

Raman spectroscopy of graphene under ultrafast laser excitation

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Abstract. The out-of-equilibrium Raman response of graphene is addressed by pulsed laser excitation. Phonon spectrum is rationalized by revisiting the electron-phonon picture in the light of a transient broadening of the Dirac cone.

1 Background

Since its isolation in 2004 [1], graphene has been in focus of intense research activities, in view of its great potential to underpin new disruptive technologies, substituting materials used in existing applications but also leading to radically new devices. Several recent results highlight the versatility in the application of this system, ranging from solar cells and light-emitting devices to touch screens, photodetectors and ultrafast lasers [2]. Clearly, understanding the light-matter interaction processes, that characterize this gapless system, is critical to technological applications in diverse areas.

For this purpose, over the last decade, non-equilibrium dynamics of charge carriers have generated great interest, leading to many theoretical and experimental studies [3]. Their main aim is to describe the different relaxation processes of the electrons (holes) in the conduction (valence) band, which can be conveniently excited by ultrashort pulsed laser. The interaction with pulsed light initially generates an out of equilibrium distribution of (hot) electrons with respect to the (cold) phonon bath. Relaxation to thermal equilibrium occurs within a few picoseconds through the fast electron-electron (e-e) and electron-phonon (e-ph) non radiative recombination channels.

Raman scattering has a pivotal role to enable the description of the equilibrium phonon properties in graphene and it is the main avenue to their characterization [4]. Nevertheless, on the laboratory timescale, continuous wave laser sources commonly used for high resolution spontaneous Raman scattering generally probe a charge carriers-lattice system

already thermally equilibrated, preventing from studying the transient regime of the non-equilibrium dynamics.

A way to impulsively localize energy into graphene's electronic subsystem is provided by sub picosecond photoexcitation. While the behaviour of hot charge carriers to such ultrafast perturbation has been thoroughly investigated [3], disclosing the behaviour of optical phonons under strongly out of equilibrium conditions remains a challenge.

2 Results

We perform spontaneous Raman measurements in graphene by using a 3-ps laser pulses, which trade off between impulsive stimulation and sufficiently narrow excitation bandwidth for an adequate spectral resolution. This experimental strategy allows us to give insights about the role of e-ph coupling as relaxation channel in presence of an electronic temperature largely exceeding that of the phonon bath.

Pulsed Raman measurements show a broad background, the hot-luminescence, originating from the inhibition of a full nonradiative recombination and directly related to the large electronic temperatures photoinduced in graphene [5]. On top of the hot luminescence, both G and 2D peaks are resolved and we determine the frequency and lifetime of phonons as function of the carriers' temperature in the range 1700-3100 K. Upon increasing temperature, we observe a broadening of both peaks, an upshift of the G band energy and a roughly independent behaviour of the 2D peak frequency.

At room temperature, the phonon lifetimes in graphene are dominated by e-ph scattering associated with inter-band carriers transitions, while anharmonicity plays a minor role [6,7]. In our case, out-of-equilibrium ps-excitation regime reveals that a transient smearing out of the Dirac cones, determined by the photoinduced large electronic temperatures, opens additional intra-band relaxation channels for the e-ph coupling, while anharmonicity is "frozen" at the negligible contribution pertaining to the much lower lattice temperature. This effect, has a pivotal role in understanding the carriers relaxation channels towards the phonon bath.

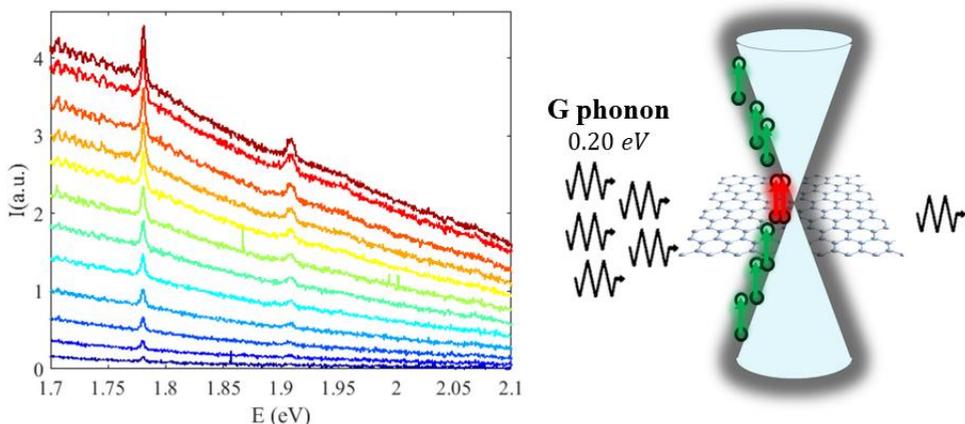


Fig. 1. (Left) Pulsed Raman spectra of graphene upon increasing electronic temperatures (from blue to red traces). (Right) Sketch of the smearing out of the Dirac cone. The red arrows indicate the

traditional inter-band ph decay channels, while the green show the additional intra-band contribution due to the broadening of the Dirac cone at large electronic temperatures.

3 Methods

An Er-doped fiber oscillator at 40 MHz was used to generate 2.5 nJ , 25 fs pulses at 1560 nm with an average power of 250 mW. This laser source, driven to a Periodically-Poled Lithium Niobate (PPLN) crystal, produces 780 nm pulses via Second Harmonic Generation (SHG), which was used for Raman photoexcitation. The beam is focused on monolayer graphene through a 20× objective (NA=0.4) and the back-scattered light is collected by the same objective, separated with a dichroic filter from the incident beam and sent to a spectrometer. The intensity of the beam can be easily attenuated in order to change the high electronic temperature photoinduced by the ps-pulses in graphene.

4 Conclusions

In summary, we demonstrated spontaneous Raman spectroscopy with pulsed excitation as a unique tool to characterize -from the phonon perspective- the role of e-ph coupling in out-of-equilibrium graphene. Accordingly, we reconsider the traditional scenario of the electron-phonon scattering [7] in a highly excited transient regime, which is critical for the emerging field of graphene-based nanophotonics and optoelectronics.

In particular, our results suggest the opening of additional relaxation channel associated to the electron-phonon coupling and due to the large electronic temperatures, which determine a smearing out of the Dirac cones [8].

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