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Extremely efficient terahertz high harmonics generation in graphene by hot Dirac fermions

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Multiple optical harmonics generation – the multiplication of photon energy as a result of nonlinear light-matter interaction, has become one of the key technologies in modern electronics and optoelectronics. Owing to its unique electronic band structure featuring massless Dirac fermions [1–3], graphene has been repeatedly predicted to possess particularly high efficiency of optical harmonics generation in the technologically important terahertz (THz) frequency range [4–6]. However, to date, numerous experiments have unfortunately failed to confirm these predictions under technologically-relevant operation conditions. Here we report on the generation of THz harmonics up to the seventh order in single-layer graphene at room temperature and under ambient conditions, driven by THz fields on the order of only 10s of kV/cm, and with field conversion efficiencies in excess of 10⁻³, 10⁻⁴, and 10⁻⁵ for the third, fifth, and seventh THz harmonics, respectively. The key to highly efficient THz harmonics generation in graphene is the collective thermal response of its background Dirac electrons to the driving THz fields. The generated THz harmonics were observed directly in the time domain as electromagnetic field oscillations at these newly synthesized frequencies. The effective THz nonlinear optical coefficients of graphene \( \chi^{(3)}_{\text{eff}} \approx 10^{-9} \text{ m}^2/\text{V}^2 \), \( \chi^{(5)}_{\text{eff}} \approx 10^{-22} \text{ m}^4/\text{V}^4 \), and \( \chi^{(7)}_{\text{eff}} \approx 10^{-38} \text{ m}^6/\text{V}^6 \) substantially exceed the respective nonlinear coefficients of typical solids by 7-18 orders of magnitude [7–9]. Our results, in particular, provide a direct pathway to highly efficient THz frequency synthesis already within the present generation of graphene electronics operating at the fundamental frequencies of only a few 100s of GHz.

A very strong demand exists in the field of modern ultrahigh-speed electronics for efficient active functional materials supporting very high, terahertz (10¹² Hz, THz), frequencies. Since the advent of graphene, several theoretical proposals (see e.g. [4–6]) have predicted efficient THz frequency multiplication or harmonics generation in single-layer graphene in realistic technologically-relevant scenarios, which includes room temperature operation. Despite considerable efforts, the experimental verification of these predictions has so far not been achieved. Bowlan et al. [10] have recently demonstrated signatures of THz harmonics in a near-intrinsic epitaxial 45-layer
graphene sample, however only observable at a cryogenic temperature. The nonlinearity mechanism in Ref. [10] critically relies on inter-band THz transitions in graphene, which at a room temperature are essentially Pauli-blocked. Further, most recently, it was suggested that efficient THz harmonics generation in graphene is unfeasible [11] due to the ultrafast relaxation of THz-excited electrons and holes, prohibiting coherent electronic response to driving THz fields, which is typically required for the generation of THz or optical harmonics in other solids [12,13]. Consequently, it was proposed to move away from the THz range to much higher infrared optical frequencies, where Yoshikawa et al. [11] successfully demonstrated the generation of multiple optical harmonics in single-layer graphene under intense optical excitation with peak electric field strengths reaching 10s of MV/cm.

Here we show that the THz high harmonics generation in single-layer graphene under realistic technological conditions is, in fact, an extremely efficient process, and that the THz nonlinearity of this atomically-thin material greatly surpasses that of other solids. We demonstrate THz harmonics generation up to the 7th order in single-layer graphene at room temperature and under ambient conditions, using THz electric fields as weak as only 10s of kV/cm, which is about three orders of magnitude lower (corresponding to one million times smaller peak powers) than that required for the observation of infrared-driven nonlinearity [11].

Previous experiments on the generation of optical harmonics in graphene critically relied on interband transitions in graphene in strong applied fields [10,11]. Here we show that the key to highly efficient THz harmonics generation in graphene is the introduction of the free background electron population, responding collectively to the driving THz field. These free background Dirac electrons, which can be easily introduced by the substrate or atmospheric doping, or by electronic gating, serve as an extremely efficient, yet highly nonlinear, intermediary energy reservoir: they facilitate and also strongly modulate the energy transfer between the THz field and graphene via a nonlinear intraband conductivity mechanism. Our experimental observations are fully reproduced by a model describing such energy transfer dynamics and the concurrent THz electromagnetic response of graphene.

Our sample is a typical chemical vapor deposition (CVD)-grown monolayer graphene deposited on a fused SiO2 substrate (see Ref. [14] and references therein). Basic characterization of the sample yielded a background free carrier concentration of \( N_c = 2.1 \times 10^{12} \text{cm}^{-2} \) and Fermi level of \( E_F = 170 \) meV at room temperature (see Methods and Extended Data Fig. 11).

Our experiment, schematically represented in Fig. 1(a), was specifically designed for the observation of the THz harmonics in graphene in the time domain (see Methods and Extended Data Fig. 1). It was enabled by the use of TELBE - a novel superconducting radio-frequency accelerator-based superradiant THz source [15]. Our measurements were performed at a repetition rate of 100 kHz, and with linearly polarized THz electric fields incident normally onto graphene. Narrow-band, multi-cycle quasi-monochromatic THz radiation pulses from TELBE (see Extended Data Fig. 2) with controllable peak field strength in the range of \( E_f = 12 - 85 \text{kV/cm} \) and FWHM bandwidth of below 70 GHz were transmitted through the single-layer graphene deposited on a SiO2 substrate, and were detected in the time-domain as the THz light-wave oscillations (see Methods and Extended Data Fig. 1). The THz transmission through a nominally identical bare SiO2 substrate served as a reference, which exhibited no sign of THz nonlinearity. The cut-off frequency
of our THz detector was 2.4 THz. All the measurements were carried out at room temperature. In Fig. 1(b,c) we show the typical results of our experiments. In Fig. 1(b) we show the amplitude spectra of the pump THz wave with a fundamental frequency of $f = 0.3$ THz and a peak electric field strength of $E_f = 85$ kV/cm, transmitted only through the bare SiO$_2$ substrate (red line), and through the single-layer graphene on the SiO$_2$ substrate (blue line). Multiple THz harmonics up to the 7$^{th}$ order are clearly visible in the spectrum of the THz signal after interaction with graphene, with a pump-to-harmonic field conversion efficiency in excess of $10^{-3}$, $10^{-4}$, and $10^{-5}$ for the third, fifth, and seventh THz harmonics, respectively. Such significant nonlinear conversion efficiencies, especially observed at THz frequencies, are quite remarkable, given that the electromagnetic interaction occurs here within just one single atomic layer. In Fig. 1(c) we demonstrate the measured THz harmonics directly in the time domain. Fig. 1(d) shows the results of the calculation based on the thermodynamic model of THz nonlinearity in graphene [14], using the experimental THz pump wave at fundamental frequency $f = 0.3$ THz as an input. We note that the calculations in Fig. 1(d) capture well all the key experimental features in Fig. 1(c), including the peak field strength in the generated harmonics, as well as the temporal shortening of the harmonic pulses with the increase in harmonic order. The essentials of our parameter-free model [14] are explained below, while the specific calculation details are provided in Methods.

The underlying physical mechanism of THz harmonics generation in graphene is the creation of nonlinear electrical currents resulting from the strongly nonlinear intraband THz conductivity of graphene background electrons. In electronic thermal equilibrium the intraband conductivity of graphene $\sigma$ is determined by the concentration $N_c$ and the temperature $T_e$ of its background electronic population. For the intraband THz excitation of graphene $N_c = const$, and the conductivity $\sigma$ is thus governed by the electronic temperature $T_e$. If graphene is sufficiently doped, so that $|E_F| > k_B T_e$, the rise in the electronic temperature leads to a reduction of conductivity [14,16–18] (here $k_B$ is the Boltzmann constant). The application of THz electric field $E$ to graphene leads to generation of a THz current $j = \sigma E$, and hence to deposition of energy into the electronic population (the power absorption coefficient of a material is directly proportional to its conductivity). One of the remarkable features of Dirac electrons in graphene is their ability to internally thermalize, i.e. exchange their kinetic energy and establish a common electronic temperature within the entire background electron population, on an ultrafast timescale below 100 femtoseconds [14,19–24], which is quasi-instantaneous as compared to the ~picosecond period of the THz field oscillation. Therefore, via such an ultrafast internal electronic thermalization, the excess energy deposited into graphene background electrons by the THz current is quasi-instantaneously converted into electronic heat – the collective kinetic energy of the entire background electron population, leading to a rise in the electronic temperature $T_e$ and to a concomitant decrease of the intraband conductivity $\sigma$. As a result of these interdependencies, the THz conductivity of graphene depends strongly nonlinearly on the driving THz field [14,17,25,26]: the stronger the field, the smaller the conductivity becomes. The subsequent energy relaxation (i.e. cooling) of the hot electron population in graphene occurs via phonon emission on a timescale of a few picoseconds (see e.g. [20,25]), i.e. with THz rate (see Methods). This phonon emission completes the energy conversion process in the THz excitation of graphene, in which the background population of Dirac electrons serves as a nonlinear intermediary in the transfer of energy from the absorbed THz field to the lattice of graphene.
The processes of heating and cooling of background Dirac electron population, leading to the reduction and recovery of the intraband THz conductivity in graphene, respectively, are schematically shown in Fig. 2(a). Here \( N(E) = D(E)f_{FD}(E,T) \) is the energy-dependent population density function for graphene background electrons, a product of the density of states \( D \) and the Fermi-Dirac distribution \( f_{FD} \). Now we arrive at a situation where the THz conductivity of graphene is not only nonlinear with the driving THz field (as facilitated by the direct conversion of absorbed THz energy into electronic heat), but also exhibits THz-rate recovery dynamics provided by the electron cooling rate (transfer of electronic heat to the lattice). The double interplay of quasi-instantaneous electron heating and THz-rate electron cooling in THz-driven graphene leads to highly nonlinear temporal modulation of the THz absorption in graphene, and hence of the THz conductivity, as illustrated in the calculations shown in Figs. 2(b,c,d) (see Methods for details).

Consequently, a nonlinear current modulated by nonlinear time-dependent conductivity, is generated in graphene in response to the driving THz field \( E(t) \). In case of a monochromatic THz driving field \( E_f(t) \) oscillating at a frequency \( f \), the resulting nonlinear current in graphene, given its centrosymmetry, will contain contributions at odd-order harmonics \( f, 3f, 5f, 7f, \ldots \), thus leading to electromagnetic re-emission at these harmonic frequencies, as illustrated schematically in Fig. 1(a), and resulting in the appearance of these harmonics in the spectrum of the transmitted THz signal. We note that in a centrosymmetric medium the even-order harmonics cancel out, and thus cannot be generated [7]. Using the above thermodynamic model [14] the nonlinear propagation of THz signals through graphene can be readily calculated, only using experimentally determined parameters as input: the incident THz waveform at the fundamental frequency \( f \); the conductivity parameters of the graphene sample measured in the linear regime in full thermal equilibrium at \( T = 300 \) K; the quasi-instantaneous electron heating (see discussion above and Refs. [19–24]), and picosecond-timescale cooling via phonon emission as measured in Ref. [20]. We also note that no adjustable parameters are used in our model (see Methods).

Now we determine the harmonic generation efficiency and estimate the effective THz nonlinear optical susceptibility of graphene from the analysis of experimentally-measured time-domain THz signals, such as those shown in Fig. 1(c). In Fig. 3(a), we show the dependency of the amplitude of the generated harmonics fields on that of the driving field. Here, in order to increase the dynamic range in the characterization of the 3rd and 5th harmonics generation processes, our THz detection scheme was optimized to detect the harmonic signal only in the spectral window around 2 THz, whereas the driving fundamental frequency \( f \) of the THz source was varied as follows: \( f = 0.68 \) THz was used to generate the 3rd harmonic at \( 3f = 2.04 \) THz, and \( f = 0.37 \) THz was used to generate the 5th harmonic at \( 5f = 1.85 \) THz. For the characterization of the 7th harmonic generation, the pump field had the central frequency \( f = 0.3 \) THz, leading to the harmonic signal at \( 7f = 2.1 \) THz, as shown in Fig. 1(b,c). Depending on the order of the generated harmonic, the peak harmonic field strength was in the range of \( 3 – 111 \) V/cm, whereas the pumping field strength was varying in the range of \( 12 – 85 \) kV/cm. The efficiency parameters of the THz harmonics generation in this work are summarized in Table 1.
Table 1. Harmonic generation efficiencies and nonlinear coefficients of graphene. Pump and harmonic peak electric field strength ranges, maximum field conversion efficiency, and the THz nonlinear coefficients of graphene of 3rd, 5th and 7th orders, established in the small-signal nonlinearity regime.

<table>
<thead>
<tr>
<th>Generated harmonic order ( m )</th>
<th>Range of pump field strength ( E_f ), kV/cm</th>
<th>Range of harmonic field strength ( E_{mf} ), V/cm</th>
<th>Max. field conversion efficiency ( E_{mf} / E_f )</th>
<th>Effective nonlinear coefficient ( \chi^{(m)}_{\text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>12 - 61</td>
<td>3 – 111</td>
<td>2x10^-3</td>
<td>~10^-9 m^2/V^2</td>
</tr>
<tr>
<td>5</td>
<td>17 - 60</td>
<td>0.4 – 15</td>
<td>2.5x10^-4</td>
<td>~10^-22 m^4/V^4</td>
</tr>
<tr>
<td>7</td>
<td>38 - 85</td>
<td>1 – 7</td>
<td>8x10^-5</td>
<td>~10^-38 m^6/V^6</td>
</tr>
</tbody>
</table>

In the same Fig. 3(a), as black solid lines, we present the results of the calculated pump-to-harmonic conversion efficiencies [14], using the parameter-free thermodynamic model as explained above. The agreement between the experimental data and the parameter-free calculation is quantitative. The pump-to-harmonics generation efficiency, shown in Fig. 3(a), saturates with the pump field increase, as caused by the dissipative nature of the interaction between the THz field and the graphene electrons. In Fig. 2(c,d) we show the calculated temporal evolution of the THz field-induced electronic heat \( \Delta Q(t) \) and the instantaneous THz power absorbance \( A(t) \) of our graphene sample, driven by the THz field at the fundamental frequency \( f = 0.3 \) THz shown in Fig 2(b), and with the field strength at the lower and upper limits of our experiment: 10 kV/cm and 85 kV/cm, respectively. At the weaker driving field of 10 kV/cm, the evolution of both \( \Delta Q(t) \) and \( A(t) \) is very small. Here, the nonlinear interaction conditions between the THz field and graphene remain approximately constant over the entire interaction period, thus manifesting the small-signal nonlinearity regime. On the other hand, as the driving THz field increases by about an order of magnitude to 85 kV/cm, the effect of the THz field on the electronic system of graphene becomes dramatic. At the peak of the interaction, the electronic heat \( \Delta Q(t) \) peaks at 0.33 \( \mu \)J/cm², leading to a reduction of the THz power absorbance of graphene by approximately 25%. Such a significant absorption saturation naturally limits the energy transfer rate from the driving THz field to the electronic system, subsequently leading to the observed saturable behavior of THz nonlinearity in graphene. The drastic difference between the THz-graphene interaction conditions for the cases of \( E_f = 10 \) kV/cm and \( E_f = 85 \) kV/cm in Fig. 2(c,d) illustrates the extremely nonlinear nature of the thermodynamic response of the Dirac electrons in graphene to the THz fields.

Importantly, at lower driving fields below approximately 20 kV/cm, both the data and the calculation of harmonics generation efficiency in Fig. 3(a) reduce to the phenomenological power-law dependencies \( E_{mf} \propto E_f^m \), where \( m \) is the harmonic order (see dashed lines in Fig. 3(a)), manifesting the small-signal nonlinearity regime. In this regime the nonlinear conversion can be described within the framework of effective odd-order nonlinear optical coefficients \( \chi^{(m)}_{\text{eff}} \), precisely as expected for the nonlinear response in a centrosymmetric medium. From the purely power-law fits to the field conversion efficiencies (dashed lines in Fig. 3), we determine the effective THz third-, fifth-, and seventh-order nonlinear coefficients of graphene as \( \chi^{(3)}_{\text{eff}} \approx 10^{-9} m^2/V^2 \), \( \chi^{(5)}_{\text{eff}} \approx 10^{-22} m^4/V^4 \), and \( \chi^{(7)}_{\text{eff}} \approx 10^{-38} m^6/V^6 \), respectively (see Methods for details). These
values of THz nonlinear optical coefficients of graphene, determined by us at room temperature
and under ambient conditions in a conventional CVD-grown single-layer graphene, exceed the
Corresponding nonlinearities of a typical solid by 7-18 orders of magnitude \[7-9\]. The third-order
nonlinearity, obtained in this work, exceeds the corresponding values measured in single-layer
graphene in the optical spectral range by 6-10 orders of magnitude \[27-29\] (we note, however,
that the theoretical prediction of stronger optical-range response exists in the literature \[30\]); and
the value reported in the infrared for the 50-layer graphene sample under cryogenic conditions
and in strong magnetic field by at least one order of magnitude \[31\]. The fifth- and seventh order
THz nonlinear coefficients of graphene have not been previously reported in the literature, to the
best of our knowledge.

We note here that the thermodynamic model of graphene conductivity does not contain any \textit{a-
\textit{priori}} defined effective nonlinear-optical coefficients of graphene, but rather describes the
temporal evolution of the THz field-induced electronic heat and, hence, the instantaneous
conductivity of graphene during its interaction with the incident THz electromagnetic wave of
arbitrary shape. A very good agreement between our parameter-free calculation and the entirety
of our data lends credence to our interpretation of the nature of the observed THz harmonics
generation in graphene.

We estimate the limits of applicability of the purely thermodynamic picture of nonlinear THz
response in doped graphene as the onset of coherent Bloch oscillations (see e.g. \[13\]), which in
graphene will occur at a pump field strength of the order of 1-10 MV/cm (see Methods). Now we
illustrate the potential for higher-order THz harmonics generation in graphene using the
thermodynamic mechanism, for some typical experimental and technological scenarios. Employing
the same material parameters of the graphene as used in this work, we apply a model quasi-
monochromatic waveform at fundamental \(f = 0.68\) THz with varying peak field strengths in the
range 100 V/cm - 1 MV/cm. This range comprises the linear regime of \(\sim\)kV/cm THz fields, the
regime of typical high-speed transistor channel fields of \(\sim\)100 kV/cm \[32\], and extends to the
TELBE operation regime under projected design parameters of 1 MV/cm \[15\]. In Fig. 3(b) we show
the corresponding calculated amplitude spectra of the transmitted THz waveform as a function of
the peak electric field strength of the incident fundamental wave. As the driving electric field
strength increases, higher-order harmonics keep appearing in the spectrum, with the 13-th
harmonic falling within the \(10^6\) dynamic range with respect to the transmitted fundamental, at the
field strength of the driving signal of 1 MV/cm.

The very high THz nonlinear coefficients of graphene, measured in this work, suggest
straightforward applications in ultrahigh-frequency (opto-)electronics. The driving electric field on
the order of 10s of kV/cm, such as used here, is about one order of magnitude smaller than the
typical channel field in ultra-high speed transistors \[32\]. Therefore, our results provide the direct
pathway way to purely electronic THz frequency synthesis already within the present generation
of graphene transistors operating at few-100s GHz fundamental frequencies \[32\]. Further, the
observed nonlinear THz response of a single layer graphene can be made scalable, for example, by
creating stratified structures with graphene-coated interfaces, or graphene-loaded waveguides or
cavities. We finally note that our results on efficient THz harmonic generation in graphene by hot
Dirac fermions can be potentially generalized to other representatives of the novel class of Dirac
materials, such as topological insulators, or Weyl and Dirac semimetals \[33\].
References


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Author contributions:
D.T. and M.G. conceived and supervised the project. H.A.H., S.K., J.C.D., Z.M., B.G., N.A., M.C., S.G., Z.W., D.T. and M.G. performed the nonlinear THz spectroscopy measurements and evaluated the experimental data. H.A.H. and D.T. performed the modeling, with contributions from Z.M. and K.J.T.. D.T., M.G. and M.B. interpreted the results, with contributions from all co-authors. Z.L., Z.C., A.N. and K.M. manufactured the samples. H.A.H. and D.T. characterized the linear THz properties of the graphene / fused silica samples. U.L. and J.T. provided for the special mode of high bunch charge operation of TELBE using the novel SRF photoinjector that enabled the observation of the 7th harmonic. M.B. initiated and supported the THz studies on graphene at MPI-P. D.T. and M.G. wrote the manuscript, with contributions from M.B., K.J.T., S.K. and H.A.H. All co-authors discussed the results and commented on the manuscript.

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Data and computer codes availability statement
The datasets generated during and/or analyzed during the current study, as well as the corresponding computer codes, are available from the corresponding authors on reasonable request.
**Main figure legends**

**Fig. 1. Schematic of the THz high harmonics generation experiment and the main results.** (a) Schematic of the experiment: quasi-monochromatic, linearly polarized THz pump wave from the TELBE source is incident onto a graphene sample, single-layer CVD-grown graphene deposited on the SiO₂ substrate. Graphene had a Fermi level \( E_F = 170 \) meV, free carrier density \( N_c = 2.1 \times 10^{12} \) cm\(^{-2} \), and electron momentum scattering time \( \tau = 47 \) fs (all parameters correspond to full thermal equilibrium at 300K). The peak electric field strength of the pump THz signal was controlled in the range of 12 - 85 kV/cm, and the central frequency was varied in the range of 0.3 – 0.68 THz. The incident THz field drives the nonlinear current in graphene, leading to the re-emission at higher odd-order harmonics that appear in the spectrum of the transmitted THz signal. The THz fields are detected in the time domain directly as oscillations of electric field, using free-space electro-optic sampling with the cut-off frequency at 2.4 THz. All the experiments are carried out at room temperature and under ambient conditions. (b) Red line: amplitude spectrum of the incident pump THz wave at the fundamental frequency \( f = 0.3 \) THz with the peak field strength \( E_f = 85 \) kV/cm, determined in the reference measurement. Blue line: the spectrum of the same THz wave transmitted through graphene on a substrate, with clearly visible generated harmonics of 3\(^{rd} \), 5\(^{th} \) and 7\(^{th} \) order. (c) Pump wave (black line) and generated 3\(^{rd} \), 5\(^{th} \) and 7\(^{th} \) THz harmonics for the case in (b). The individual higher harmonics were Fourier filtered from the complete nonlinear signal containing all the generated harmonics at once. (d) Thermodynamic model calculation, corresponding to the measurements in (b,c), using the experimental fundamental pump wave at the frequency \( f = 0.3 \) THz (black line), and the basic parameters of graphene in full thermal equilibrium at 300 K as an input.

**Fig. 2 Illustration of the mechanism of THz harmonics generation in graphene, based on the calculations using the thermodynamic model of intraband nonlinear THz conductivity of graphene.** (a) Temporal asymmetry of electron heating and cooling rates in graphene leads to a situation where the application of (b) a THz driving field to the graphene electron population results in (c) the electronic heat accumulation \( \Delta Q(t) \) and hence in the temporal modulation of (d) the THz absorbance \( A(t) \) and of the conductivity of graphene \( \sigma(t) \). In these calculations the driving field (b) oscillates at the fundamental frequency \( f = 0.3 \) THz. Blue and red lines in (c,d) correspond to the driving field peak amplitude of 10 kV/cm and 85 kV/cm, respectively. The 10 kV/cm field strength represents the regime of small-signal nonlinearity (no significant modification of the sample properties on the timescale of the interaction with the THz wave), while the THz wave with 85 kV/cm field strength leads to significant electron heating and thus to a substantial decrease in the absorption of graphene at the peak of interaction.

**Fig. 3. THz high harmonics generation efficiency.** (a) Dependency of the generated harmonic field strength on the fundamental pump field strength. For the third, fifth and seventh harmonics the fundamental field frequency was \( f = 0.68 \) THz, \( f = 0.37 \) THz, and \( f = 0.3 \) THz, respectively, leading to the corresponding higher harmonics of 3\(^{rd} f = 2.04 \) THz, 5\(^{th} f = 1.85 \) THz, and 7\(^{th} f = 2.1 \) THz, respectively. Symbols – data, black lines – parameter-free calculations using the thermodynamic model, dashed lines, power of 3 (red), power of 5 (green), and power of 7 (blue) fits corresponding to the small-signal nonlinearity regime below the driving field of ca. 20 kV/cm, which allows estimation of the
3rd, 5th and 7th order THz effective nonlinear susceptibilities of graphene $\chi^{(3)}_{\text{eff}}$, $\chi^{(5)}_{\text{eff}}$, and $\chi^{(7)}_{\text{eff}}$, as indicated in the figure. The error bars for the pump fields are defined by the width of the chosen pulse intensity distribution. The error bars for the harmonic fields are derived from the sum of the standard deviations from multiple measurements and the background noise. (b) Calculation of higher-order harmonic generation in graphene using the thermodynamic mechanism: amplitude spectra of the THz field transmitted through the graphene sample. The calculation was performed with sample parameters as used in this work ($N_c = 2.1 \times 10^{12} \text{cm}^{-2}$ and $E_F = 170 \text{ meV}$), using the model incident THz field at $f = 0.68 \text{ THz}$ with the peak strength in the range of 100 V/cm - 1 MV/cm. The harmonics up to the 13th order appear in the spectrum within the $10^6$ dynamic range with respect to the transmitted fundamental.
**Methods**

**Basic experimental setup.** The experiments were performed at the TELBE THz facility, which is providing tunable, narrow-band (bandwidth of 20% (FWHM)), spectrally dense THz pulses in the frequency range between 0.1 THz and 1.2 THz with adjustable repetition rates up to the few 100 kHz regime. The few multicycle THz pulses are generated in an undulator through the process of superradiance from ultra-short relativistic electron bunches accelerated and compressed in a quasi-CW superconducting radio frequency accelerator [15].

In these specific experiments linearly polarized THz pulses with 0.3 THz, 0.37 THz, and 0.68 THz central frequencies were employed separately as input fundamental driving field. The input THz beam was focused onto the graphene sample at normal incidence and the transmitted (i.e. re-emitted) THz waves were detected behind the sample (see Extended Data Fig. 1). All the measurements were carried out at room temperature and under ambient atmosphere. The higher harmonic background was suppressed by appropriate shaping of the longitudinal electron bunch form and by additional narrow bandpass filters [34] before the sample, creating highly monochromatic pump fields with a bandwidth of roughly 10% (FWHM) (Extended Data Fig. 2). Upon transmission through the sample, the THz signal containing the remainder of the fundamental field, as well as the generated harmonics, was again sent through a set of band-pass filters with the transmission band centered at the generated harmonic to be detected. The resulting THz field was measured directly in the time-domain by free-space electro-optic sampling (FEOS) in a 1.9 mm thick ZnTe crystal [35], with the peak THz field strength not exceeding $\approx 0.6 \text{ kV/cm}$. For FEOS THz detection, gating pulses of 100 fs duration, central wavelength of 805 nm, from a commercial Ti:sapphire laser system [36] were used, which is synchronized and timed to the TELBE source [15]. The uncertainty in the timing between the THz pulses generated by the superradiant THz source and the probe laser pulses was less than 30 fs (FWHM) [37]. We note that the specific choice of the 1.9 mm thick ZnTe crystal enables sensitive THz field sampling only in the frequency range below 2.5 THz, which in turn motivated our choice of the fundamental frequencies of $f = 0.68 \text{ THz}$, $f = 0.37 \text{ THz}$, and $f = 0.3 \text{ THz}$ for the harmonics generation at $3f = 2.04 \text{ THz}$, $5f = 1.85 \text{ THz}$, and $7f = 2.1 \text{ THz}$ respectively.

To achieve the optimal dynamic range required for measuring the field dependence of these different harmonics shown in Fig. 3(a) of the main text, specifically chosen bandpass filter combinations were used in the individual experimental configurations which are described later in more detail. Combined with the advanced pulse-resolved data acquisition scheme [37], a dynamic range of better than $10^3$ in the time-domain detection of seventh and third harmonic fields, and $10^9$ in case of the fifth harmonic measurement was achieved.

**Pulse-resolved determination of THz intensities and fields.** Depending on the tuning of the TELBE THz source, intensities can fluctuate between 10% and 50% with respect to the average value. The intensity of each THz pulse is recorded using a fast pyro detector with a bandwidth of 1 MHz in front of the first bandpass filter (see Extended Data Fig. 1). The THz pulses are thereafter grouped and evaluated in separate ranges around a certain pyro detector level. The width of these ranges defines the error bar in the pump fields in Fig. 3(a) of the main text. The actual absolute values for the intensity and the corresponding THz field are derived from a careful cross-calibration that has been carried out prior to the experiment. For this, the intensity seen by the pyro detector was compared to that of the FEOS measurement at different pyro detector levels. The THz intensity was dimmed in front of the pyro detector and in front of the ZnTe crystal.
to avoid nonlinearities in both detection schemes. The resulting dependence between the THz intensities obtained from the FEOS signal and the pyro detector level has subsequently been used to derive the THz intensity/THz field for every single pulse. The peak fields at the sample position were determined from a combination of the beam profile, as measured by a commercial pyroelectric camera [38], the THz pulse shape, as measured by FEOS, and the THz power, as determined by a commercial calibrated THz power-meter [39–41].

**Simultaneous detection of the third, fifth and seventh harmonic.** In this experiment, a fundamental frequency of 0.3 THz was chosen for generation and detection of the seventh harmonic at 2.1 THz. The repetition rate of the TELBE THz source was 100 kHz, the fs-laser had a corresponding rate of 200 kHz. The particular configuration of bandpass filters, as shown in Extended Data Fig. 3, allowed not only the detection of the 7th harmonic but also to simultaneously observe the 3rd and 5th harmonics at 0.9 THz and 1.5 THz (see Fig. 1 of the main text). Two 0.3 THz bandpass filters were used to suppress the harmonic background of the undulator, leading to a maximum field strength of 85 kV/cm at the sample. The resulting suppression factor in intensity is $10^8$ for the 3rd, $10^6$ for the 5th, and $10^4$ for the 7th harmonic. The filtered THz beam was focused onto the sample, employing an off-axis parabolic mirror in combination with an additional Teflon lens, which yielded a THz spot size of 560 µm (FWHM). A 2.1 THz bandpass filter was utilized behind the sample to enable optimal sensitivity for the 7th harmonic in the EOS measurement, while still allowing a detectable portion of the lower harmonics and the fundamental to pass through.

The as-measured HHG spectrum from graphene is shown in Extended Data Fig. 4 (red curve), clearly showing the fundamental and harmonics up to the 7th order. The raw signal originating from the bare SiO2 substrate as a reference is shown in black. To determine the corresponding electric fields quantitatively, the transmission function of the 2.1 THz filter, as well as the frequency-dependent sensitivity of the ZnTe detection crystal have to be included. The former has been measured and is displayed in the Extended Data Fig. 4 as the grey curve, showing the substantial suppression of frequencies below 1.9 THz. We note that the spectra presented in Fig. 1 (b) of the main text were obtained by deconvoluting the response functions of both the ZnTe detection crystal and the 2.1 THz filter from the measured FEOS signals (see further discussion in the next section of reconstructing the harmonic fields from the measured FEOS signals and Extended Data Fig. 9). We also note that in order to not overly amplify the noise above 2.2 THz in the graphene sample and reference spectra, the ZnTe sensitivity curve was assumed to be flat for values above 2.2 THz in this case. This does not affect either the overall peak shape in Fig. 1 of the main text, or the peak field values that were used to calculate the HHG efficiencies (see Fig. 3(a) and Table 1 in the main text).

**Separate detection of the third and fifth harmonic at 2.04 THz and 1.85 THz.** The repetition rate of the TELBE THz source was set to 101 KHz, the fs-laser used for FEOS detection had a repetition rate of 202 kHz. To explicitly measure and quantify (cf. Fig. 3(a) of the main text) the signals from THG and FHG, we chose the fundamental frequencies of 0.68 THz and 0.37 THz, respectively. Sets of narrow bandpass filters [34] were tailored correspondingly. These filters suppress the higher harmonic background to less than $10^{-7}$ for 0.68 THz and to less than $10^{-11}$ for 0.37 THz in intensity. Thereby, we reached an optimal dynamic range in the FEOS detection of the harmonic field, despite the fact that the harmonic field is weaker than the fundamental field by a factor of $10^3$ (THG) and $10^4$ (FHG). Beam diameters (FWHM) on the sample surface were 1 mm for 0.68 THz and 0.6 mm for 0.37 THz. In the latter case an additional Teflon lens was used to optimize the spot size.
In Extended Data Fig. 5(a), we show a schematic of the beampath in the THG experiment. Here a single 1.93 THz bandpass filter \[34\] was introduced after the sample to attenuate the fundamental at 0.68 THz, while allowing transmission of the THG signal at 2.04 THz. The spectral transmission function of the 1.93 THz filter is shown in the Extended Data Fig. 6(a). Extended Data Fig. 6(b) shows the as-measured amplitude spectra of the detected FEOS signals: the reference (pump field transmitted through a bare SiO\(_2\) substrate) and that from the sample (pump field transmitted through graphene on a SiO\(_2\) substrate). We note that the pump field contains a small spurious contribution at the THG frequency (black line in Extended Data Fig. 6(b)), which is, however, one order of magnitude smaller than the THG generated in graphene (red line in Extended Data Fig. 6(b)).

In case of the THG experiment, the leaking intensity/field at the fundamental frequency \(f = 0.68\) THz measured through the bare SiO\(_2\) substrate (geometry as shown in Extended Data Fig. 5(a)) serves as a representative for the fundamental THz excitation field in Extended Data Fig. 10 and was used as a reference input pulse in the theoretical model.

In the FHG experiment, we employed the beampath as schematically shown in Extended Data Fig. 5(b). To ensure a larger sensitivity for the detection of the fifth harmonic field, the number of bandpass filters before and after the sample was doubled for all fields except for the three highest field values shown in Fig. 3(a) for which the 0.4 THz filter was removed. Extended Data Fig. 7 shows the as-measured amplitude spectra of the detected reference and sample FEOS signals. The transmission at the fundamental frequency is strongly suppressed, while no spurious contribution of the pump field at the FHG frequency is observed.

Because of the overly small signal of the 0.37 THz fundamental in this configuration it was – in contrast to the THG experiment – not suitable to derive the waveform of the fundamental THz pulse from the leaking fundamental. Instead, the waveform was measured with an additional experimental configuration shown in Extended Data Fig. 5(c). This waveform was also utilized as a reference input pulse for the theoretical calculation of the nonlinear response of graphene.

**Reconstruction of the harmonic fields from the measured FEOS signals.** The complex-valued (i.e. containing both amplitude and phase) field transmission functions of all optical elements in the THz beampath of our experiments (sample substrate, bandpass filters), as well as the FEOS detector (THz Fresnel insertion losses, and the frequency-dependent acceptance function of the FEOS ZnTe crystal which is described in [42,43]) have been characterized, as summarized below. As a result, the rigorous reconstruction of the measured FEOS signals back to the actual, calibrated THz electric field transients at all frequencies of interest (fundamental, THG and FHG) was made possible. Our reconstruction from the FEOS signals back to the actual fields follows the same general protocol reported in Ref. [44], while taking into account all elements in the THz beampath. Here we exemplify the field reconstruction from the measured EOS on the example of the THz THG experiment with \(f = 0.68\) THz \(\rightarrow 3f = 2.04\) THz.

Extended Data Fig. 6(a) shows the amplitude transmission spectrum of the 1.93 THz bandpass filter, while Extended Data Fig. 8 below shows the phase and thereby time difference added to the signals at all frequencies of interest due to the propagation through this optical element. A THz time-domain spectroscopy measurement of the SiO\(_2\) substrate yielded the values of frequency-dependent power absorption coefficient of 7.6 cm\(^{-1}\) (2.04 THz), 6.6 cm\(^{-1}\) (1.85 THz), 2.3 cm\(^{-1}\) (0.68 THz), and 1.3 cm\(^{-1}\) (0.37 THz), and spectrally flat refractive index of 1.98, in good agreement with the literature [45].
In Extended Data Fig. 9(a), we show the frequency-dependent transmission response function (amplitude transmission and phase shift) of the bare SiO\(_2\) substrate, while in Extended Data Fig. 9(b) we show the acceptance function (amplitude and phase shift) of our FEOS unit: 1.9 mm thick ZnTe crystal, gated by the 100 fs pulses at 805 nm central wavelength.

Taking all the above elements used in the THz transmission and detection in our experiment, we are now able to rigorously reconstruct the as-measured THz FEOS signals back into the actual THz-field waveforms, as shown in Extended Data Fig. 10 (example of THG measurement with \(f = 0.68 \text{ THz} \rightarrow 3f = 2.04 \text{ THz}\)).

Extended Data Fig. 10(a) shows the measured FEOS signals transmitted through the bare substrate (the black pulse), through the graphene/substrate sample (the red pulse), both normalized to the peak of the substrate pulse, and the difference between the two normalized FEOS signals (the blue pulse). The difference pulse (the blue one) clearly shows oscillations at the THG frequency of 2.04 THz. Extended Data Fig. 10(b) shows the corresponding reconstructed fields (the fields at the point just after the graphene/substrate interface) after compensating for the field losses and deconvoluting the response functions, described above, of the optical elements after the graphene/substrate interface. We note that deconvoluting the phase shift induced by these optical elements after the graphene film from the FEOS signals in Extended Data Fig. 10(a) results in a time-shift of ~17.8 ps to the reconstructed fields in Extended Data Fig. 10(b). Further, in the reconstructed fields in Extended Data Fig. 10(b), the fundamental field is upscaled to its original values before the bandpass filter attenuation after the sample, and in turn dominates over the THG. Thus, the oscillation at the THG frequency included in the difference field pulse (the blue pulse) in Extended Data Fig. 10(b), compared with that in Extended Data Fig. 10(a), is now less pronounced. Now, if we spectrally remove the fundamental signal at 0.68 THz from the field difference pulse shown in Extended Data Fig. 10(b), we arrive at the THG field waveform (Extended Data Fig. 10(c)).

### Sample preparation and characterization

Our sample is a typical CVD-grown monolayer graphene transferred onto a fused silica substrate. The graphene quality was tested via Raman spectroscopy that showed a single layer identity with a large-scale homogeneity (Extended Data Fig. 11(a) for the Raman spectra of the sample). The characteristic graphene 2D and G peaks are observed at 2703 cm\(^{-1}\) and 1591 cm\(^{-1}\), respectively. The Gaussian shape of the 2D band with a FWHM of ~47 cm\(^{-1}\) along with the relative ratio of the 2D peak to the G peak denotes single layer identity of the graphene sample. The very weak D band at 1300 cm\(^{-1}\) is indicative of a low defect density.

The linear conductivity of our graphene sample was characterized via THz time-domain spectroscopy using a ZnTe crystal as a THz emitter pumped by 800 nm laser pulses with a pulse width of 40 fs, and a repetition rate of 1 kHz. The experimental data revealed Drude-type conductivity, providing the Fermi level energy of 170 meV and electron momentum scattering time of 47 fs (see Extended Data Fig. 11(b) for the linear THz characterization of the sample).

We note here that our graphene sample is, in fact, \(p\)-type, as is typical for the CVD-grown material deposited onto fused SiO\(_2\) substrate in the presence of ambient atmosphere (see e.g. [53]). However, due to the symmetry of the band structure for Dirac electrons and holes in graphene, for simplicity, we depict the Fermi level in the conduction rather than in the valence band.

### Calculations

The (nonlinear) complex-valued THz field transmission from the free space through graphene into the substrate is described by the Tinkham equation.
where $n_s$ is the refractive index of the substrate, $Z_0$ is the free-space impedance and $\tilde{\sigma}(\omega)$ is the complex THz conductivity of the conductive film. The conductivity $\tilde{\sigma}(\omega)$ is nonlinear on the driving THz field [14,18,25,26,55,56], see also the discussion below.

The intraband conductivity of conduction band electrons of graphene at THz frequencies $\tilde{\sigma}(\omega)$ can generally be described by the solution of Boltzmann equation [3,14,57]:

$$\tilde{\sigma}(\omega) = -\frac{e^2 v_F}{2} \int_0^\infty D(E) \frac{\tau(E)}{1 - i\omega\tau(E)} \frac{\partial f_{FD}(E, \mu, T_e)}{\partial E} dE$$

(\text{M2})

where $v_F = 1 \times 10^6 m/s$ is the Fermi velocity of the relativistic Dirac-fermions in graphene, $\tau(E)$ is the carrier energy-dependent scattering time, $D(E) = 2|E|/\pi(hv_F)^2$ is the density of states of the graphene energy bands, and $f_{FD}(E, \mu, T_e) = 1/[\exp\left(\frac{E-\mu}{k_BT_e}\right) + 1]$ is the Fermi-Dirac distribution function for a chemical potential $\mu$ and carrier temperature $T_e$.

The dominating electron momentum scattering mechanism in CVD-grown graphene deposited on fused silica substrate is the scattering via Coulomb interactions with charged impurities (long-range Coulomb scattering) [3,14,58–61], which is defined by linear dependence of scattering time on energy $\tau(E) = \gamma E$ (see also [62]). The proportionality constant $\gamma = \tau_0/E_F = 47 fs/170 meV$ can be obtained from the linear response described above (see also [14] and Extended Data Fig. 11(b)). In terms of the THz induced heat density $\Delta Q$, one can express $\Delta Q = \gamma(E_F + \Delta Q/N_c)$, where $N_c = \int_0^\infty D(E)f_{FD}(E, \mu, T_e)dE$.

In order to compute the time-dependent THz field-induced heat $\Delta Q$ accumulated in the electronic system of graphene during the (nonlinear) interaction with the driving THz wave, the split-step time-domain calculations as common in nonlinear optics, must be performed (see e.g. [63]). For this, the inverse Fourier transforms of Eq. (M1) with the conductivity $\tilde{\sigma}(\omega)$ described by Eq. (M2) must be taken at every time step during numerical propagation. In order to speed up the calculations, a linear parameterization of the Eq. (M2) has been used, under the conditions of energy (all absorbed THz energy is adding to $\Delta Q$) and free carrier density ($N_c = \int_0^\infty D(E)f_{FD}(E, \mu, T_e)dE = const.$) conservation, yielding the following expression

$$\tilde{\sigma}(\omega) \approx \frac{(ev_F)^2 \gamma N_c/E_F}{1 - i\omega\tau(\Delta Q)}$$

(\text{M3})

Now, the time domain expression of the THz field transmission of graphene, by taking the inverse Fourier transform of Eq. (M1) with the conductivity $\tilde{\sigma}(\omega)$ described by Eq. (M3), results in a time-dependent response function

$$T(t) = \left[\frac{2\delta(t)}{n_s + 1} - \frac{2Z_0(ev_F)^2\gamma N_c}{(\tau_0 + \gamma\Delta Q(t)/N_c)(n_s + 1)^2}\exp\left\{\frac{-Z_0(ev_F)^2\gamma N_c + n_s + 1}{(\tau_0 + \gamma\Delta Q(t)/N_c)(n_s + 1)}t\right\}\right]$$

(\text{M4})

where $\delta(t)$ is the Dirac delta. The convolution of this function with the temporal THz driving field $E_{in}(t)$ yields the corresponding temporal field transmitted through the graphene film into the SiO$_2$ substrate

$$E_{t}(t) = T(t) * E_{in}(t)$$

(\text{M5})

where *-sign denotes the convolution.
In order to accommodate for the electron cooling due to phonon emission, we use the following cooling rate as directly measured in Ref. [20]

\[
R(t) = 0.001 \exp \left( -\frac{t}{\tau_1} \right) + 0.46 \exp \left( -\frac{t}{\tau_2} \right) + 0.539 \exp \left( -\frac{t}{\tau_3} \right) \tag{M6}
\]

with time constants \(\tau_1=13\) fs, \(\tau_2=80\) fs and \(\tau_3=0.86\) ps. This relaxation process leads to a recovery toward the initial linear conductivity of the graphene after the incident THz pulse ceases. The calculation of the THz induced heat is thus based on the following convolution:

\[
\Delta Q(t) = \frac{1}{2} \varepsilon_0 c R(t) \ast \left[ E_{inc}^2(t) - n_s E_r^2(t) - (E_r(t) - E_{inc}(t))^2 \right] \tag{M7}
\]

where \(\varepsilon_0\) is the vacuum permittivity.

As a result, the time-dependent induced electronic heat given by Eq. (M7) leads to the temporal modulation of conductivity and results in the nonlinear response function of graphene described by Eq. (M4), which in turn leads to harmonics generation.

**The nonlinear THz refractive index of graphene.** The dielectric function of the graphene film can be expressed by [64,65]

\[
\varepsilon_r = \varepsilon_\infty + \frac{i\sigma}{\omega \varepsilon_0} \tag{M8}
\]

where \(d = 0.3\) nm is the thickness of the graphene film and \(\varepsilon_\infty \approx 1\) [64,65]. We calculate the real part of the refractive index using \(n = \text{Re}\{\sqrt{\varepsilon_r}\}\). Substituting into Eq. (M8) for the conductivity by the linear Drude conductivity shown in Extended Data Fig. 11(b), we first obtained the linear (field-independent) refractive index (for fields less than 1 kV/cm). When the graphene film interacts with higher fields, the conductivity decreases as explained above, leading to a reduction in the refractive index [Extended Data Fig. 12]. In Extended Data Fig. 12(a), we show the calculated field-dependent THz index when the graphene film is pumped by THz fields at a fundamental frequency of 0.3 THz. In Extended Data Fig. 12(b), we show the THz field dependence of the nonlinear refractive index at the harmonics \(3f = 2.04\) THz generated by \(f = 0.68\) THz pump, \(5f = 1.85\) THz generated by \(f = 0.37\) THz pump, and \(7f = 2.1\) THz generated by \(f = 0.3\) THz pump. From this field dependence of the refractive index, we estimated the third, fifth and seventh order susceptibilities \(\chi^{(3)}, \chi^{(5)}\) and \(\chi^{(7)}\), respectively, as explained in the next section.

**Extraction of nonlinear coefficients of graphene.** The conservative, low-boundary estimate of the third, fifth and seventh-order THz nonlinear optical coefficients of graphene, based on the experimentally measured field conversion efficiencies in small-signal regime (power law fits to the data and the results of thermodynamic model in Fig. 3(a)) is done as follows. Ignoring both the pump field depletion (given \(~90\%\) field transmission through graphene in the most absorptive limit of small driving THz fields), and the phase mismatch in \(f\rightarrow mf\) conversion processes (negligible within one atomic layer), the conversion from the pump to the harmonic field is defined as \(E_{mf} = \gamma L |E_f|^m\) with \(\gamma = k_m \frac{\pi f}{c n_{mf} \lambda_{eff}} \chi^{(m)}_{eff}\) [7,66]. Here \(m = (3,5,7)\) is the harmonic order; \(E_r\) and \(E_{mf}\) are peak electric field strengths of the incident fundamental and generated \(m\)-th harmonic field, respectively; \(k_m = (3/4, 5/16, 7/64)\) is a numerical coefficient for harmonics \(m = 3, 5\) and \(7\), respectively; \(L = 0.3\) nm is the thickness of graphene layer [67]; \(c\) is the speed of light in vacuum; and \(n_{mf}\), \(n_{sf}\) and \(n_{sf}\) represent the refractive index of graphene at the harmonic frequencies, which at the target
harmonic frequency around 2 THz is chosen to be $\sim 10$ (see below). From the measured 3rd harmonic generation with $f = 0.68$ THz $\rightarrow 3f = 2.04$ THz, the field conversion coefficient of $\gamma L = \left| E_{3f} / \left| E_f \right| \right|^3 = 1.79 \times 10^{-16}$ m$^2$/V$^2$, and an estimate of the effective third-order THz nonlinear susceptibility of graphene is $\chi^{(3)}_{\text{eff}} \sim 1.7 \times 10^{-9}$ m$^2$/V$^2$. For the measured 5th harmonic generation with $f = 0.37$ THz $\rightarrow 5f = 1.85$ THz, the field conversion coefficient $\gamma L = \left| E_{5f} / \left| E_f \right| \right|^5 = 2.68 \times 10^{-30}$ m$^4$/V$^4$ and the effective fifth-order THz nonlinear susceptibility of graphene is estimated as $\chi^{(5)}_{\text{eff}} \sim 1.2 \times 10^{-22}$ m$^4$/V$^4$. In the same fashion, for the 7th harmonic generation process with $f = 0.3$ THz $\rightarrow 7f = 2.1$ THz, the field conversion coefficient $\gamma L = \left| E_{7f} / \left| E_f \right| \right|^7 = 1.8 \times 10^{-46}$ m$^6$/V$^6$ and the estimate of the effective seventh-order THz nonlinear susceptibility of graphene is $\chi^{(7)}_{\text{eff}} \sim 1.7 \times 10^{-38}$ m$^6$/V$^6$.

We note that the value for the refractive index of graphene of $n_{3f,5f,7f} \sim 10$ (at the frequency around 2 THz, and at high electron temperature) used in our calculations is a conservative order-of-magnitude estimate, as the actual values can be as high as $n \sim 20-80$ (Extended Data Fig. 12(b)), which will increase the values of the retrieved nonlinear coefficients of graphene even further.

**Limits of the thermodynamic model of THz response of graphene in terms of driving THz field strength.**

The electron response, following the heating-cooling dynamics of electron population as described in this paper, will dominate the THz intraband nonlinearity of graphene until the regime of coherent Bloch oscillations will be reached. In this regime (see e.g. [13,68]), the conduction band electron reaches the Brillouin zone boundary in the time faster than the typical electron momentum scattering (Drude) time, providing for the coherent nonlinear Bloch oscillations in the k space of the Brillouin zone between the $k = \pi/a$ and $-k = -\pi/a$ points, where $a$ is the lattice constant. We use the acceleration theorem $\frac{dk}{dt} = -\frac{eE}{\hbar}$ which can be further simplified to $\frac{\Delta k}{\tau} = -\frac{eE}{\hbar} \tau$, where $\Delta k = \pi/a$ is the Brillouin zone half-width, $a = 0.14$ nm is the lattice constant of graphene, and $\tau$ is the electron momentum relaxation time. For the typical electron momentum relaxation time in the range $\tau = 10-100$ fs (see e.g. [3]) we arrive at the electric field strength range $E = 1 – 10$ MV/cm. This field strength thus sets the estimated upper validity limit for our model.

**References / Methods**


40. A. Steiger, M. Kehrt, C. Monte, and R. Müller, "Traceable terahertz power measurement from 1 THz to 5 THz," Opt. Express 21, 14466 (2013).


Incident quasi-monochromatic THz field \( E_f(t) \)

Electron heating and cooling: nonlinear current \( j(t) \)

Re-emitted THz field

Time-dependent conductivity \( \sigma(\Delta Q,t) \) →

temporal current modulation

\[ j(t) = \sigma(\Delta Q,t) \cdot E_f(t) \]

Spectral amplitude (normalized)

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Electric field

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Pump field

Harmonics

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Time (ps)

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Population density $N = D \cdot f_{FD}$

Energy

Heating $< 100$ fs

Cooling $\sim 1$ ps

Cold high $\sigma_{\text{THz}}$

Hot low $\sigma_{\text{THz}}$

THz electric field $E(t)$ (a.u.)

THz-induced heat $\Delta Q(t)$ ($\mu$J/cm$^2$)

THz power absorbance $A$ ($\%$)

THz conductivity modulation: $\sigma_{\text{THz}}(t)$

Energy Population density $N = D \cdot f_{FD}$

Time (ps)

- $E_f = 10$ kV/cm
- $E_f = 85$ kV/cm

$\Delta Q(t)$ ($\mu$J/cm$^2$)

THz conductivity modulation: $\sigma_{\text{THz}}(t)$

Time (ps)
Fundamental electric field $E_f$ [kV/cm]

Harmonic electric field [V/cm]

$$\chi^{(3)}_{\text{eff}} \approx 10^{-9} \text{ m}^2/\text{V}^2$$

$$\chi^{(5)}_{\text{eff}} \approx 10^{-22} \text{ m}^4/\text{V}^4$$

$$\chi^{(7)}_{\text{eff}} \approx 10^{-38} \text{ m}^6/\text{V}^6$$

$$\propto E_f^3$$

$$\propto E_f^5$$

$$\propto E_f^7$$

(a) Thermodynamic model

(b) Decimal Log of spectral amplitude [a.u.]
Extended Data Fig. 1: Experimental set-up. Tunable multicycle THz pulses (red) from the undulator of the TELBE facility are used to irradiate the graphene sample. 100-fs pulses from a Ti:sapphire laser system (brown) are used to probe the transmitted and emitted THz pulses by free-space electro-optic sampling. PD, photodiode; BS, beamsplitter; Pol., polarizer.

Extended Data Fig. 2: Fundamental frequencies after bandpass filtering. The bandwidths were determined from Gaussian fits to the spectra. MSA, mean square amplitude.
Extended Data Fig. 3: Scheme of the set-up for detection of multiple harmonics up to the seventh order. Two 0.3-THz bandpass filters (BP) are used to suppress the undulator harmonic background. A single 2.1-THz bandpass filter after the sample attenuates the fundamental, third and fifth harmonics to an extent that they can still be detected by the EOS set-up.

Extended Data Fig. 4: HHG signal from graphene, reference signal from the SiO2 substrate and filter function of the 2.1-THz bandpass. The red curve shows the as-measured HHG spectrum of the graphene sample. The black curve shows the reference spectrum taken from the bare SiO2 substrate. The measured transmission function of the 2.1-THz bandpass filter is also shown (grey line).
Extended Data Fig. 5: Schemes of the experimental configurations to determine the electric fields of the fundamental, THG and FHG pulses. Measurements were performed with graphene/SiO2 and with the bare SiO2 substrate. a, Set-up for the THG experiment used to measure the fundamental and harmonic simultaneously. b, Set-up to measure the harmonic in the FHG experiment. Two filters were used before the sample and two after the sample, to optimize the signal-to-noise ratio. c, Set-up to determine the electric fields for the fundamental in the FHG experiment.

Extended Data Fig. 6: Filter function of the 1.93-THz bandpass and raw spectra from the THG experiment. a, Amplitude transmission function of a single 1.93-THz bandpass filter. b, As-measured spectral amplitude in arbitrary units (a.u.), as determined from the bare SiO2 substrate (black) and from the graphene sample (red). The incident THz peak field of the fundamental at 0.68 THz was 61 kV cm⁻¹.
Extended Data Fig. 7: Raw spectra from the FHG experiment. These as-measured spectra show the spectral amplitude as determined from a measurement with the bare SiO2 substrate as a reference and a measurement of the graphene sample. The incident THz peak field in the fundamental at 0.37 THz was 40 kV cm\(^{-1}\) when using two filters in the incident beam. Insignificant transmission at the fundamental frequency and no spurious background at the FHG frequency band is observed in the reference field measurement.

Extended Data Fig. 8: Frequency-dependent phase difference induced by the 1.93-THz bandpass filter.
Extended Data Fig. 9: The frequency-dependent response function.

a, The bare substrate described by the amplitude transmission (black line) and the substrate-induced phase shift (blue line).
b, A simulated acceptance function of the 1.9-mm-thick ZnTe detection crystal; amplitude (black curve) and phase shift (blue curve). Arrows indicate relevant axis.

Extended Data Fig. 10: Reconstruction of the harmonic fields from the measured FEOS signals. This is an example of THG measurement with $f = 0.68 \text{ THz} \rightarrow 3f = 2.04 \text{ THz}$. 

a, Measured FEOS signals (dimensionless).
b, The corresponding fields transmitted through the incidence interface of the sample after deconvoluting the response functions of all the elements after the graphene film, including the 1.9-mm-thick ZnTe detection crystal, the 1.93-THz filter and the fused silica substrate from the FEOS signals in a. Black pulse is for the bare substrate, red for the graphene sample and blue for the difference.
c, The pure THG field extracted from the blue field pulse in b.
Extended Data Fig. 11: Characterization of the graphene sample.

a, Raman spectrum of the graphene sample. b, Linear conductivity, real and imaginary, of the graphene film normalized to the universal conductivity $\sigma_0 = e^2/(4\hbar)$. The symbols represent the experimental data; the solid lines represent the Drude fit with a Fermi level energy $E_F = 170$ meV (corresponding to a doping concentration $N_c = 2.1 \times 10^{12}$ cm$^{-2}$) and a scattering time $\tau_0 = 47$ fs as fitting parameters. The error bars are the standard deviation in the measurements.

Extended Data Fig. 12: The nonlinear (THz-field-dependent) refractive index of the graphene film. a, The THz refractive index of the graphene film as a function of frequency at various peak electric fields for the THz pump at 0.3 THz, showing reduction in the refractive index with both frequency and exciting field strength. b, The field dependence of the nonlinear THz refractive index at the harmonics $3f = 2.04$ THz generated by $1f = 0.68$ THz pump, $5f = 1.85$ THz generated by $1f = 0.37$ THz pump, and $7f = 2.1$ THz generated by $1f = 0.3$ THz pump.