

Local Structure and Dynamics of Hydrogen in Defective Graphene

D. Pontiroli^{1}, C. Cavallari², S. Rols², G. Magnani¹, M. Gaboardi¹, S. Sanna³, G. Bertoni⁴,
R. Verucchi⁵ and M. Riccò¹*

¹ Dipartimento di Fisica e Scienze della Terra, Università degli Studi di Parma, 43124 Parma, Italy

² Institut Laue Langevin, 38042 Grenoble Cedex, France

³ Dipartimento di Fisica “A. Volta”, Università di Pavia, 27100 Pavia, Italy

⁴ Istituto IMEM-CNR, 43124 Parma, Italy

⁵ Istituto dei Materiali per l'Elettronica e il Magnetismo, IMEM-CNR, 38123 Povo (Tn), Italy

^{1*} Dipartimento di Fisica e Scienze della Terra, Università degli Studi di Parma, 43124 Parma, Italy. Email: daniele.pontiroli@fis.unipr.it

The interest on the hydrogen interaction with carbon nanomaterials is wide-ranging and embraces fundamental problems, such as the interstellar formation of H₂, or the onset of magnetism in carbon [1]. The understanding of the peculiar state of hydrogen on the graphene surface is also important for technological reasons, such as graphene-based electronics and energy-storage. In this context, the thermal exfoliation of graphite oxide has attracted large attention, since it is an easy and low-cost method to produce single-layer graphene nanosheets with high rate, potentially scalable at the industrial level [2]. Thanks to its large specific surface area (2630 m²/g), graphene is able to adsorb considerable amount of hydrogen, although at rather low temperatures, due to the small H₂ binding energy. Besides physisorption, atomic hydrogen can also bind to graphene via a chemisorption process. DFT calculations have been shown that H₂ dissociation should be energetically favorable in presence of catalysts (metal nanoparticles), or even defects at the graphene plane [3]. This process could in principle feed the progressive H covering of the whole graphene surface (H-spillover effect), reaching up to 7.7 wt% of stored hydrogen (graphane), provided that H atoms are able to diffuse onto the graphene plane. A large debate on the possibility of H diffusion on graphene exists in the recent literature, but a clear description of this phenomenon is still missing. Although scanning tunneling microscopy has shown the absence of diffusion of atomic deuterium on clean HOPG [4], recent Raman and IR investigations on Pt-doped carbon systems evidenced the presence of H spillover on graphenic surfaces [5]. In this work [6], we performed a detailed study of the hydrogen interaction with defective graphene obtained via thermal expansion of graphite oxide (TEGO), part of which was enriched with about 0.7 wt % hydrogen by a further thermal annealing at 1273 K under H₂ flux at ambient pressure (H-TEGO). The macroscopic availability (grams) of such graphene made possible the investigation with techniques requiring bulk amount of samples, such as Solid State Nuclear Magnetic Resonance (SSNMR) and Inelastic Neutron Spectroscopy (INS), both of them extremely sensitive to hydrogen dynamics. Complementary investigation of samples was performed by TEM, SAED, XPS and UPS spectroscopy.

Figure 1a) shows the temperature evolution of ¹H SSNMR spectra measured on H-TEGO at $\mu_0H = 5.6$ T. The spectrum profiles consist of the superimposition of a large (30 kHz) T-independent Gaussian contribution and a Lorentzian one, whose width clearly narrows upon heating. The broad Gaussian component was reasonably attributed to clusters of hydrogens covalently bound to the graphene planes, in particular saturated armchair edges and graphane nano-islands, in which the observed broadening arises from their homonuclear dipolar interaction. On the contrary, the narrower component appears compatible with H in more dilute zigzag edges and mixed sp²/sp³ regions. Noticeably, the clear motional narrowing affecting the NMR linewidth of this latter contribution witnesses a H diffusive dynamics active already at T = 150 K, characterized by an activation energy barrier of just 29(4) meV and correlation times of the order of 1 μ s.

In order to better clarify these findings, INS spectra in a wide temperature range were collected on both TEGO and H-TEGO at the IN4C and Lagrange beamlines at the Institut Laue Langevin, Grenoble (see Figure 1b)). The TEGO and H-TEGO spectra are dominated by intense band located around 105 and 150 meV, which enhance in the hydrogenated sample. Such contributions falls in the range of C-H bending modes and are compatible with the presence of atomic H covalently bound to the graphene plane. The high resolution of spectra collected at Lagrange, assisted with DFT calculations, allowed to discriminate among different types of H attached in various positions on the graphene planes. In particular, the detected H dynamics seems to be promoted at the edges of not-completely saturated single-atom and extended vacancies of the graphene planes (see in Figure 1c)), produced during the exfoliation process, through the detachment of some C atoms. We suggest that this process should be likely supported by H incoherent quantum tunneling.

In conclusion, we evidenced the presence of hydrogen dynamics chemisorbed on the graphene plane already at low temperature. Both NMR and INS performed on bulk amount of defective graphene indicated that this system is effective to dissociate the H₂ molecule and to support H motion with a surprisingly low energy barrier of 30 meV, which has probably a quantum origin.

References

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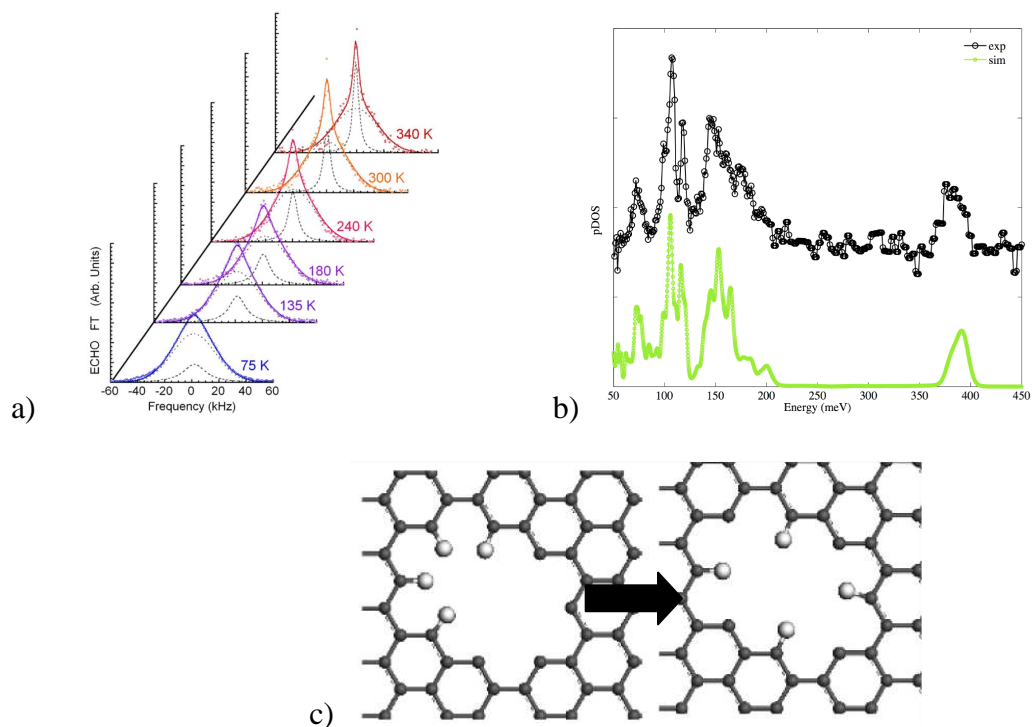


Figure 1: a) NMR spectra on H-TEGO. b) INS spectra of H-TEGO collected on Lagrange (ILL, Grenoble) at 5 K (black circles), compared with the simulated spectrum (green solid line). c) H configurations in not-completely saturated extended C vacancies giving rise to the probed dynamics.