Ultrafast two-dimensional terahertz spectroscopy of elementary excitations in solids

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Abstract. Recent experimental progress has allowed for the implementation of nonlinear two-dimensional (2D) terahertz (THz) spectroscopy in the ultrafast time domain. We discuss the principles of this technique based on multiple phase-locked electric field transients interacting in a collinear geometry with a solid and the phase-resolved detection of the THz fields after interaction with the sample. To illustrate the potential of this new method, 2D correlation spectra of coupled intersubband-longitudinal optical phonon excitations in a double quantum well system and a study of ultrafast carrier dynamics in graphene are presented.

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1. Introduction

Nonlinear two-dimensional (2D) spectroscopy in the ultrafast time domain has become an important tool for unravelling the dynamics and couplings of elementary excitations in condensed-phase systems. Experiments have addressed a wide range of electronic and vibrational excitations in solids, liquids and (bio)molecular systems [1–7]. Combined with theoretical calculations and simulations of the transient nonlinear response, such work has given detailed insight into the microscopic equilibrium fluctuations, e.g., of liquid structure [8], as well as into non-equilibrium vibrational and chemical dynamics [9, 10], excitonic and electronic excitations [11] and processes of system–bath interactions.

Nonlinear time-resolved spectroscopy in the frequency range 1–25 THz, corresponding to photon energies between approximately 4 and 100 meV, provides access to low-energy excitations in bulk and nanostructured solids such as phonons, electronic interband, impurity-related and intraexcitonic transitions, as well as intersubband excitations [12–16]. Moreover, it allows for exploring nonlinear charge transport processes most directly [17, 18]. In liquids, intermolecular vibrations and translations, which are sensitive probes of structural dynamics, occur in this range. While nonlinear THz methods have recently made substantial progress, 2D techniques have found very limited application so far. Their use requires subpicosecond THz sources strong enough to induce a nonlinear system response and interaction geometries not hampered by the comparably large diameter of THz beams and/or focal spots. Both optical rectification of near-infrared femtosecond pulses in nonlinear crystals [19–21] and plasma sources driven by two-colour femtosecond light fields [22–27] provide THz transients with field strengths up to megavolts per centimetre. Free-space electrooptic (EO) sampling allows for a full characterization of such pulses in amplitude and absolute phase [19, 28, 29]. Implementing such components in a novel experimental scheme, 2D spectroscopy in the range of 1–30 THz was recently demonstrated [30–33]. This method is based on a collinear interaction geometry of two phase-locked pulses with a solid sample and the field-resolved detection of the transmitted THz field. First applications have included intersubband Rabi flopping in semiconductor quantum wells, the measurement of intersubband correlation spectra and the analysis of correlated electronic and lattice excitations in a double quantum well (DQW) system.

In this paper, we discuss both methodological aspects and applications of 2D THz spectroscopy in solid-state physics. Section 2 gives an introduction to the 2D THz method, followed by a discussion of experiments on coupled intersubband and longitudinal optical (LO) phonon excitations in quantum wells (section 3). In section 4, we present the results on the nonlinear THz response of graphene excited at electric field strengths in the non-perturbative regime. The conclusions and a brief outlook are given in section 5.

2. Concepts of two-dimensional (2D) terahertz (THz) spectroscopy

So far, 2D spectroscopy has been based on femtosecond pump–probe and photon-echo methods probing the third-order nonlinear response of a sample in the time domain [34]. The pump–probe implementation of 2D spectroscopy uses a tunable narrow-band pump pulse and a spectrally broad probe pulse travelling in a different spatial direction with a time delay $T$ relative to the pump. There are two simultaneous interactions with the pump electric field at $T = 0$ generating the excitation in the sample and a third interaction with the probe field at the time delay $T$. The probe field induces a polarization and serves as the local oscillator for the field.
radiated by the sample. The resulting signal is detected spectrally resolved as a function of the detection frequency \( \nu_3 \). The pump–probe signal is measured for different frequency positions \( \nu_1 \) of the pump pulses to generate a 2D spectrum of the third-order response as a function of the excitation frequency \( \nu_1 \) and the detection frequency \( \nu_3 \).

The third-order photon echo method is based on a sequence of three pulses schematically shown in figure 1(a). The three pulses interact with the sample in a non-collinear geometry with wavevectors \( k_1, k_2 \) and \( k_3 \) (figure 1(b)). The first two interactions with the sample are separated by the coherence time \( \tau \). The first pulse generates a coherent polarization of the sample, which is transformed into a transient population by the interaction with the second pulse. After the waiting period \( T \), during which the population evolves freely, the nonlinear signal is generated by interaction with the electric field of the third pulse. Nonlinear signals occur in the directions \(-k_1 + k_2 + k_3\) and \( k_1 - k_2 + k_3\), which are different from those of the three pulses interacting with the sample. Such signals are detected phase resolved, e.g. by heterodyning them with a fourth synchronized pulse serving as the local oscillator. A spectrally resolved detection of the heterodyned signal, i.e. the interferogram of the local oscillator and the signal field, provides the signal as a function of detection frequency \( \nu_3 = \nu_3 \). A Fourier transform of interferograms taken for different coherence times \( \tau \) along the \( \tau \)-coordinate gives the signal as a function of the excitation frequency \( \nu_1 = \nu_1 \). Details of this procedure have been discussed in [34].

The non-collinear geometries of the third-order pump–probe and photon-echo methods are difficult to implement in the THz range because of the comparably large diameter of freely propagating THz beams and the large optical spot size of focused THz pulses. We, thus, developed a method of THz 2D spectroscopy based on a sequence of two phase-locked pulses A and B (figure 1(c)) and the collinear interaction scheme with wavevectors \( k_A \) and \( k_B \) depicted in figure 1(d) [30, 31]. The THz pulses A and B are separated by the delay time \( \tau \) and induce the nonlinear response of the sample. The THz field transmitted through the sample is detected by a phase-resolving detector based on free-space EO sampling. In this way, the electric field is measured as a function of real time \( t \). To separate the nonlinear signal from the transmitted excitation fields, the following sequence of measurements is carried out: (i) the total electric field with both pulses A and B interacting with the sample, (ii) electric field with only pulse A interacting and (iii) electric field with only pulse B interacting. The electric field of the nonlinear signal, \( E_{NL} \), is then extracted as the difference \( E_{NL} = E_{AB} - E_A - E_B \), where \( E_{AB}, E_A \) and \( E_B \) are the results of measurements (i)–(iii). A double Fourier transform of the signal field \( E_{NL} \) along the time coordinates \( \tau \) and \( t \) then provides 2D spectra as a function of the excitation frequency \( \nu_1 \) and detection frequency \( \nu_3 \). While the present scheme with two phase-locked pulses is limited to measurements with a waiting time \( T = 0 \), the extension to sequences of three or even more pulses is straightforward.

An important difference between non-collinear and collinear interaction geometries exists with respect to different third-order contributions such as pump–probe and photon echo signals and to signals of higher (\( >3 \)) nonlinear order, which arise from multiple interactions with the pulses of the incoming sequence. In the non-collinear case, such signals are separated in space due to the different superpositions of the wavevectors of the pulses generating them. In contrast, all nonlinear contributions are present in the signal measured in the collinear geometry of 2D THz spectroscopy. Nevertheless, the different nonlinear orders can be separated in the frequency domain as will be discussed below.

Figure 1(e) shows a schematic representation of the experimental setup, which is based on an amplified Ti:sapphire laser system and has been described in detail elsewhere [19].
Figure 1. (a) Pulse sequence applied in three-pulse photon echo experiments. The intensity envelopes $I(t)$ of pulses 1–3 (black lines) are plotted together with a signal (red line) as a function of time. Pulses 1 and 2 are separated by the coherence time $\tau$, and pulses 2 and 3 by the population time $T$. (b) Non-collinear wavevector diagram applied in three-pulse photon echo experiments. The wavevectors $k_1$, $k_2$, $k_3$ of the three pulses and the wavevector $k_{LO}$ of the local-oscillator pulse are shown. The photon echo signals are emitted in the directions $-k_1 + k_2 + k_3$ and $k_1 - k_2 + k_3$. For detection, the signal is heterodyned with the local-oscillator pulse. (c) Two-pulse sequence applied in collinear THz 2D spectroscopy. The electric fields $E(t)$ of the two pulses and the nonlinear signal are plotted as a function of time, and $\tau$ represents the delay/coherence time. (d) Collinear geometry of THz 2D spectroscopy with wavevectors $k_A$, $k_B$. 
Figure 1. (Continued) and the phase-resolving detector based on EO sampling.
(e) Schematic representation of the experimental setup based on a Ti:sapphire oscillator/amplifier system including a pulse shaper. Pulses A and B are generated by optical rectification in GaSe crystals. Although pulses A and B are initially parallel to each other, because of the high divergence in the THz range they are collinear when reaching the sample. The field-resolved detection is based on EO sampling in ZnTe using 12 fs probe pulses from the laser oscillator.

The mode-locked oscillator provides linearly polarized 12 fs pulses at a 72 MHz repetition rate. The major fraction of the oscillator output travels through a pulse shaper (Dazzler) and feeds a multipass amplifier working at a 1 kHz repetition rate. The second part of the oscillator output serves as a probe pulse for EO sampling. The amplifier provides 25 fs pulses around 800 nm with an energy of up to 600 µJ. From such pulses, the intense THz transients with electric field amplitudes of up to 1 MV cm\(^{-1}\) are derived by optical rectification in a nonlinear crystal or by implementing THz generation in a laser-induced plasma driven simultaneously at the laser fundamental and second-harmonic frequency. In the setup of figure 1(e), the THz pulses A and B are generated by optical rectification in two separate GaSe crystals. The delay time \(\tau\) between them is varied with an optical delay line. The two THz beams are combined and focused onto the sample by an off-axis parabolic mirror. The transmitted THz field is imaged onto the nonlinear EO sampling crystal (ZnTe or GaP) with two other off-axis parabolic mirrors. In the EO sampling setup, the polarization change of the 12 fs probe pulses from the oscillator is measured as a function of delay relative to the THz transient with a polarization-sensitive detection scheme that consists of a \(\lambda/4\) plate, a Wollaston prism (W) and two balanced photodiodes PD1 and PD2. The different measurements (i)-(iii) providing the fields \(E_{AB}, E_A\) and \(E_B\) are carried out with two mechanical choppers synchronized to the 1 kHz repetition rate of the laser system.

To illustrate the experimental concept, simulated time-domain THz data are plotted in figure 2. Part (a) shows the total electric field \(E_{AB}\) transmitted through the sample as a function of real time \(t\), (b) the transmitted fields \(E_A\) and \(E_B\) of pulses A and B and (c) the extracted nonlinear signal \(E_{NL} = E_{AB} - E_A - E_B\). In figure 2(d), the total field \(E_{AB}\) is plotted as a function of the two time coordinates \(t\) and \(\tau\). The field of the first pulse A depends only on \(t\) and, thus, its phase fronts are parallel to the \(y\)-axis of this plot. In contrast, the field of the second pulse B depends on both \(t\) and \(\tau\), resulting in phase fronts tilted by 45°. As causality is fulfilled in generating the nonlinear signal, the corresponding electric field \(E_{NL}\) plotted in figure 2(e) occurs only in an area of the 2D plot limited toward shorter \(t\) and \(\tau\) by the phase fronts of pulses A and B.

A scheme of the so-called frequency vectors allows for an analysis and separation of the different nonlinear signals in the frequency domain. The definition of the two-component frequency vectors is illustrated in figure 3(a). The left panel shows the wavefronts of the two pulses A and B in the time domain as a function of \(t\) and \(\tau\). A 2D Fourier transform along \(t\) and \(\tau\) provides the pulse spectra (right panel), which are located around \(\tilde{v}_A = (\nu_\tau, \nu_t) = (0, \nu_0)\) and \(\tilde{v}_B = (-\nu_0, \nu_0)\) in the frequency-domain 2D plot with axes \(\nu_t = \nu_1\) and \(\nu_\tau = \nu_3\) (figure 3(b); \(\nu_0\) is the centre frequency of the THz pulses). The electric field of pulse A depends on \(t\) only, resulting in a vanishing \(\nu_\tau\) component of the vector \(\tilde{v}_A\). In contrast, the electric field of pulse B depends...
Figure 2. Results of a simulation of THz 2D spectroscopy in the time domain. (a) The total electric field $E_{AB}$ consisting of the two THz pulses and the field radiated by a two-level system. (b) Electric fields of the individual THz pulses $E_A$ and $E_B$. (c) Nonlinear signal $E_{NL} = E_{AB} - E_A - E_B$. (d) Contour plot of the total field $E_{AB}$ plotted as a function of delay (coherence) time $\tau$ and real time $t$. (e) Contour plot of the nonlinear signal $E_{NL}$ plotted as a function of $\tau$ and $t$.


In figure 3(b), examples of interaction sequences/Liouville space pathways of different nonlinear orders are illustrated applying the frequency vector picture. In figure 3(c), the results of theoretical simulations of coherent Rabi flopping in a two-level system are shown. The total nonlinear response is decomposed into the different nonlinear interaction sequences of different order. As Rabi oscillations include arbitrary nonlinear orders, the total nonlinear response breaks up in many contributions with non-zero amplitudes. The results of an experiment on intersubband Rabi flopping are shown in figure 3(d). In an n-type modulation-doped GaAs/AlGaAs multiple quantum well sample, the dipole allowed intersubband transition between the $n = 1$ and 2 conduction subbands (transition frequency 25 THz) was resonantly driven with strong pairs of THz pulses, resulting in Rabi oscillations of the intersubband polarization and population inversion. The measured 2D spectrum consists of the broad range of signals shown in figure 3(d), in agreement with the theoretical results of figure 3(c).
Figure 3. (a) Left panel: electric field of two THz pulses A and B as a function of delay time $\tau$ and real time $t$. Right panel: Fourier transform of the time-dependent field plotted along the frequency axes $\nu_t$ (conjugate to real time $t$) and $\nu_\tau$ (conjugate to delay time $\tau$). The frequencies are given in units of the THz carrier frequency $\nu_0$. (b) Sequences of frequency vectors $\vec{\nu}_A = (\nu_\tau, \nu_t)$ representing different types of nonlinear signals in the ($\nu_\tau, \nu_t$) plane. Sequences composed of three vectors represent third-order photon echo signals, while the sequence of five vectors stands for a fifth-order nonlinear signal. (c) Simulation of a coherent Rabi flop in a two-level system decomposed into the different nonlinear orders. The vector sequences shown in (b) contribute to the total signals shown at the different $\nu_\tau$. All signals shown occur at $\nu_t = \nu_0$. (d) Result of an experiment on intersubband Rabi flopping in GaAs/AlGaAs quantum wells [30]. PE stands for photon echo, 6 WM for six-wave mixing, r for rephasing and nr for non-rephasing.

This example demonstrates that signals of different nonlinear orders are readily separated, allowing for an analysis of the individual contributions, e.g. the third-order four-wave mixing signals. In other words, selecting the four-wave mixing signals from the overall 2D spectrum and plotting them on extended frequency scales for $\nu_\tau = \nu_1$ and $\nu_t = \nu_3$ is equivalent to the third-order 2D spectra measured in non-collinear pump–probe and photon-echo experiments.
Figure 4. (a) Potential energy diagram and conduction subband envelope wavefunctions of a GaAs/Al\textsubscript{0.35}Ga\textsubscript{0.65}As DQW system. On the right-hand side, a schematic LO phonon potential with oscillator quantum states is shown. (b) The measured third-order time-domain nonlinear response $E_{\text{NL}}$ plotted as a function of real time $t$ and delay (coherence) time $\tau$. (c) Fourier transform of the third-order time-domain signal in the $(\nu_\tau, \nu_t)$ plane. The $\chi(2)$ signals originate from frequency mixing in the bulk GaAs substrate. Because of different group velocities, the two pulses have temporal overlap at some point in the substrate for a large range of $\tau$.

3. Correlated intersubband-longitudinal optical-phonon excitations in GaAs/AlGaAs double quantum wells

An important application of 2D THz spectroscopy is coupled electronic and lattice excitations in solids. For sufficiently strong microscopic interaction, the properties of the individual excitations undergo significant changes, which are reflected in a strongly modified linear and/or nonlinear response. The coupling of electrons to a polar lattice via the Coulomb interaction leads to the formation of polarons, which can be visualized as an electron surrounded by a cloud of LO phonons. In the following, we discuss the behaviour of intersubband excitations of electrons strongly coupled to LO phonons. The 2D spectra of this system display a large manifold of diagonal and off-diagonal peaks, which originate from the polaronic character of the nonlinear response [32].

The sample investigated consists of nine GaAs/Al\textsubscript{0.35}Ga\textsubscript{0.65}As DQWs with the potential energy diagram sketched in figure 4(a). In each period of the sample, a 9 nm wide quantum well (NW) couples through a 2 nm thick AlGaAs barrier to a 12 nm wide quantum well (WW), resulting in the envelope wavefunctions of the subbands $n = 1$–5 plotted in figure 4(a).
Figure 5. (a), (b) Rephasing and non-rephasing third-order photon echo signal in the time domain. (c) 2D THz correlation spectrum of the DQW system shown in figure 4(a). The absolute value of the photon echo signal, i.e. the sum of the rephasing and non-rephasing signals, is plotted as a function of excitation frequency \( \nu_1 = \nu_\tau \) and of detection frequency \( \nu_3 = \nu_t \). The break-up of the spectrum in many diagonal and off-diagonal peaks is caused by the strong polaronic coupling between intersubband and LO phonon excitations. Right panel: intersubband absorption spectrum of the DQW sample (solid line) and spectra of the THz pulses A and B (dashed and dotted lines).

The individual DQWs are separated by 15 nm thick AlGaAs barriers with Si doping layers at their centres, resulting in an electron density of \( 10^{12} \) cm\(^{-2} \) per DQW. The dipole-allowed transitions between subbands 1 and 3 and subbands 2 and 4 give rise to two strong absorption lines centred at 17 THz (transition energy 70 meV) and 24 THz (99 meV). The linear absorption spectrum of the sample at room temperature is shown in the right panel of figure 5(c). On the right-hand side of figure 4(a), we show a schematic harmonic potential of LO phonons with quantized oscillator states separated by an energy of 36 meV, corresponding to a transition frequency of 8.8 THz. The \( v = 2 \) state at 17.4 THz and the \( v = 3 \) state at 26.1 THz are close to the minima of the \( n = 3 \) and 4 subbands of the DQW, respectively, favouring a coupling between electronic subbands and LO phonon states.

In the 2D experiments, pulses A and B were centred at spectral positions of 20 and 24 THz and covered both intersubband absorption lines shown in figure 5(c). The maximum electric field amplitude of the two pulses was between 70 and 90 kV cm\(^{-1} \). The total nonlinear signal from the DQW sample is plotted in figure 4(b) as a function of the real time \( t \) and the delay time \( \tau \). Decomposition of this signal in the frequency space by applying the frequency vector method described in section 2 gives the signals plotted in figure 4(c). The second-order contributions
marked by $\chi^{(2)}$ originate from frequency mixing in the thick GaAs substrate and will not be discussed further. The two third-order photon echo signals B–A–A and A–B–B, for which the frequency vector sequences are plotted in figure 3(b), represent the so-called rephasing and non-rephasing third-order response of the DQW sample [36]. In the B–A–A sequence, the $\nu_i$ components of the frequency vectors in the first and the third interaction have opposite sign, corresponding to phase factors in the nonlinear response function with opposite signs of their exponents. As a result, the emitted signal has a carrier wave proportional to $\exp(-i2\pi \nu_0(t - \tau))$, i.e. the phase fronts of this signal are perpendicular to those of pulse B. This is shown in figure 5(a), where the rephasing signal is plotted as a function of the real time $t$ and the delay time $\tau$. This plot was generated by a Fourier back-transformation of the frequency-domain B–A–A signal in figure 4(c) into the time domain. In the A–B–B interaction sequence, the $\nu_i$ components of the frequency vectors have the same sign and the phase fronts of the emitted non-rephasing signal (figure 5(b)) are parallel to those of pulse B.

Figure 5(c) shows the absorptive 2D correlation spectrum, which represents the (real part of the) sum of the rephasing and non-rephasing photon-echo signals. The 2D spectrum displays a highly complex pattern of diagonal and off-diagonal peaks of both positive and negative sign. In particular, there is a rich variety of peaks at excitation frequencies $\nu_i$ in between the diagonal peaks originating from the 1–3 and 2–4 intersubband transitions at 17 and 24 THz. Coupling between such two intersubband dipoles is weak as is evident from the absence of cross peaks in the 2D spectrum. Overall, purely electronic intersubband transitions occurring in the DQW structure (cf figure 4(a)) cannot account for the large number of additional diagonal and off-diagonal peaks and for their particular frequency positions.

The multitude of 2D peaks is caused by a strong polaronic coupling between the intersubband and LO phonon excitations. Such a pronounced coupling originates from the polar optical interaction between electrons and LO phonons and the energetic resonance between individual LO phonon states and subband states as shown in figure 4(a). A theoretical analysis of the 2D spectrum and the linear intersubband absorption spectrum has been performed within a model considering single-particle intersubband excitations coupled to LO phonons [32]. For vanishing electron–LO-phonon coupling, the model gives the purely electronic 2D spectrum of the intersubband excitations, which has been presented in [32] and which displays a peak pattern much simpler than that of figure 5(c). For a strong electron–LO-phonon coupling, one finds a shift of the 1–3 and 2–4 intersubband transitions caused by a renormalization of the electronic subband states as well as a multitude of LO-phonon-assisted additional transitions, for instance, $(1+\text{LO}) - 4$ and $2 - (3+\text{LO})$. The renormalized electronic and phonon-assisted transitions display a significant mutual coupling, which gives rise to the multitude of off-diagonal peaks in the 2D spectrum. In the linear absorption spectrum, the polaronic character leads to a shift of the purely electronic absorption lines and the occurrence of additional weaker components due to the LO-phonon-assisted transitions. Due to the substantial spectral broadening present at room temperature, the different contributions overlap and give rise to the broad envelopes of the linear absorption spectrum shown in the right panel of figure 5(c).

While the theoretical analysis identifies the basic mechanism behind the complex 2D spectrum, the measured peak pattern is not fully reproduced by the calculations (see figure 2(c) of [32]). This fact points to limitations of the single-particle picture of electronic excitations and calls for a treatment including Coulomb-mediated many-body effects. Nevertheless, the calculations allow for an estimate of the electron–LO-phonon interaction energy in the DQW sample of approximately 200 meV. This value is much larger than the polaron binding energy.
of 5 meV in bulk GaAs. The strong coupling originates from the very high intersubband dipole moment $d_{IS} \approx e \times 10 \text{ nm}$ ($e$ is the elementary charge) and the dynamic in-plane localization of the electrons to their thermal deBroglie wavelength, which has a value of approximately 3.5 nm at a temperature of 300 K.

4. THz 2D spectroscopy of graphene in the non-perturbative limit

Graphene, a single layer of carbon atoms in a honeycomb spatial arrangement, has a peculiar bandstructure with a vanishing energy gap between the highest valence and the lowest conduction bands at the so-called Dirac points [$\mathcal{E}(K) = \mathcal{E}(K') = 0$] [37]. Because of the linear dispersion of such bands in $k$-space, graphene allows for the study of ‘massless’ charge carriers with a velocity independent of their energy [38]. Charge transport in graphene has been widely explored, but there is still much to be learned about carrier dynamics on the ultrafast time scale, in particular at very small energies close to the Dirac points $K$ and $K'$ (figure 6(a)). So far, ultrafast pump–probe studies of graphene at photon energies exceeding 1 eV have provided information on non-equilibrium carrier dynamics [39–42]. Thermalization into separate Fermi distributions of electrons and holes occurred within 250 fs, due to Coulomb and optical phonon scattering. This process is followed by carrier cooling via emission of optical and finally acoustic phonons. Eventually, electrons and holes recombine in the picosecond time domain. Carrier dynamics at energies close to the Dirac points and well below the optical phonon energy should be quite different, as shown by recent mid-infrared measurements [43].

From a transport point of view, one expects graphene to be extremely nonlinear in the THz frequency range. In figure 6(a) the Dirac-cone-like bandstructure of graphene is shown close to the $K = (K_x, K_y)$ point. According to the acceleration theorem, i.e. $dk/dt = e E(t)/\hbar$, a THz pulse polarized in the $x$-direction moves an electron back and forth along $k_x$ on a trajectory $k_x(t) = e A_x(t)/\hbar$ (green curve) determined by the transient vector potential $A_x(t)$. Since $k_y$ remains constant during this motion, the band structure $\mathcal{E}(k_x, k_y = \text{const.} \neq 0)$ as a function of $k_x − K_x$, follows two hyperbolas (valence and conduction band) similar to that of a narrow gap semiconductor. For an electron residing initially at a $k$ vector with $|k_y − K_y| \gg \omega_{\text{THz}}/2v_F$ the intraband motion of the carrier (blue double arrow in figure 6(a)) dominates the response to the applied THz field.

This behaviour changes drastically for electrons residing initially at $k$ vectors with $|k_x − K_x| \ll \omega_{\text{THz}}/2v_F$. Such particles experience an almost vanishing periodic Coulomb potential of the crystal lattice due to destructive interference of its Fourier components at the $K$ and $K'$ points. As a result, they perform predominantly interband trajectories similar to free electrons as visualized by the red double arrow in figure 6(a). Around the $K$ and $K'$ points, the interband dipole matrix element diverges, i.e. $|d(k)| \propto |k − K|^{-1}$.

As a result, the interband transition dipole moment in the THz range is huge with a value of $|d| = e \times 80 \text{ nm}$ at an interband transition frequency of 2 THz. The extremely strong transition dipole leads to an interband Rabi frequency $\Omega_{\text{Rabi}} = |d| \cdot E_{\text{THz}}/\hbar$, which is equal to the 2 THz carrier frequency already

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2 ‘Massless’ refers to the similarity of the energy dispersion of graphene around $K, K'$ with that of a relativistic fermion with rest mass zero (e.g. a neutrino). For any $k \neq K, K'$ graphene electrons do have an effective mass relevant for acceleration processes.

3 This is most easily seen from the momentum matrix element, which has a constant magnitude, namely $|p| = mv_F$. From the relation between the dipole and the momentum matrix elements, $|p| = mω|d|/e$, we obtain with $ω = 2v_F/|k − K|, |d| = ev_F/ω$. 

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Figure 6. (a) Dirac-cone-like bandstructure of graphene close to the \( K = (K_x, K_y) \) point. The energy \( E(k_x, k_y) \) is plotted as a function of \( k_x - K_x \) for three different distances \( k_y - K_y \). Green curve: trajectory of \( k_x(t) = eA_x(t)/\hbar \).

(b) Nonlinear signal \( E_{NL} \) (red line) reconstructed from the pump A–probe B nonlinear signal in (e). The black line gives the field \( E_B \) of the second THz pulse.

(c) 2D contour plot of the total field \( E_{AB} \) as a function of real time \( t \) and delay time \( \tau \). (d) Nonlinear THz signal \( E_{NL} \) as a function of \( t \) and \( \tau \). (e) 2D Fourier transform of the third-order nonlinear signals in the \((\nu_\tau, \nu_t)\) plane. Pump–probe signals are present, while four-wave mixing signals are absent.

at a field strength \( E_{THz} \approx 1 \text{ kV cm}^{-1} \). At such field amplitudes, the light–matter interaction is automatically in the non-perturbative regime, where interband carrier wave Rabi oscillations occur. This mechanism allows for an efficient electron–hole pair generation and recombination by coherent interband tunnelling [44, 45].

In the following, we present the first THz 2D study of graphene. A phase-locked pair of pulses centred at 2 THz propagates parallel to one another and are focused onto the graphene sample where they spatially overlap. We investigated a ten-layer C-face epitaxial graphene sample on SiC (from Graphene Works) at temperatures between 10 and 300 K. Pulses A and B had field strengths of 9 and 18 kV cm\(^{-1}\), respectively. The nonlinear response of the graphene sample is mapped by the 2D method described in section 2. For an extended planar sample of a thickness \( l \) small compared to the wavelength of the THz pulses—a condition perfectly fulfilled in our case—the emitted nonlinear field \( E_{NL}(t) \) is proportional to the current density \( j(t) \) in the sample, i.e. \( E_{NL}(t) = -Z_0j(t)/2 \), where \( Z_0 \) is the vacuum impedance [17].

In figure 6(c), the total electric field \( E_{AB} \) is plotted as a function of real time \( t \) and delay time \( \tau \). The time-domain nonlinear signal \( E_{NL} = E_{AB} - E_A - E_B \) is presented in figure 6(d), while figure 6(e) shows the corresponding third-order signals in the frequency domain as a function of excitation frequency \( \nu_\tau \) and detection frequency \( \nu_t \). The third-order response is
Figure 7. 2D contour plots of the amplitude of the reconstructed complex pump A–probe B nonlinear signal (black ellipses in figure 6(e)) measured at different cold finger temperatures. We observe exclusively pump-induced absorption of the THz probe pulse. Rightmost panel: temperature dependence of the amplitude of the pump–probe signal.

dominated by pump–probe signals, which are non-rephasing. In contrast, rephasing photon echo signals are absent. Selecting the pump-A–probe-B nonlinear signal and Fourier transforming it back into the time domain gives the oscillatory trace shown as a red line in figure 6(b). This signal displays a phase shift of \( \pi \) relative to the field of the probe pulse B (black line) indicating an induced transient absorption of the sample.

The enhanced absorption as a function of pump–probe delay \( \tau \) was measured at several sample temperatures. The 2D contour plots of figure 7 show the amplitude of the reconstructed pump-A–probe-B nonlinear signal for different temperatures. In all cases, we observe exclusively pump-induced absorption of the THz probe pulse. The temperature dependence of the amplitude of the pump–probe signal is shown in the rightmost panel of figure 7. With increasing temperature, the picosecond decay of the enhanced absorption becomes faster and the maximum in the differential transmission decreases drastically from 0.015 to 0.002, see figure 7.

Considering the transport mechanisms shown in figure 6(a), i.e. intraband motion and interband tunnelling of electrons, the interpretation of the nonlinear THz response of graphene is straightforward. In our experiments the amplitude of the trajectories in \( k \) space \( |k_x(t)| = |eA_x(t)/\hbar| \) is many times larger than both the wavevector at which the 2 THz interband transition occurs \( (\omega_{\text{THz}}/2v_F \ll |k_x(t)|) \) and the Fermi wavevector \( k_F = \mu/v_F \ll |k_x(t)| \) determined by the quasi-Fermi level \( \mu \) due to a possible unintentional doping of some layers. Thus, we are definitely in the non-perturbative regime, in which the periodic motion of electrons between states in the lower and upper cone allows for an ultrafast electron–hole pair generation. The energy absorbed from the THz pump pulse leads directly or indirectly, e.g. via impact ionization and Auger recombination, to a multiplication of carriers. Since the oscillator strength of THz intraband absorption is directly proportional to the area density of both holes in the valence band and electrons in the conduction band, the THz probe pulse experiences always an induced absorption after the pump pulse has injected energy into the electronic system of graphene. In a photon picture (which is definitely inappropriate to describe the non-perturbative regime) one could say that multi-photon transitions, which lead to induced absorption, are much stronger...
than one-photon THz transitions, for which the excited sample would display a decrease of absorption caused by Pauli blocking of the optically coupled electron and hole states.

Both the induced absorption and the absence of the photon-echo signals are explained by a model using a pseudopotential bandstructure for graphene including the electron–light coupling via the vector potential \[\text{eq}\]. The model further includes radiative damping and coupling between graphene layers. The model, which will be discussed in detail elsewhere, reproduces our experimental results very well, without having to introduce extremely fast decoherence processes or other scattering mechanisms. Both the enhanced absorption and the absence of photon-echo signals have their origin in the huge transition dipole moments. Since the Rabi frequencies are different at each point in \(k\)-space, the superposition of all photon-echo components leads to a negligible total signal. The model also explains the picosecond recombination of the generated electron–hole pairs by collective radiative damping, an issue which is beyond the scope of this paper.

5. Conclusions

In conclusion, the work discussed here extends ultrafast 2D spectroscopy into the THz frequency range. The collinear interaction geometry and the detection of electric fields in absolute phase and amplitude allow for measuring the nonlinear response of a sample at frequencies between 1 and approximately 40 THz up to arbitrarily high order in the electric field. Using a scheme of frequency vectors, which is equivalent to Feynman diagrams in the time domain, the total nonlinear signal can be decomposed into different nonlinear orders. Moreover, different Liouville space pathways occurring at the same nonlinear order are distinguished. This approach was applied for decomposing an intersubband Rabi flop in semiconductor quantum wells into different nonlinear orders as well as for deciphering the line shapes of polaronic excitations in quantum wells and determining the underlying polar–optical coupling between electrons and LO phonons. In graphene, the nonlinear THz response is already at small driving fields in the non-perturbative regime. It was shown that in this regime the coupling of carriers to the electromagnetic field dominates over all other scattering processes.

The method presented here allows for a straightforward extension to more complex pulse sequences, in particular for a full implementation of the three-pulse photon-echo method with non-zero waiting times. As the THz pulses are inherently synchronized with ultrashort pulses in other spectral ranges derived from the same laser system, optical excitation of the sample before performing the 2D THz measurements is readily implemented. With THz driving fields up to \(1\,\text{MV cm}^{-1}\) at hand, a broad range of resonant and non-resonant nonlinear optical phenomena is accessible. Beyond applications in solid-state physics, an extension of this research toward disordered fluctuating systems such as liquids will be most interesting.

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