High Frequency, Pulsed and HYSCORE Electron Spin Resonance Investigations on Unzipped Graphene Nanoribbons

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Introduction

Graphene has emerged as a promising and versatile material, with outstanding electronic and spintronic properties that could be useful in many device applications, owing to its high carrier mobility and long spin life time resulting from low spin-orbit coupling (SOC) (~ 10^{-4} eV) and low hyperfine (hf) interaction. Recently, the demonstration of room temperature electron spin transport and spin precession in single layer graphene (SLG), discovery of large band gap in graphene nanoribbons (GNRs) and the observation of room temperature long relaxation times (~ 2 ns) and lengths (~ 0.7 μm) in bi-layer graphene (BLG) have suggested that graphene-based materials could play a pivotal role in spintronic devices that manipulate electron spin rather than charge.

ESR spectroscopy is a powerful technique to interrogate unpaired electron spins in paramagnetic materials and has been applied to pure graphite and carbon nanotubes. The objective of the present work is to address the nature of edge spins and spin dynamics in detail through a broad multi-frequency continuous wave (cw), pulsed ESR and HYSCORE spectroscopy carried out on pristine unzipped (split) GNRs.

Experimental

High frequency ESR experiments were performed at 239.2 and 336 GHz using the quasioptical spectrometer that has been developed at NHMFL. Pulsed ESR experiments were performed using a Bruker Elexsys 680 X-band ESR spectrometer. X-band (~9.7 GHz) HYSCORE spectroscopy was carried out at T = 12 K.

Results and Discussion

Important experimental findings include: (a) the multi-frequency cw ESR data infer the presence of only carbon-related paramagnetic non-bonding states, with g ≈ 2.003, independent of microwave frequency and temperature; (b) a linear broadening of the ESR signal as a function of microwave frequency; (c) the electron spin relaxation process is found to be characterized by slow and fast components, the temperature dependence of spin relaxation rate could be well described by tunneling level states (TLSs) model, as demonstrated in **Figure** 1; (d) HYSCORE data infer the presence of ^{1}H, weakly coupled to carbon-based paramagnetic centre with the hyperfine coupling (hfc) strength of ~25 MHz. Much of our work has been published recently.[1,2] The spin density at the carbon that couples to hydrogen is estimated at ~ 33%.

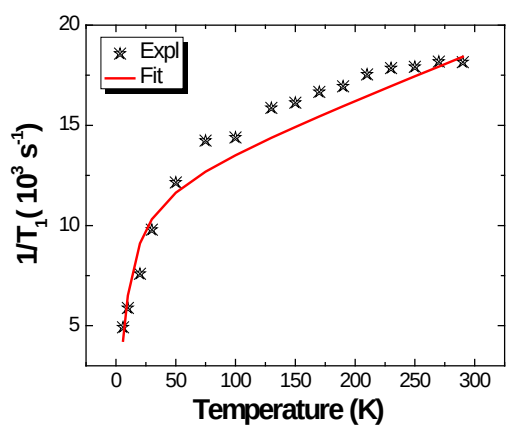

Figure 1. Spin-lattice relaxation rate at 9.7 GHz as a function of temperature.

Conclusions

We have been able to address several important questions pertaining to the nature and dynamics of spin states in GNRs using broadband ESR spectroscopy. The present experimental work could help in advancing the present understanding on the edge-spin (or magnetic)-based properties and spin relaxation rate in GNRs.

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References

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[2] Rao, S.S., *et al*., ACS Nano., **6**, 7615-7623 (2012).