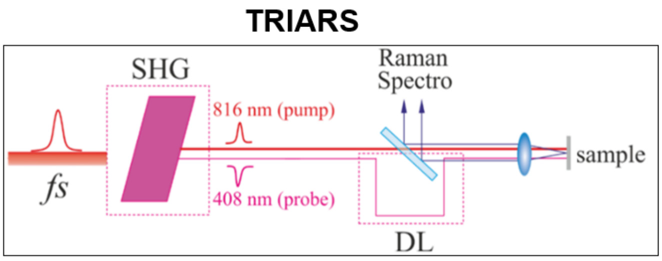
# Time-Resolved Raman scattering in exfoliated and CVD graphene crystals

S. Katsiaounis[1,2], Nikos Delikoukos[1,2], J. Parthenios[1], K. Papagelis[1,3]

[1]Foundation of Research and Technology Hellas, Institute of Chemical Engineering Sciences, P.O. Box 1414, GR-26504 Patras, Greece
[2]Department of Physics, University of Patras, GR-26504 Patras, Greece
[3] School of Physics, Department of Solid-State Physics, Aristotle University of Thessaloniki, Thessaloniki 54124, Greece

We have developed an experimental set-up to perform Time-Resolved Incoherent Anti-stokes Raman Scattering (TRIARS) experiments in graphene crystals to directly investigate the ultrafast dynamics of G- phonons [1]. In this technique an intense pump beam generates a non-equilibrium population of G phonons which decays to lower energy phonons via anharmonic interactions [2]. This decay process is monitored by the intensity of the anti-Stokes Raman signal, induced by the less intense probe beam, as a function of the delay-time between the pump and probe beams. We performed measurements in HOPG, 1-3L exfoliated graphene samples on $Si/SiO_2$ as well as CVD polycrystalline monolayers and stacks of monolayers onto $Si/SiO_2$ and quartz substrates.

We have found that the underlying substrate strongly reduces the G phonon lifetime of exfoliated and CVD monolayer via the provision of additional relaxation channels. In thicker exfoliated samples the G-mode lifetimes are close to that of graphite, implying that anharmonic coupling between phonon modes is insensitive to weak interplanar interactions. The electron -phonon (*e-ph*) coupling strength of graphite is found to be ~10.6 $cm^{-1}$ in excellent agreement with first principles calculations [2]. Polycrystalline monolayer and layer decoupled 2L, 3L CVD samples exhibit systematically smaller lifetimes than exfoliated ones. Measurements on stacks of two or three CVD monolayers gave almost similar results. The measured G phonon lifetimes in CVD graphene samples on quartz exhibit systematically higher lifetimes compared to the corresponding ones on $Si/SiO_2$ [1]. Very recently, we have extended the applicability of TRIARS to investigate the influence of hole doping by means of $HNO_3$ doped CVD graphene on the ultrafast dynamics of G phonons. A reduction of G phonon lifetime with doping is observed, resulting in an increased *ph-ph* contribution and a concomitant considerable reduction of the *e-ph* contribution to the G band linewidth.



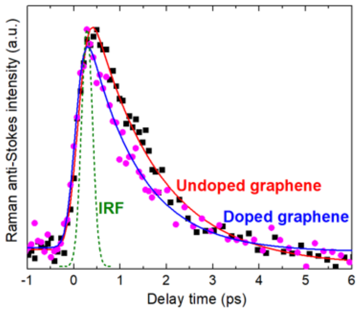




Figure 1: (Left) Simplified schematic representation of TRIARS set-up. fs: femtosecond pulse, SHG: Second Harmonic Generation, DL: Delay Line. (Right) Characteristic normalized anti-Stokes Raman intensity of G phonons as a function of delay-time for graphene, before and after doping. The green dashed curve corresponds to instrument response function (IRF).

## References

1. S. Katsiaounis, A. V. Sharkov, E. V. Khoroshilov, G. Paterakis, J. Parthenios and K. Papagelis, *The Journal of Physical Chemistry C*, 2021, **125**, 21003-21010.
2. N. Bonini, M. Lazzeri, N. Marzari and F. Mauri, *Phys Rev Lett*, 2007, **99**.