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# A direct view onto the carrier dynamics in graphite at the H point

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**Abstract.** Time-resolved XUV photoemission spectroscopy is employed to monitor the dynamics of photo-excited carriers in graphite at the boundary of the Brillouin zone. The experiment provides direct access to the momentum region relevant for optical excitation and relaxation.

## 1 Introduction

The ultrafast dynamics of electronic excitations in graphite has attracted continuous attention over the last decade in experiment and theory. A variety of pump-probe techniques based on pure optical approaches as well as photoemission have been used to disentangle the different time-scales characterizing processes such as carrier thermalization, carrier recombination or carrier-lattice interaction [1-3]. Despite substantial progress, data interpretation is limited by the fact that the different probes applied in previous work provided only indirect access to the electronic states involved in the excitation and relaxation processes. For instance, in pure optical experiments it is difficult to disentangle electron and hole dynamics, whereas photoemission studies have been restricted to probing photon energies in the visible and near ultra-violet spectral region limiting electron momentum-space access to states in the vicinity of the Γ point. For graphite, however, all electronic states in the relevant energy regime near the Fermi energy are located at the boundary of the Brillouin zone.

In a recent study on phase-transition dynamics in 1*T*-$TiSe_2$ we have proven that time- and angle-resolved photoemission spectroscopy (TR-ARPES) operated with femtosecond XUV pulses from a high-harmonic light source can provide the missing direct experimental access to the dynamics of high momentum electron states [4]. Here we employ this technique to directly map the energy- and momentum-dependent relaxation of photo-excited carriers in graphite in the vicinity of the H-point. The experimental approach enables us to monitor the dynamics of hot electrons and hot holes separately. Our data give evidence for ultrafast carrier thermalization on a sub-30 fs time-scales followed by efficient carrier cooling within several 100 fs supporting recent results reported in [3].

## 2 Experiment

Time- and angle-resolved photoemission experiments were performed using a hemispherical electron energy analyzer mounted in an ultrahigh vacuum (UHV) chamber and equipped with an efficient 2D detection unit for parallel energy and momentum detection. The highly ordered pyrolytic graphite (HOPG) sample, which was cleaved *in-situ* under UHV prior to the experiment, is optically excited

using light pulses from a 3 kHz CPA multipass amplifier (30 fs, 785 nm, 1.3 mJ pulse energy) at (absorbed) fluences of several $mJcm^{-2}$ per pulse. The femtosecond XUV pulses used to probe the ultrafast dynamics in photoemission were generated in argon in a fiber-based high harmonic cell [5]. A double mirror monochromator consisting of two multilayer mirrors selects the 27th harmonic ($h\nu$ = 42.8 eV) out of the harmonic spectrum providing a measured photon flux in the $10^9$ photons/s regime at the sample position. The overall time resolution of the experiment is 32 fs as determined from surface LAPE (laser assisted photoemission) cross-correlation measurements [6]. The energy resolution of the experiment is limited by the spectral width of the high-harmonic light pulses to a value of about 400 meV. All experiments were conducted at an equilibrium sample temperature of 120 K.

## 3 Results and Discussion

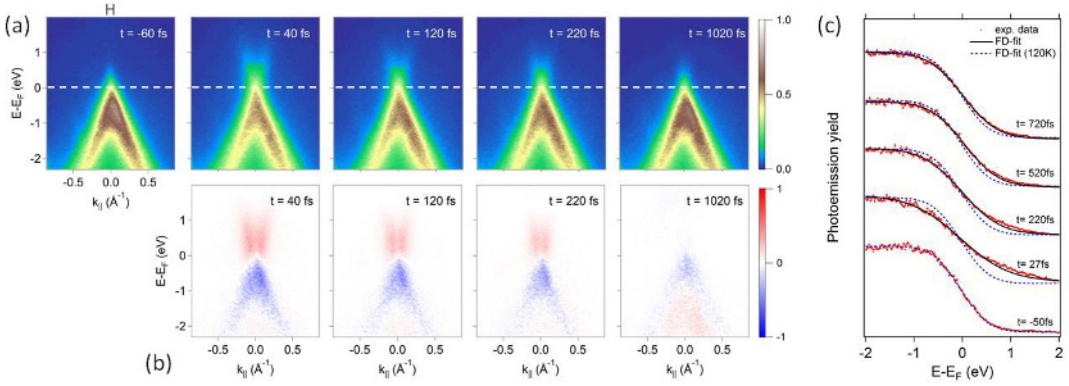


**Fig. 1.** (a) Photoemission snap shots of graphite recorded at the H-point at different temporal delays after photo-excitation with 800 nm, 30 fs laser pulses. The absorbed fluence in this experiment was 9 $mJcm^{-2}$. (b) Photoemission intensity difference maps (in reference to $\tau$ = - 60 fs) deduced from the snap shots shown in (a). Red color (bright grey) coding is indicative for the presence of excess electrons, blue color (dark grey) coding is indicative for the presence of excess holes. (c) Momentum-integrated spectra at different delays in comparison to Fermi-Dirac fits convoluted with the energy resolution function of the experiment.

Fig. 1 (a) displays time-resolved ARPES intensity snap shots of graphite at different temporal delays $\tau$ after photo-excitation with 800 nm laser pulses. In addition, a reference spectrum is shown which was recorded 60 fs prior to the excitation. Despite the limited energy resolution, the downward dispersing valence band, characteristic for the band structure of graphite, is reasonably well resolved [7]. Upon absorption of the IR excitation pulse, spectral weight is transferred to energies above the Fermi energy indicative of the instantaneous generation of hot electrons. The series of snap shots shows that the dominating part of the hot electron population decays out of the probing region above $E_F$ well within the first picosecond. The probed population decay can either arise from electron-hole recombination processes or, more likely, the scattering of the electrons into other excited state regions in momentum space. Fig. 1 (b) shows photoemission intensity difference maps which have been generated by subtraction of the reference ARPES map recorded at $\tau$ = - 60 fs. These maps provide a distinct view onto the dynamics associated with the transient generation of holes in the valence band (see photoemission intensity decrease color-coded in blue/dark grey). Fermi-Dirac (FD) fits to the momentum integrated raw data (see Fig. 1(c)) indicate a distinct asymmetry between electron and hole distribution. Static reference measurements of doped graphite show that this asymmetry results from a difference in the photoemission spectral weight between $\pi$ and $\pi$*-band.

After correction of the data for this mismatch we find that the thermalization of the electron and the hole distribution is completed within the 32 fs time resolution of the experiment. Spectrally resolved population transients give, furthermore, evidence for rapid carrier cooling on a few 100 fs time-scale most likely because of efficient coupling to optical phonons.

In summary, TR-ARPES was used to monitor the transient population of hot carriers in graphite excited at the boundary of the Brillouin zone. The direct access to this momentum region, provided by the use of femtosecond XUV pulses, reveals details of the relaxation process that can barely be resolved by alternative, more indirect techniques. One particular example is the capability to probe the momentum redistribution dynamics of the hot carriers following the momentum selective excitation by a polarized pump pulse. In general, the results will provide new insights into the complex processes associated with hot carrier relaxation in graphite and graphite-derived systems.

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