Ultrafast Non-Thermal Electron Dynamics in Single Layer Graphene

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Abstract: We study the ultrafast dynamics of non-thermal electron relaxation in graphene upon impulsive excitation. The 10-fs resolution two color pump-probe allows us to unveil the non-equilibrium electron gas decay at early times.
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The dynamics of elementary optical excitations in graphene has been the object of a great deal of studies, aimed at understanding the fundamental relaxation mechanisms[1,2]. According to the band structure of graphene (Fig. 1(a) absorption of a photon of frequency ν promotes an electron from an energy hν/2 below the Fermi level in the valence band to an energy hν/2 above the Fermi level in the conduction band. Ultrafast photoexcitation, therefore, creates a strongly non-equilibrium (non-thermal) distribution of electrons in the conduction band (and holes in the valence band), consisting of two peaks at ±hν/2 with respect to the Fermi level (see Fig. 1(a)). The primary relaxation process is thermalization due to electron-electron (e-e) interaction, giving rise to an equilibrated Fermi-Dirac (FD) electron distribution with a well defined temperature, higher than that of the lattice. The hot electrons subsequently reach thermal equilibrium with the colder lattice via electron-phonon (e-ph) scattering. These equilibration processes change the transient absorption spectrum over a wide range of energies and an ultrafast timescale. Their time-domain observation calls therefore for the combination of very short pulsewidths and broad spectral tunability.

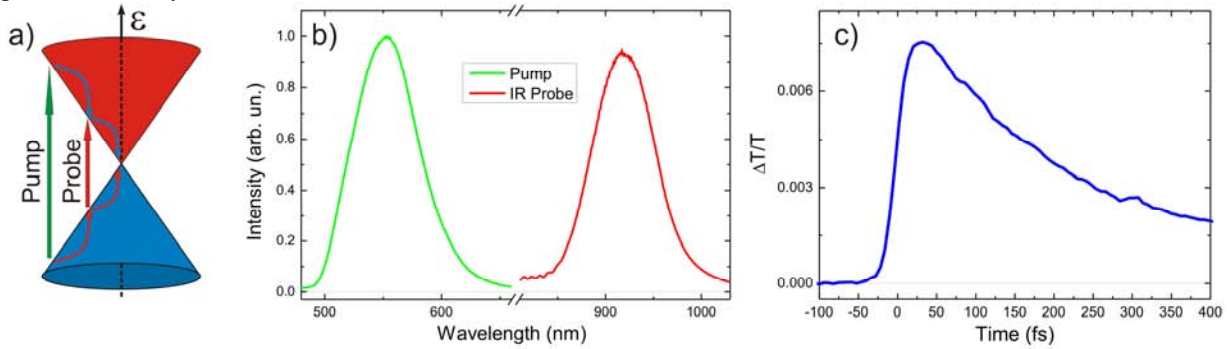

Fig.1. (a) Sketch of the pump-probe experiment: the pump pulse excites a non-thermal electronic distribution that is probed at lower energies; (b) pump and probe pulse spectra; (c) ΔT/T time trace at the 860 nm probe wavelength.

A large body of experimental work on ultrafast spectroscopy of graphene is available [1-4] .However, so far, most studies have been performed with a time resolution which is too low to observe e-e scattering dynamics and thus have probed an equilibrated hot electron/hole distribution, established within the pump pulse duration (~100-150 fs). These studies have revealed the dynamics of carrier cooling through interaction with the lattice. A number of theoretical studies [5] and indirect experimental evidence [4] however point to an extremely fast e-e relaxation, occurring on the 10-fs timescale. Here we perform pump-probe spectroscopy on graphene using two-color few-optical-cycle pulses. We impulsively excite optical transitions with an ultra-broadband 7-fs pulse centered at 2.25 eV (2-2.5 eV bandwidth) and probe with a red-shifted 13-fs pulse covering the 1.45-1.2 eV range. The instrumental response function (IRF) of our apparatus (full width at half maximum of the pump-probe cross-correlation) is ~15 fs [6,7]. The combination of high time resolution and broad spectral coverage allows to capture the transition from the non-thermal to a FD electron/hole distribution.

Pump-probe experiments are carried out on single-layer graphene films grown by chemical vapor deposition and transferred onto a 100-μm-thick fused silica substrate. A portion of the substrate is not covered with graphene, thus

allowing to measure the substrate contribution to the nonlinear response by a simple transverse translation of the sample. In our experiments we observe a prompt rise of the photobleaching signal in the near-IR, that already points out to an ultrafast e-e relaxation, taking place over a timescale comparable to our IRF. Time traces at selected probe wavelengths display a biexponential decay (fig. 1(c)), with a first time constant τ_1 ~160 fs, and a second longer time constant that is not addressed in this study. The first decay is assigned to cooling of the hot electron/hole distribution via interaction with optical phonons, while the longer decay is due to relaxation of the thermalized electron/phonon bath by anharmonic decay of the hot phonons.

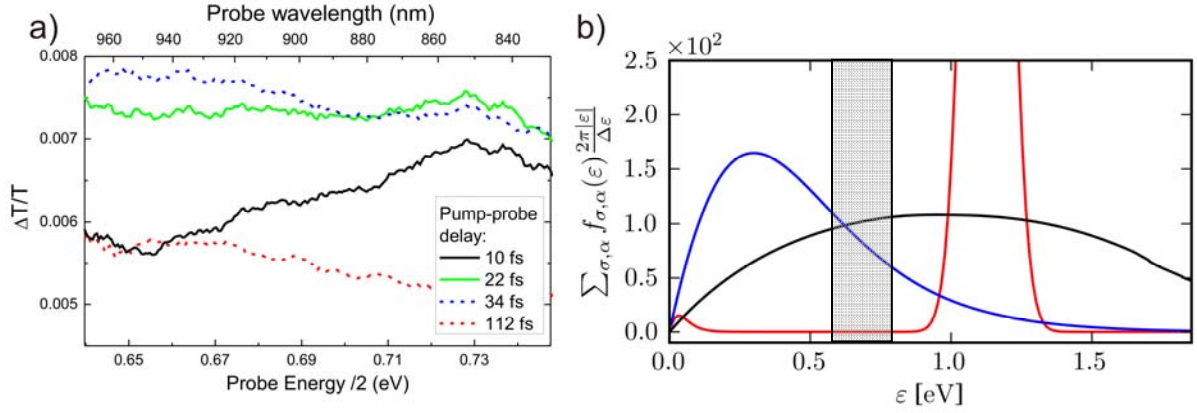

Fig. 2. (a) Transient spectra at selected delays after pumping with a 7-fs visible pulse. The change in slope shows the evolution of the impulsively excited electron distribution to the thermal equilibrium; (b) calculations of the electronic distribution at different delays (red, τ_0=0; black τ_1, blue τ_2). The probe window is marked with the shaded area.

A deeper insight into the dynamical processes leading to e-e thermalization can be obtained by plotting ΔT/T spectra at selected probe delays (Fig. 2(a)). At early times (10 fs), the ΔT/T spectrum has a positive slope, peaking at higher energy; then it progressively flattens (22 fs) and changes to a negative slope, which is retained and then magnified at longer delays. To understand the data we recall that the ΔT/T signal for single-layer graphene is the difference between the transient electron/hole distribution function at time τ and the equilibrium distribution function before the pump pulse. The sub-10-fs pump pulse creates an electron distribution peaking at ~1.12 eV above the Fermi level, while the probe pulse interrogates the 0.6-0.72 eV interval. At early times, therefore, we will observe the tail of this distribution, which has a positive slope. On the other hand for a thermal distribution the ΔT/T spectrum has a negative slope peaking at lower photon energies. The change of slope of the ΔT/T spectrum thus captures the transition from the non-thermal to the thermal regime, which is completed within ~30 fs. Fig. 2(b) reports a calculation of the transient electronic distribution above Fermi level that shows how, at early times, the electronic distribution (black line) is still peaked at higher energy and then relaxes to a thermal distribution only at longer times (blue line). The observed dynamics do not exhibit a significant dependence on the excitation density. By moving from multichannel to single-wavelength detection, we were able to reduce the fluence by a factor of 20, and saw a substantially unchanged dynamics.

In conclusion, we exploit the very high temporal resolution of our two-color pump-probe scheme to observe the early times in the relaxation dynamics of out-of-equilibrium electrons in single layer graphene. The ultrafast timescale of this process is strongly related to the peculiar band structure and the electronic properties of this fascinating material.

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