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Ultrafast low-energy dynamics of graphite studied by nonlinear multi-THz spectroscopy

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Abstract: Ultraintense few-cycle THz pulses are employed to study the nonlinear response of graphite. A phase sensitive 2D spectroscopy setup is capable of detecting pump-induced transient changes as well as multi-wave mixing processes. The observed strong THz-pump THz-probe signals provide insight into ultrafast dynamics and the spectral response of the low-energy carriers. Here we report the observation of a pump-induced transmission in graphite. The relaxation dynamics shows three distinct time scales, which are assigned to carrier thermalization, phonon emission and a slow cooling down back to equilibrium.

Graphite and graphene feature exceptional electronic and lattice properties that are important for applications in optoelectronics as well as for fundamental physics [1]. The electronic band structure of both materials shows a vanishing energy gap between valence and conduction bands which enables the study of massless charge carriers in the graphene case. THz pump / THz probe experiments performed with picosecond pulses from a free-electron laser have demonstrated an anomalous nonlinear response of carriers in the vicinity of the Dirac point of graphene [2].
Winnerl and coworks observed a pump-induced bleaching for a fluence of $\Phi \approx 1$ μJ/cm^2 and photon energies exceeding twice the Fermi energy. Important insights into the relaxation dynamics in graphite have been obtained using near-infrared (NIR) excitation [3,4]. Two-dimensional femtosecond spectroscopy is expected to allow for a particularly direct observation of ultrafast dynamics and spectral correlations. At THz frequencies this technique promises access to the intriguing low-energy interband dynamics of graphite and graphene. In fact, lead-off experiments on THz multi-wave mixing have been proposed recently [5]. Latest advances in the multi-THz technology pave the way towards a systematic investigation of extreme THz nonlinearities utilizing ultraintense phase-stable laser pulses with peak electric fields exceeding 100 MV/cm [6,7]. Furthermore, electro-optic detection warrants a direct observation of the time trace of the carrier field with absolute amplitude and phase resolution.

Here we employ our high-field multi-THz source to study the nonlinear response of a thin graphite flake using a two-dimensional spectroscopy setup. A highly oriented pyrolytic graphite (HOPG) crystal is exfoliated down to a thickness of approximately 130 nm (Figure 1(a)). The

sample is bonded to a 250-µm-thick diamond window via van der Waals forces. All experiments are performed at room temperature and the THz peak fields were chosen as high as 2.5 MV/cm per branch, corresponding to a fluence of 2 mJ/cm^2.

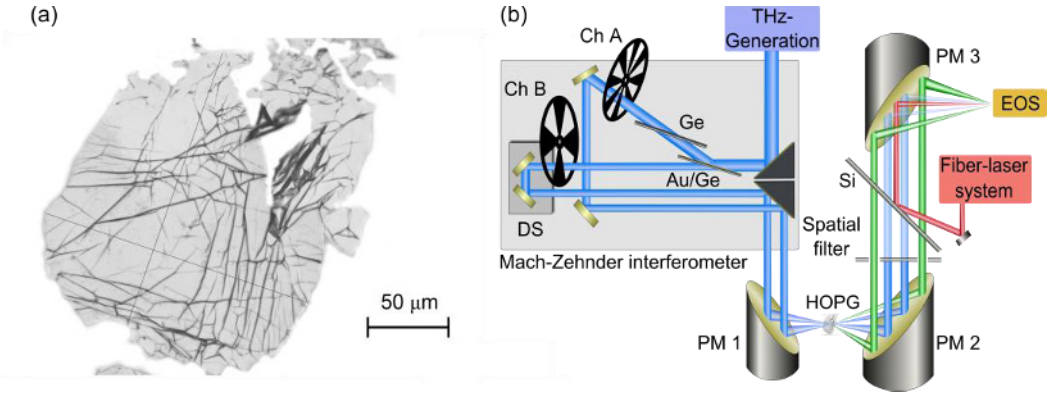

Fig. 1. (a) Optical microscope image of the 130-nm-thick graphite sample. (b) Two-dimensional multi-THz spectroscopy setup.

In our system, difference frequency mixing of two NIR pulse trains takes place in a GaSe crystal, thus providing intense THz transients centered at a frequency of 25 THz with a bandwidth of 5 THz. A Ge beam splitter set at Brewster's angle and coated with a thin gold layer (Au/Ge) provides two identical copies of the THz transient (Figure 1(b)). The reflected transient E_1 propagates through an additional Ge wafer to match the dispersion of the transmitted pulse E_2 which is delayed by a linear stage. Both beams are tightly focused onto the sample with an off-axis parabolic mirror. An electro-optic detection scheme is used to sample the emerging linear and nonlinear fields by a NIR gating pulse of a duration of 8 fs. The total transmitted field E_{12} is retrieved as a function of the electro-optic sampling delay t and the relative temporal offset τ between the THz pulses. The nonlinear signal E_{NL} is acquired by subtracting the individual transients E_1 and E_2 from the total response: $E_{NL} = E_{12} - E_1 - E_2$. We disentangle different nonlinear contributions, such as pump-probe and four-wave mixing signals, by two-dimensional spectral filtering of E_{NL} [5]. An appreciable pump-probe signal is clearly observed in our experiment (Figure 2(a)) whereas four-wave mixing and higher order multi-wave mixing signatures are too weak to be resolved, at present.

Figure 2(a) shows the transient change in E_1 induced by the field of E_2. A strong response in the temporal region where both transients overlap ($\tau = 0$ ps) is followed by a slower relaxation process. Owing to the field-resolved detection provided by electro-optic sampling we are able to extract the spectral profile of the pump-probe signal in the frequency range between 23 and 29 THz, covered by our broadband THz transients. Figure 2(b) depicts the amplitude spectrum of the normalized relative transmission change $\Delta T/T$ as a function of the pump-probe delay time. The dash-dotted line marks the change of sign. The ultrafast dynamics of $\Delta T/T$ at selected frequencies are plotted in Figure 2(c). Remarkably, at frequencies above 25 THz the transmission change is *negative* in contrast to a *positive* differential transmission of multi-layer graphene in a similar frequency range that was reported recently [4]. This qualitative difference in the nonlinear THz response of graphite and graphene is likely related to the significant interlayer coupling in graphite which results in a modification of the band structure and additional interband optical transitions [8]. Theoretical modeling of the optical response of photodoped graphite is currently in progress.

The observed relaxation dynamics demonstrates at least three distinctly different time scales (Figure 2(c)): The fast initial relaxation within ≈200 fs reflects the thermalization of the electron and hole distributions. The following decay of negative differential transmission on a 1-ps time scale is tentatively assigned to the cooling of the photogenerated charge carriers via electron optical-phonon scattering. Although the pump-photon energy is clearly below the optical-phonon emission threshold

of 200 meV the efficient carrier generation and strong electron-electron interaction lead to an extremely hot electron hole plasma with significant occupation of states with energy above 200 meV. At longer delay times the pump-probe spectrum demonstrates a rather stable shape with a zero-crossing at a frequency of 24 THz as shown in Figure 2(c) (τ = 1.5 ps). At earlier times, the electron cooling dynamics results in the evolution of the pump-probe spectrum clearly revealed by the shift of the zero-crossing point depicted in Figure 2(b). For τ > 1.5 ps, the intensity of the pump-probe signal decays slowly with a time constant distinctly larger than the measurement window of 3.5 ps. This relaxation reflects the cooling of charge carriers with a kinetic energy below the optical phonon emission threshold.

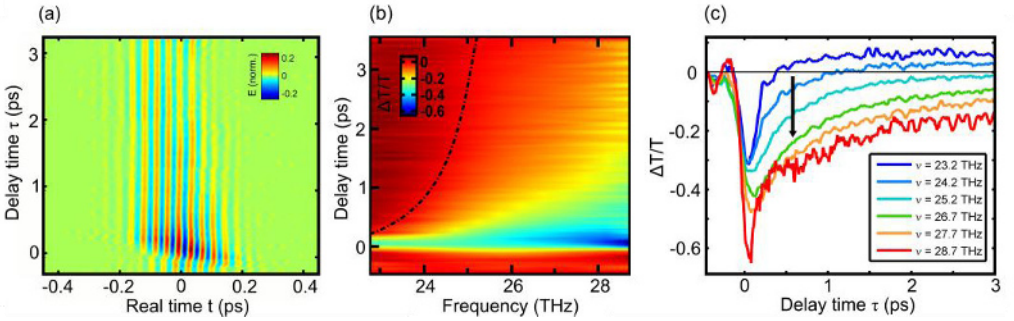

Fig. 2. (a) Pump-probe signal plotted as a function of the sampling time t and the delay time τ. (b) Relative transmission change $\Delta T/T$ of the probe transient plotted as a function of the frequency ν and the delay time τ. The dashed-dotted line corresponds to $\Delta T/T$ = 0. (c) $\Delta T/T$ as a function of the delay time τ for different frequency components of the driving field. The arrow marks increasing frequencies.

Furthermore, we have performed measurements with THz transients centered at 30 THz. Surprisingly, the zero-crossing of the transient transmission spectra shifts towards higher frequencies by 5 THz, i.e. the same amount by which the THz pump pulse is changed (not shown). Thus, the THz pump-probe response in graphite is strongly dependent on the energy of the pump photons indicating a strong contribution of interband optical transitions compared to the response of the photogenerated plasma.

In conclusion, ultraintense few-cycle THz transients are used to study carrier dynamics in graphite. A strong pump-probe signal reveals three distinct relaxation processes of the THz-induced transmission change. The transient transmission spectra demonstrate a characteristic zero-crossing which shifts on a picosecond time scale and depends on the central frequency of the pumping THz pulse. Our results demonstrate the high potential of the high-field multi-THz nonlinear spectroscopy for investigation of ultrafast carrier dynamics in graphite, graphene and related carbon-based materials.

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