Femtomagnetism in graphene induced by core level excitation of organic adsorbates and the role of electron transfer

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Abstract

We predict the induction or suppression of magnetism in the valence shell of physisorbed and chemisorbed organic molecules on graphene occurring on the femtosecond time scale as a result of core level excitations and electron transfer at the interface [1]. For physisorbed molecules, where the interaction with graphene is dominated by van der Waals forces and the system is non-magnetic in the ground state, numerical simulations based on density functional theory show that the valence electrons relax towards a spin polarized configuration upon excitation of a core-level electron with the LUMO shifting closer to the Fermi level to accommodate the additional charge and screen the positive core hole. The system is magnetic until the core electron de-excites via one of the several electronic decay channels [2,3]. The magnetism depends on efficient electron transfer from graphene and the corehole lifetime is in the femtosecond (fs) time scale. On the other hand, when graphene is covalently functionalized, the system is magnetic in the ground state showing two spin dependent mid gap states localized around the adsorption site [4].
The influence of a substrate is then considered for charge transfer between molecules and supported graphene. We focus on the resonant charge transfer lifetime of N-1s core excited 1,1' Bipyridine adsorbed on epitaxial graphene/ Ni(111). In the ground state, even though the system is magnetic, there is no magnetic moment on the molecule. Upon photoexcitation, our calculations predict that charge transfer may occur bidirectionally to/ from the LUMO on a few-fs timescale in good agreement with experimental results [2] and differently from unsupported graphene where no itinerant states are available at the Fermi level. [1] Ravikumar, A. et al. Femtomagnetism in graphene induced by core level excitation of organic adsorbates. Sci. Rep. 6, 24603; doi: 10.1038/srep24603 (2016).

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