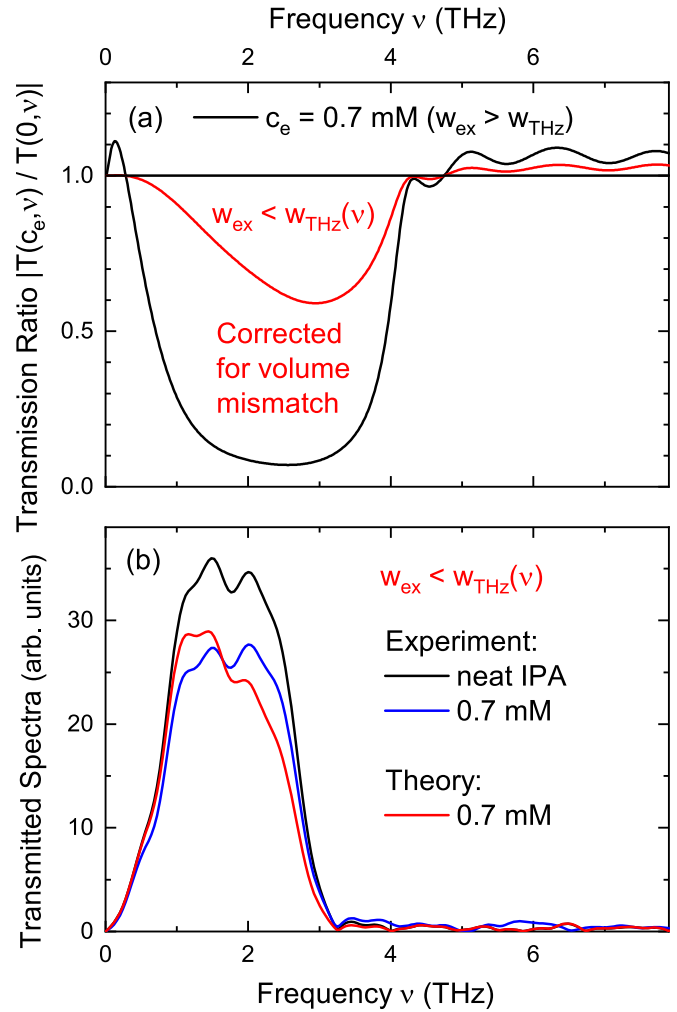


FIG. 9. (a) Black curve: calculated frequency-dependent transmission ratio between an IPA sample containing electrons ($c_e = 0.7 \text{ mM}$) and that of neat IPA for a THz beam with a diameter smaller than that of the excited volume $w_{\text{THz}} < w_{\text{ex}}$, i.e., no volume mismatch. Red curve: transmission ratio corrected for the frequency-dependent volume mismatch $w_{\text{THz}}(\nu) > w_{\text{ex}}$ occurring in the experiment. (b) Spectra of THz pulses transmitted through the neat IPA sample (black), through that containing electrons (blue, $c_e = 0.7 \text{ mM}$), and the theoretically expected spectrum (red) including frequency-dependent volume mismatch.

present experiments, the results of such treatment are shown in Fig. 6. Despite the fact that such a treatment neglects any nonlinear diffraction of the THz beam the agreement between experiment and theory is surprisingly good.

The steplike response is dominated by transient absorption. Here, one has to pay special attention to both the finite thickness of the IPA sample and the volume mismatch between that containing photogenerated electrons (characterized by diameter w_{ex} in Figs. 6 and 9) and that determined by the beam profile of the THz probe pulse (characterized by diameter w_{THz} in Figs. 6 and 9). Both constraints modify the transient absorption in a frequency-dependent fashion, two phenomena, which we already discussed in detail in Ref. [27] and its Supplemental Material.

Even for THz frequencies exhibiting no volume mismatch in the experiment, i.e., $w_{\text{ex}} > w_{\text{THz}}$, one has to consider radiative coupling between different sheets of the IPA sample arranged along the propagation direction. In the spectral range with a negative dielectric function $\epsilon < 0$, the THz response is similar to the inductive behavior of an epsilon-near-zero (ENZ) material [27]. With the theoretical concept described in Ref. [27] we calculated the frequency-dependent transmission ratio between an IPA sample containing electrons at a concentrations $c_e = 0.7$ mM and that of neat IPA. The result for $w_{\text{ex}} > w_{\text{THz}}$ is shown as a black line in Fig. 9(a), while the red line gives the result corrected for the experimental $w_{\text{ex}} < w_{\text{THz}}$ case. In panel (b) we show the experimental spectra of our THz pulse transmitted through neat IPA (black

line) and the sample with $c_e = 0.7$ mM (blue line), together with a spectrum calculated for the $w_{\text{ex}} < w_{\text{THz}}$ case (red line). A comparison of the black and blue line reveals a stronger decrease of electric-field amplitude at low THz frequencies, in line with the rise of $\text{Im}(n)$ toward lower frequencies [cf. Fig. 1(c)]. This behavior is reversed by the correction for $w_{\text{ex}} < w_{\text{THz}}$ (red line). Due to the larger spot size of the low-frequency components of the THz pulse, a larger unexcited sample volume contributes to the overall transmission, thus enhancing the transmitted low-frequency components (red curve). Apparently, for the high concentrations generated in the present experiments, the steplike transient absorption response occurs predominantly at detection frequencies $\nu_t > 1.5$ THz.

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- [1] L. D. Landau, E. M. Lifshitz, and L. P. Pitaevskii, *Electrodynamics of Continuous Media*, 2nd ed. (Butterworth-Heinemann, Oxford, 1984).
 - [2] J. J. Hopfield and D. G. Thomas, Theoretical and experimental effects of spatial dispersion on the optical properties of crystals, *Phys. Rev.* **132**, 563 (1963).
 - [3] V. Ballenegger and J.-P. Hansen, Dielectric permittivity profiles of confined polar fluids, *J. Chem. Phys.* **122**, 114711 (2005).
 - [4] V. M. Agranovich and Y. Gartstein, Spatial dispersion and negative refraction of light, *Phys.-Usp.* **49**, 1029 (2006).
 - [5] G. E. H. Reuter and E. H. Sondheimer, The theory of the anomalous skin effect in metals, *Proc. R. Soc. Lond. A* **195**, 336 (1948).
 - [6] R. G. Barrera, A. Reyes-Coronado, and A. García-Valenzuela, Nonlocal nature of the electrodynamic response of colloidal systems, *Phys. Rev. B* **75**, 184202 (2007).
 - [7] P. A. Bopp, A. A. Kornyshev, and G. Sutmann, Static nonlocal dielectric function of liquid water, *Phys. Rev. Lett.* **76**, 1280 (1996).
 - [8] P. A. Bopp, A. A. Kornyshev, and G. Sutmann, Frequency and wave-vector dependent dielectric function of water: Collective modes and relaxation spectra, *J. Chem. Phys.* **109**, 1939 (1998).
 - [9] D. C. Elton and M. Fernández-Serra, The hydrogen-bond network of water supports propagating optical phonon-like modes, *Nat. Commun.* **7**, 10193 (2016).
 - [10] L. Turi and P. J. Rossky, Theoretical studies of spectroscopy and dynamics of hydrated electrons, *Chem. Rev.* **112**, 5641 (2012).
 - [11] B. C. Webster, The polaron viewpoint of solvated electrons, *Nat. Phys. Sci.* **239**, 79 (1972).
 - [12] G. A. Kenney-Wallace and C. D. Jonah, Picosecond spectroscopy and solvation clusters. The dynamics of localizing electrons in polar fluids, *J. Phys. Chem.* **86**, 2572 (1982).
 - [13] X. Shi, F. H. Long, H. Lu, and K. B. Eisenthal, Electron solvation in neat alcohols, *J. Phys. Chem.* **99**, 6917 (1995).
 - [14] I. A. Taub, D. A. Harter, M. C. Sauer, and L. M. Dorfman, Pulse radiolysis studies. IV. the solvated electron in the aliphatic alcohols, *J. Chem. Phys.* **41**, 979 (1964).
 - [15] A. Migus, Y. Gauduel, J. L. Martin, and A. Antonetti, Excess electrons in liquid water: First evidence of a prehydrated state with femtosecond lifetime, *Phys. Rev. Lett.* **58**, 1559 (1987).
 - [16] J. C. Alfano, P. K. Walhout, Y. Kimura, and P. F. Barbara, Ultrafast transient-absorption spectroscopy of the aqueous solvated electron, *J. Chem. Phys.* **98**, 5996 (1993).
 - [17] M. F. Emde, A. Baltuška, A. Kummrow, M. S. Pshenichnikov, and D. A. Wiersma, Ultrafast librational dynamics of the hydrated electron, *Phys. Rev. Lett.* **80**, 4645 (1998).
 - [18] J. Savolainen, F. Uhlig, S. Ahmed, P. Hamm, and P. Jungwirth, Direct observation of the collapse of the delocalized excess electron in water, *Nat. Chem.* **6**, 697 (2014).
 - [19] H. Fröhlich, Electrons in lattice fields, *Adv. Phys.* **3**, 325 (1954).
 - [20] T.-D. Lee and D. Pines, Interaction of a nonrelativistic particle with a scalar field with application to slow electrons in polar crystals, *Phys. Rev.* **92**, 883 (1953).
 - [21] A. Ghalgaoui, B. P. Fingerhut, K. Reimann, T. Elsaesser, and M. Woerner, Terahertz polaron oscillations of electrons solvated in liquid water, *Phys. Rev. Lett.* **126**, 097401 (2021).
 - [22] P. Singh, J. Zhang, A. Ghalgaoui, K. Reimann, B. P. Fingerhut, M. Woerner, and T. Elsaesser, Coherent polaron dynamics of electrons solvated in polar liquids, *PNAS Nexus* **1**, pgac078 (2022).
 - [23] M. Woerner, B. P. Fingerhut, and T. Elsaesser, Field-induced electron generation in water: Solvation dynamics and many-body interactions, *J. Phys. Chem. B* **126**, 2621 (2022).
 - [24] M. Runge, K. Reimann, M. Woerner, and T. Elsaesser, Non-linear terahertz polarizability of electrons solvated in a polar liquid, *Phys. Rev. Lett.* **131**, 166902 (2023).
 - [25] K. Reimann, M. Woerner, and T. Elsaesser, Two-dimensional terahertz spectroscopy of condensed-phase molecular systems, *J. Chem. Phys.* **154**, 120901 (2021).
 - [26] J. H. Hannay, The Clausius-Mossotti equation: An alternative derivation, *Eur. J. Phys.* **4**, 141 (1983).
 - [27] M. Runge, M. Woerner, D. I. Bondar, and T. Elsaesser, Solvated electrons in polar liquids as ϵ -near-zero materials tunable in

- the terahertz frequency range, *Phys. Rev. Lett.* **134**, 056901 (2025).
- [28] T. D. Lee, F. E. Low, and D. Pines, The Motion of slow electrons in a polar crystal, *Phys. Rev.* **90**, 297 (1953).
- [29] F. M. Peeters and J. T. Devreese, Radius, self-induced potential, and number of virtual optical phonons of a polaron, *Phys. Rev. B* **31**, 4890 (1985).
- [30] P. Gaal, W. Kuehn, K. Reimann, M. Woerner, T. Elsaesser, and R. Hey, Internal motions of a quasiparticle governing its ultrafast nonlinear response, *Nature (London)* **450**, 1210 (2007).
- [31] P. Bowlan, W. Kuehn, K. Reimann, M. Woerner, T. Elsaesser, R. Hey, and C. Flytzanis, Nonlinear electron transport in an electron-hole plasma, *Phys. Rev. B* **85**, 165206 (2012).