

# Ultrafast terahertz self-induced absorption and phase modulation on a graphene based thin film absorber

Anastasios D. Koulouklidis,<sup>\*,†</sup> Anna C. Tasolamprou,<sup>†</sup> Spyros Doukas,<sup>‡</sup> Eudokia Kyriakou,<sup>†,¶</sup> M. Said Ergoktas,<sup>§,||</sup> Christina Daskalaki,<sup>†</sup> Eleftherios N. Economou,<sup>†,⊥</sup> Coskun Kocabas,<sup>§,||,#</sup> Eleftherios Lidorikis,<sup>‡,@</sup> Maria Kafesaki,<sup>†,△</sup> and Stelios Tzortzakis<sup>†,△,∇</sup>

<sup>†</sup>*Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas (FORTH), N. Plastira 100, Heraklion, Crete, 71110, Greece*

<sup>‡</sup>*Department of Materials Science and Engineering, University of Ioannina, Ioannina, 45110, Greece*

<sup>¶</sup>*Department of Materials Science and Technology, University of Crete, Heraklion, Crete, 70013, Greece*

<sup>§</sup>*Department of Materials, University of Manchester, Manchester, M13 9PL, United Kingdom*

<sup>||</sup>*National Graphene Institute, University of Manchester, Manchester, M13 9PL, United Kingdom*

<sup>⊥</sup>*Department of Physics, University of Crete, Heraklion, Crete, 70013, Greece*

<sup>#</sup>*Henry Royce Institute for Advanced Materials, University of Manchester, Manchester, M13 9PL, United Kingdom*

<sup>@</sup>*Institute of Materials Science and Computing, University Research Center of Ioannina (URCI), Ioannina, 45110, Greece*

<sup>△</sup>*Department of Materials Science and Technology, University of Crete, Heraklion Crete, 70013, Greece*

<sup>∇</sup>*Science Program, Texas A&M University at Qatar, P.O. Box 23874 Doha, Qatar*

## Abstract

Interaction of intense terahertz (THz) waves with graphene based modulation devices holds great potential for the opto-electronic applications of the future. Here we present a thin film graphene based THz perfect absorbing device, whose absorption and phase characteristics can be modulated through THz self-actions in the sub-ps time scale. The device consists of a single layer graphene placed on an ionic liquid substrate, back-plated by a metallic back-reflector, with the graphene doping level mediated through electrostatic gating. We experimentally record an absorption modulation of more than three orders of magnitude from the initial perfect absorption state, when the device is illuminated with THz field strengths in the range of 102 kV/cm to 654 kV/cm. Furthermore, an absolute phase modulation of  $130^\circ$  is recorded. Detailed theoretical analysis indicates that the origin of the THz nonlinear response is the THz induced heating of the graphene's carriers, that leads to a reduction of its conductivity, and consequently to reduced absorption of the THz radiation. Our analysis also maps the temporal dynamics of the THz induced temperature elevation of the graphene carriers, illustrating the ultrafast, sub-ps nature of the overall process. These results can find applications in future dynamically controlled flat optics and spatiotemporal shaping of intense THz electric fields.

## Keywords

nonlinear THz graphene, hot carriers, thermalization, terahertz self-induced modulation, graphene, perfect absorption

## Introduction

Terahertz (THz) radiation technology aims to bridge the realms of electronics and photonics, and therefore it attracts increasing attention over the last two decades. Due to their

unique characteristics, i.e., non ionizing nature, transparency of many non-conductive materials, direct probing of vibrational and rotational modes in molecules, THz waves have been extensively utilized for a variety of applications, such as medical diagnostics, industrial quality control, food inspection, and many more.<sup>1-3</sup> Important applications refer to THz wireless communication systems, particularly within the landscape of the fast emerging 5G and 6G technologies<sup>4,5</sup> where THz waves promise increased bandwidths for the data demanding systems. In the quest of achieving the necessary tunability to efficiently undertake THz modulation, various materials and devices have been explored, such as diodes,<sup>6</sup> phase changing materials<sup>7</sup> and more.<sup>8,9</sup> One of the most promising such materials is graphene, whose unique mechanical and optical properties stand in the center of the research attention in recent years.<sup>10</sup> So far, graphene has been proposed for a plethora of opto-electronic THz components controlling both propagating and localized surface plasmons on graphene-based waveguide modulators,<sup>11</sup> emitters and detectors for terahertz radiation,<sup>12,13</sup> topological routing,<sup>14</sup> and metasurfaces with exotic functionalities. Additionally, graphene is expected to play a key role in space-time-modulation, which further expands the wave interaction impact.<sup>15-18</sup>

Graphene predominantly exhibits a Drude-like response in the THz part of the spectrum, due to its easily generated and controlled free carriers. Its optical properties can be largely modulated through chemical doping and/or external electrostatic or magnetic fields.<sup>19,20</sup> Additionally, graphene optical response can be modified in an ultrafast manner; hot electrons driven by the excitation by optical pulses can lead to a sub-ps transient modulation of its conductivity.<sup>21</sup> Similar effects are observed under intense THz pulse excitation, where hot carrier nonlinear effects dominate the response.<sup>22</sup> In fact, graphene is considered to be a particularly highly nonlinear material at THz frequencies.<sup>22</sup> The nature of this nonlinear response has been related to the collective thermodynamic response of the background Dirac electrons under the application of intense THz fields, resulting in THz-induced carrier heating.<sup>23</sup> Many interesting nonlinear features of graphene have been observed, which may be

further facilitated by the rapid development of high power THz sources.<sup>24–26</sup> Experimental studies have demonstrated the emission of THz induced high harmonics,<sup>27</sup> graphene plasmon nonlinear absorption,<sup>28</sup> saturable absorption,<sup>29</sup> and the electric tunability of the graphene’s nonlinearity.<sup>30</sup>

An efficient modulator involves the tunable and near unity (perfect) absorption which can be achieved in a simple Salisbury screen configuration, where a uniform graphene sheet is placed on top of a dielectric substrate, back plated by a metallic back-reflector. Such a structure has been shown to provide perfect absorption mediated by electrostatic gating.<sup>31</sup> Recently, we demonstrated that such a configuration can also provide ultrafast THz modulation, in the order of a few ps, when optically excited.<sup>21</sup> Here we demonstrate an electrically gate-tuned graphene-based Salisbury screen device, whose absorption and phase characteristics can be self-modulated when the intensity of the incident THz field is high enough to drive the graphene layer in the non-linear regime. We record an amplitude modulation of more than three orders of magnitude in the resonant absorption of our device, and an absolute phase modulation of  $130^\circ$  when the THz field strength increases from 102 to 654 kV/cm. To unveil the origin of this nonlinear response, we perform a detailed theoretical analysis based on the dynamics of single layer graphene (SLG) hot carriers,<sup>32,33</sup> and we attribute it to a THz induced temperature increase of graphene carriers, that is followed by a drop in the conductivity and a reduction in the THz absorption. Through our analysis, the temporal dynamics of this THz induced temperature elevation is mapped, illustrating an ultrafast, sub-ps response of the entire phenomenon.

## Experimental implementation

For the excitation of the graphene device we employ a powerful THz Time Domain Spectrometer (THz-TDS), which is based on two-color filamentation of ultrashort laser pulses in air, and operates in reflection mode.<sup>34</sup> This source provides ultra-broadband THz pulses

( $>18$  THz) with peak electric field strength values up to 700 kV/cm. Figure 1 (a) shows the incident THz electric field measured through an air-biased coherent detection (ABCD) technique<sup>34,35</sup> together with its corresponding power spectrum (inset of Figure 1 (a)). The THz beam illuminates the sample at an angle of  $16^\circ$  with a TM (Transverse Magnetic) polarization. In the experiments we have chosen electro-optic detection in a 100  $\mu\text{m}$  thick Gallium phosphide (GaP)  $\langle 110 \rangle$  crystal, as it offers better signal to noise ratio compared to the ABCD scheme. The detection crystal was optically contacted to a 2 mm thick GaP  $\langle 100 \rangle$  crystal in order to avoid any Fabry-Perot spectral oscillations, extending the available temporal window to 12 ps. The strength of the THz field on the graphene sample was controlled with a pair of wire grid polarizers, and the device was characterized in the range of field strengths between 102 kV/cm and 654 kV/cm. The lowest peak field strength was limited by the noise level of the detection system. Finally, water vapor absorption by the THz radiation was avoided by enclosing the whole experimental setup in a purge gas chamber.

Figure 1 (b) presents a schematic of the graphene-based device. The THz cavity is formed by chemical vapor deposition (CVD) grown single layer graphene as top electrode, a 25  $\mu\text{m}$ -thick porous polyethylene membrane containing room temperature ionic liquid electrolyte (DEME-TFSI)<sup>31</sup> as cavity layer, and a gold electrode as a back reflector.<sup>18,31</sup> The Fermi energy of graphene can be fine tuned through an external electric gating between the graphene layer and the grounded back gold electrode. When no voltage is applied to the device the graphene layer is positively doped due to the nature of growth and transfer processes.<sup>18,31</sup> The doping level is enough to satisfy the coherent perfect absorption conditions<sup>21,31</sup> without any electrostatic gating (0 V).

Figure 2 (a) shows normalized measured THz electric fields for the cases of the lowest and highest available THz field strengths. Due to the high bandwidth of our THz-TDS system we are able to resolve both reflective interfaces of the device that manifest themselves as two distinct peaks on the THz field: one at -0.25 ps originating from the reflection of the THz pulse on the graphene layer and one at 0 ps that originates from the gold back reflector (see

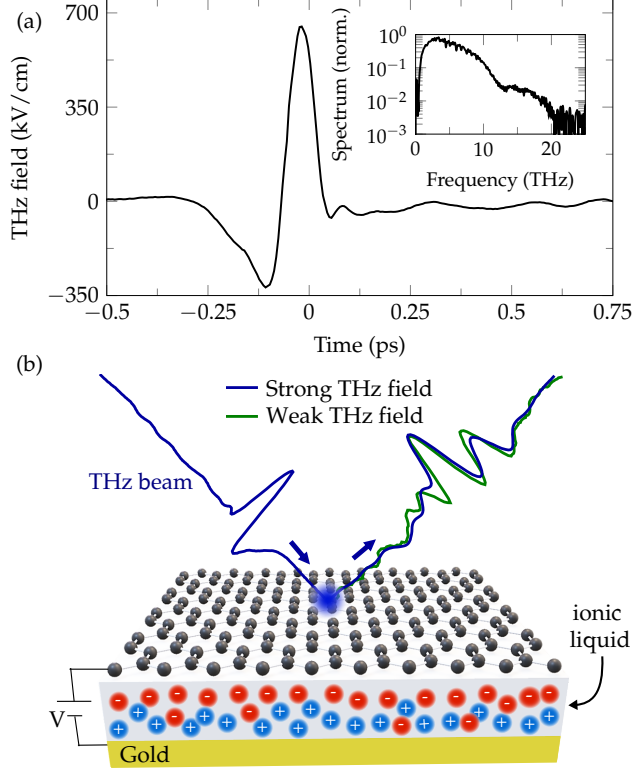


Figure 1: Schematic representation of the graphene absorber structure. The device is composed of: a single layer graphene, a membrane soaked with room-temperature ionic liquid electrolyte of thickness  $d = 25 \mu\text{m}$  and a metallic back-reflector. Fermi energy of graphene can be controlled through electrostatic gating. The THz beam illuminates the sample at an angle of  $16^\circ$ .

Figure 2 (b)). From Figure 2 (a) we see that as the THz field strength increases, we record a drop on the THz reflectivity of the graphene layer compared to the one from the gold back reflector. This indicates a THz induced negative photoconductivity on the graphene layer. Additionally, we observe an overall modulation of the THz electric field shape indicating also a modulation of the THz field phase.

The nonlinear behaviour is depicted more clearly in the electrical response of the graphene layer in the presence of the external electrostatic gating. Therefore, we measured the THz reflectivity variation only of the graphene layer, by recording the peak of the THz electric field that corresponds to the graphene layer (time = -0.25 ps) as a function of the gate voltage. Figure 2 (c) shows the reflectivity variation for different incident peak electric fields in the range of 102 to 654 kV/cm. All curves are normalized to the charge neutral point (CNP)

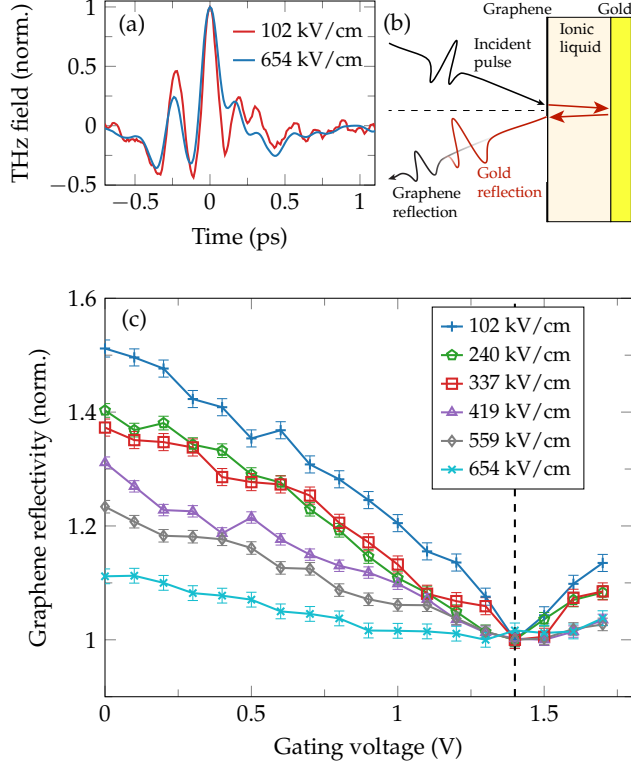


Figure 2: (a) Normalized THz electric fields in the case of 102 kV/cm (red curve) and of 654 kV/cm (blue curve). (b) Schematic representation of the formation of the THz field shape after its reflection on the graphene device. (c) THz reflectivity of the gated graphene layer alone, as a function of both the THz field strength and the Fermi energy level, defined by the gating voltage. All curves are normalized to the response at the CNP of graphene indicated with dashed line at 1.4 V.

of graphene (dashed line at 1.4 V) defined as the gating voltage, at which the graphene resistance becomes maximum and consequently the THz reflectivity becomes minimum due to the increased transmission. We observe that the graphene THz reflectivity induced by the gating voltage, depends non-linearly on the THz field strength. At low THz fields, we record a modulation of the THz reflectivity up to 50 % at 0 V. However, at high THz field strengths, this modulation drops to 10 %. All the following measurements were performed at 0 V, where the maximum modulation on the graphene reflectivity was observed.

The aforementioned THz induced photoconductivity modulation, is expected to impact the absorption and phase characteristics of the whole device. The reflectance - normalized to the reflectance at the CNP - and associated phase spectra of the device for varying THz

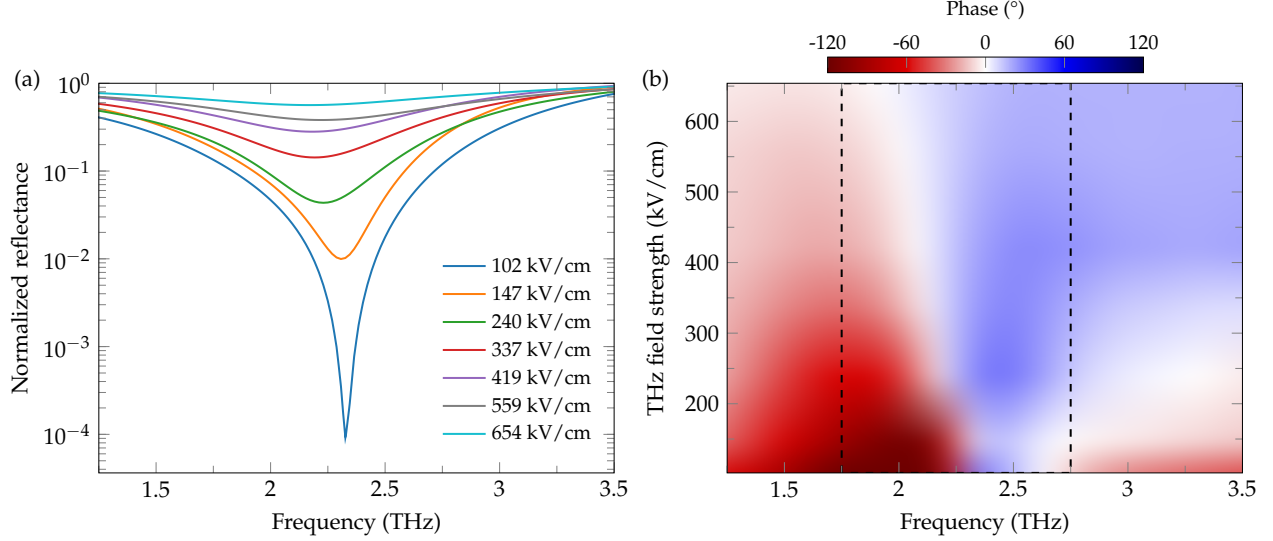


Figure 3: Experimentally measured reflectance (a) and phase (b) spectra for the cavity structure presented in Figure 1, for various values of THz field strength in the range of 102–654 kV/cm. All spectra are normalized at the CNP.

field strengths, are shown in Figs. 3 (a) and (b) respectively. At low THz field strengths our device operates at the perfect absorption conditions presenting a resonance at frequency  $f = 2.33$  THz, defined by the device design and the angle of incidence of the THz radiation. The reflectance of the device at this frequency drops down to  $9.2 \times 10^{-5}$ . However, as the THz field strength increases, the perfect absorption conditions are disrupted and the reflectance of the device increases to 0.57, for the maximum available THz field strength. This corresponds to a THz induced absorption modulation of more than three orders of magnitude. Moreover, a slight red shift of the resonance with increasing THz field strength is observed. In Figure 3 (b) we observe also a significant phase modulation at frequencies around the resonance (region between dashed lines in Figure 3 (b)). We recorded an absolute THz induced phase modulation of  $130^\circ$ . This large phase modulation is responsible for the THz pulse reshaping (see Figure 2 (a)) when the THz field strength scales up. In order to exclude any nonlinearities induced by the intense THz fields on the ionic liquid substrate, we investigated separately a similar sample without the graphene layer, and we didn't observe any THz nonlinear response.



## Discussion and interpretation

In order to understand the origin of the observed nonlinear response, we performed a detailed modeling of the graphene's response to THz excitation. Figure 4 shows a schematic representation of this response. After the absorption of the incoming THz radiation, graphene carriers thermalize in an ultrafast ( $\sim 20$  fs)<sup>36,37</sup> timescale. Heat dissipation occurs in a much slower ( $\sim$  ps)<sup>32,38</sup> timescale, via emission of optical phonons<sup>38,39</sup> and disorder assisted supercollisions.<sup>38,40,41</sup> This leads to heat accumulation in the graphene carrier bath, raising the electronic temperature  $T_e$ . The elevated  $T_e$  results in a reduced graphene chemical potential, due to net carrier density conservation (i.e.,  $n_e(\mu, T_e) - n_h(\mu, T_e) = \text{const}$ , where  $n_e(\mu, T_e)$ ,  $n_h(\mu, T_e)$  the graphene electron and hole densities respectively and  $\mu$  the graphene chemical potential<sup>32</sup>), and a broadened Fermi-Dirac distribution of graphene carriers. This reduces the intraband transitions, as explicitly evaluated by the Kubo formula,<sup>32</sup> leading to a reduced intraband conductivity,<sup>23,42</sup> and thus to a reduced THz absorbance of graphene.<sup>32</sup>

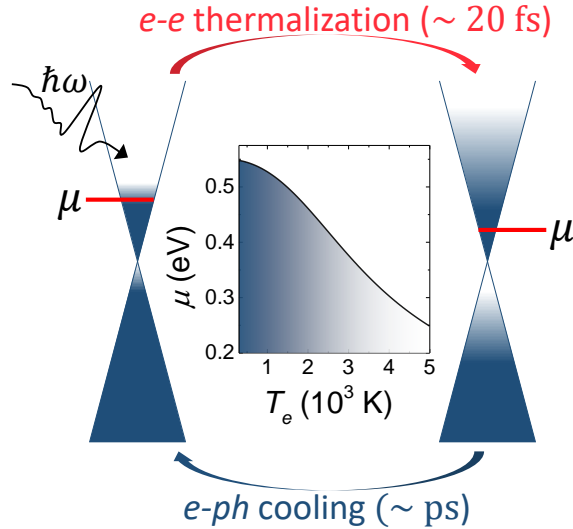


Figure 4: Schematic representation of graphene carriers upon heating, following THz excitation. Chemical potential (red line) and carrier distribution are sketched at room temperature (left) and  $T_e \gg 300$  K (right). The middle graph plots the reducing graphene chemical potential with increasing  $T_e$ , as a consequence of carrier conservation.

In order to quantitatively describe the above, graphene carrier and temperature dynamics

are time integrated using a 4<sup>th</sup> order Runge-Kutta method (4RK).<sup>32</sup> To do so we assume a two-temperature model<sup>32,43</sup>

$$c_e \frac{\partial T_e}{\partial t} = \alpha_{SLG}(\omega, T_e) P_{in}(\omega, t) - J_{e-ph}(T_e, T_l) \quad (1)$$

$$c_l \frac{\partial T_l}{\partial t} = J_{e-ph}(T_e, T_l) - \Gamma_{SLG-sub}(T_l - T_{sub}) \quad (2)$$

where  $c_e$  and  $c_l$  are the electronic and lattice graphene thermal capacities,<sup>32,44</sup>  $T_e$  and  $T_l$  the graphene carrier and lattice temperatures, which are generally different,<sup>32,43</sup>  $\alpha_{SLG}(\omega, T_e)$  the graphene absorption, which depends on  $T_e$  and light frequency  $\omega$ ,  $P_{in}(\omega, t)$  the input power density of the THz source,  $J_{e-ph}(T_e, T_l)$  the thermal current density from the electron to the phonon bath,  $\Gamma_{SLG-sub} \approx 20 \text{ MWm}^{-2}\text{K}^{-1}$  the cooling rate of graphene lattice into the substrate<sup>32</sup> and  $T_{sub}$  the substrate temperature, assumed for simplicity fixed at 300 K. For the input power density we assume a Gaussian pulse profile, i.e.  $P_{in}(\omega, t) = P(\omega) \exp(-B(t/\tau_w)^2)$  with  $B = 4 \ln(2)$ ,  $\tau_w \approx 150$  fs the full width at half maximum of the pulse and  $P(\omega)$  the spectral profile of the input pulse. The spectral profile  $P(\omega)$  is determined experimentally (see inset of Figure 1a) and is normalized so that  $\int_0^\infty P_{in}(\omega, t) dt$  yields the pulse fluence measured in the experiment. Terms  $c_e$ ,  $c_l$  and  $J_{e-ph}(T_e, T_l)$  are calculated as described in Ref. 32. For  $J_{e-ph}(T_e, T_l)$ , we explicitly account<sup>32</sup> for electron - optical phonon scattering<sup>32,38,39</sup> as well as supercollision scattering.<sup>32,40,41</sup> For the latter we assume short-range scatterers with a mean free path  $l$ ,<sup>32,40,41</sup> yielding a supercollision thermal current density scaling with  $l^{-1}$ . THz light absorption in graphene is governed by intraband absorption, described by the frequency dependent intraband graphene conductivity:<sup>23,32,45</sup>

$$\sigma(\omega) = \frac{ie^2}{\pi \hbar^2} \int_0^\infty dE \frac{E}{\omega + i\tau^{-1}(E)} \left[ \frac{\partial f_{FD}(-E; \mu_{SLG}, T_e)}{\partial E} - \frac{\partial f_{FD}(E; \mu_{SLG}, T_e)}{\partial E} \right] \quad (3)$$

where  $f_{FD}(E; \mu_{SLG})$  is the Fermi-Dirac distribution and  $\tau(E)$  the energy dependent momentum scattering time.<sup>23</sup> The latter is modeled assuming unscreened long-range scattering in Coulomb impurities, i.e.  $\tau(\epsilon) = \gamma \epsilon$ , as expected in CVD grown graphene,<sup>22,23,42,46</sup> where  $\gamma = n_i \pi^2 e^4 / \hbar \epsilon_{sub}^2$  with  $\epsilon_{sub}$  the substrate dielectric constant, depends on impurity concentration  $n_i$ <sup>46</sup> and will be treated as a free parameter. A full microscopic description can be used to account for effects of screening<sup>47</sup> and electron-phonon scattering<sup>48</sup> on the relaxation time. However, at the high Fermi levels ( $\geq 0.2$  eV) and substrate supported graphene with low ( $< 10^4$  cm<sup>2</sup>/Vs) mobility used in our study, it is found to result in an overall linear dependence with carrier energy.<sup>42,49</sup> This linear scaling has also been successfully implemented in describing conductivity changes upon carrier heating.<sup>22,23</sup> Thus, to avoid the addition of extra free parameters (which could lead to overfitting the experimental data) we follow the simplified linear scaling model of the unscreened case and fit the proportionality constant  $\gamma$  and graphene  $E_F$  to the experimental results. Using Eq. 3 for graphene Drude conductivity, we calculate the dielectric function from which graphene's absorption  $\alpha_{SLG}(\omega, T_e)$  can be determined.<sup>32</sup> The substrate's contribution to the optical response is determined by fitting the device's reflectivity, prior to graphene placement, assuming a 25  $\mu$ m substrate thickness. We fit the substrate's dielectric response using a single Lorentz oscillator.<sup>50</sup> The extracted Lorentz parameters are:  $\epsilon_\infty = 3.29$ ,  $\Delta\epsilon = 1.45$  eV,  $\hbar\Omega = 5.42$  meV and  $\hbar\Gamma = 9.28$  meV, where  $\epsilon_\infty$  is the value of the dielectric function at infinite frequency,  $\Delta\epsilon$  the oscillator strength,  $\hbar\Omega$  the transition frequency and  $\hbar\Gamma$  the decay rate of the Lorentz term. The overall optical response of the proposed device, including the contributions of the substrate and the back-mirror, is calculated by employing the Fresnel equations using the transfer matrix method (TMM). Finally, the reflection spectrum of the device is calculated as:

$$R(\omega) = \frac{\int_0^\infty P_{in}(\omega, t) R(\omega, t) dt}{\int_0^\infty P_{in}(\omega, t) dt} \quad (4)$$

where  $R(\omega, t)$  is the time-dependent reflection resulting from TMM, which includes all the

definitions of Eqns. 1-3, self-consistently updated during the time integration within the 4RK scheme.<sup>32</sup>

Therefore, the only free parameters for our model are the graphene Fermi level  $E_{F,SLG}$ , the proportionality constant  $\gamma$  for long-range Coulomb scattering<sup>22,23</sup> and the mean-free path for supercollision scattering  $l$ .<sup>32,40,41</sup> We scan a wide range of these three parameters in order to minimize the deviations between our calculations and the experimental measurements. Good quantitative agreement between calculations and experiment (see Fig. 5b) is found for  $E_{F,SLG} \approx 0.56$  eV,  $l \approx 75$  nm and  $\gamma \approx 170$  fs/eV. The latter yields a momentum relaxation time of  $\tau \approx 95$  fs at room temperature, which corresponds to a carrier mobility of  $\mu_q \approx 1700$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The values for  $E_{F,SLG}$  and  $\tau$  extracted from our model match very well to previous reports in similar devices.<sup>18,31</sup> Moreover, the supersollision mean free path is within the range of previous reported values<sup>40,41</sup> for graphene on a dielectric substrate. These demonstrate the usefulness of our model as a reliable tool for extracting graphene's parameters using as input the experimental optical measurements.

Figure 5 (a) shows the reflectance spectra, for different THz field strengths, as calculated from our model. The above spectra are acquired after normalization of the reflectance at zero bias to the reflectance at CNP (1.4 V bias). For this normalization, we assumed  $E_{F,SLG} \approx 200$  meV at CNP. The above value was determined after fitting the calculated spectra to experimental measurements under 1.4 V bias and is in line with previously reported values of graphene residual doping on ionic liquid substrates.<sup>18,31,51</sup> We observe a similar behaviour with the experimental findings (see Fig. 3). As the THz field increases, so does the calculated reflectance, presenting also the characteristic red shift of the resonance observed in the experiment. This absorption resonance is due to critical coupling of light<sup>19</sup> into the Fabry – Perot cavity formed by the graphene reflector and the back mirror, and is sharper in theory compared to experiment. The latter can be attributed to inhomogeneous broadening originating from substrate thickness and graphene doping fluctuations across the measurement spot size. At frequencies far from resonance, on the other hand, an anti-

resonance is expected, where the total reflection of the graphene-mirror system is larger than the reflection at CNP (where graphene is non-reflecting) and thus the normalized reflectance reaches above unity. We note that this behavior is observed in the theoretical spectra but not in the experimental spectra, which is most likely due to the aforementioned inhomogeneous broadening. In Figure 5 (b) we plot the minimum reflectance, as a function of peak THz field strength, alongside the experimental results. The final results for the on resonance reflectance modulation shows a good agreement between theory and experiment.

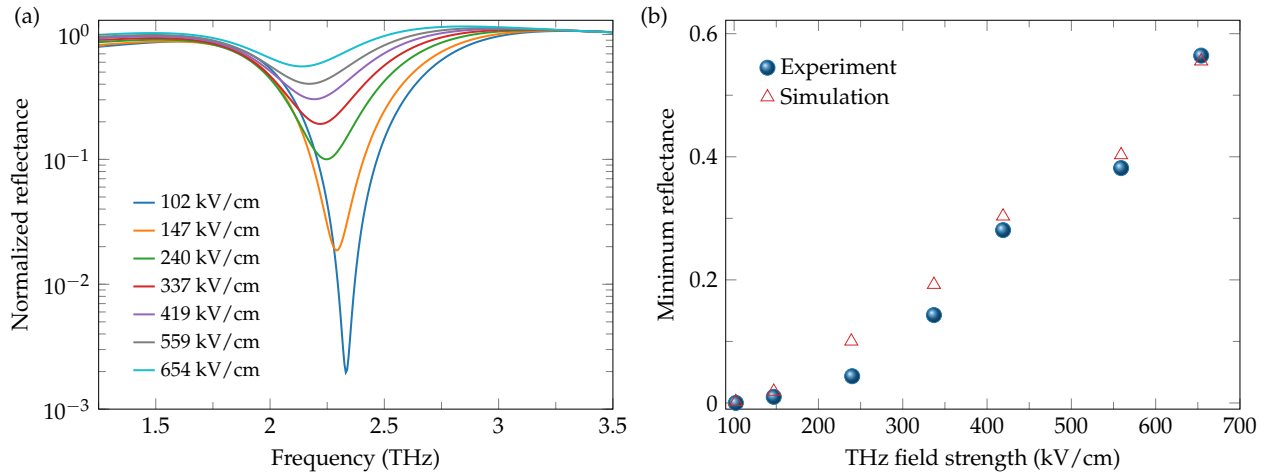


Figure 5: (a) Reflectance spectra, for different THz field strengths for the cavity structure presented in Figure 1, as calculated from our model using  $E_{F,SLG} = 0.56$  eV,  $l = 75$  nm and  $\gamma = 170$  fs/eV. All spectra are normalized at the CNP. (b) Experimental and calculated minimum reflectance of the proposed device, as a function of THz field strength.

It is evident that a higher THz field strength, yields larger overall reflectance. As discussed, this can be attributed to the heating of graphene carriers and the subsequent lowering of graphene chemical potential and the reduction of its intraband conductivity. Therefore, graphene absorbance is reduced, and as a result reflectance of the incoming THz radiation increases. The temporal evolution of the differential reflectance at resonant frequency during THz excitation can be found in the supplementary material. There, we also extract a relationship between peak relative reflectance increase at resonance as a function of incoming THz field strength, yielding  $\Delta R_{max} \approx \beta E_{max}$ , with  $\beta = 3.4 \times 10^{-4}$  cm/kV.

Our theoretical framework allows one to gain insight into the carrier temporal dynamics,

during THz excitation. Figure 6 (a) shows the temporal evolution of carrier temperature, during, and shortly after the THz excitation. In Figure 6 (b) we plot the respective temporal evolution of the real part of intraband conductivity (which is directly proportional to THz graphene absorbance), at the resonant frequency. This elucidates how the near instantaneous thermalization of graphene carriers, in combination with their retarded cooling, leads to vanishing conductivity at higher THz field strengths. The latter is the source of the non-linear absorption modulation observed in this work. Furthermore, we observe that the overall phenomenon occurs on the sub-ps time scale, illustrating the ultrafast nature of the observed modulation. The temporal evolution of the differential conductivity is also included in the supplementary material, along with the photoconductivity minima relation on the excitation THz field strength, yielding  $\sigma_{min} = 0.035E_{max}^{-\alpha}$ , with  $\alpha = 0.63$ .

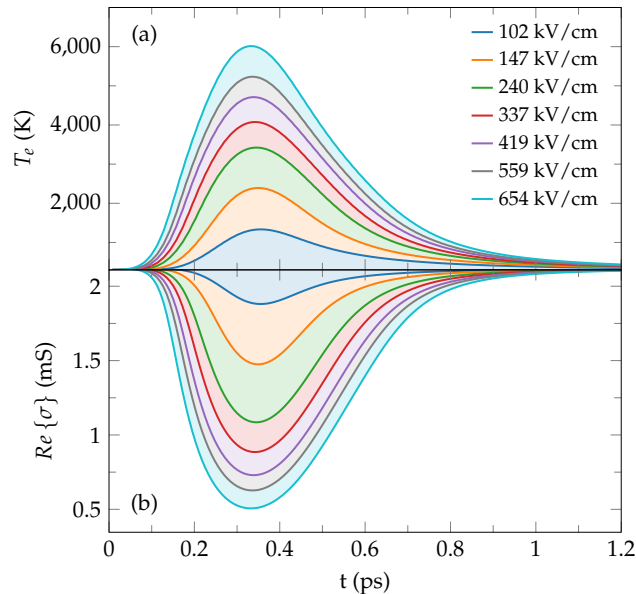


Figure 6: Calculated temporal evolution of (a) graphene carriers' temperature and (b) real part of intraband conductivity at the resonant frequency.

## Conclusion

We have demonstrated that under the excitation of intense THz pulses, a graphene-based Salisbury screen perfect absorbing device can be self-modulated in terms of its absorption

properties. In our experiments, we observed an absorption modulation of more than three orders of magnitude at 2.33 THz and an absolute phase modulation of  $130^\circ$  when the THz field strength scaled from 102 kV/cm up to 654 kV/cm. Our detailed theoretical analysis based on the dynamics of the THz induced hot carriers in a single layer graphene, shed light on the origin of the observed nonlinear response of the device: the irradiation of intense THz fields, results in heating of the graphene's carriers and a subsequent decrease of its chemical potential and intraband conductivity. The carrier temporal dynamics during THz excitation, obtained through our split-time algorithm, reveals the ultrafast nature of the non-linear response since the entire phenomenon lasts less than a picosecond. These results, demonstrate a new mechanism of modulating the absorption and phase properties of graphene based perfect absorbing devices, that of THz self-actions. Such devices could find applications in future dynamically modulated flat optics devices. Additionally, devices based on our work can serve for custom beam and pulse shaping of intense THz sources.

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## Supporting Information Available

THz nonlinearity dependence on excitation field strength

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# Graphical TOC Entry

