Hydrogen on graphene investigated by inelastic neutron scattering

Journal of Physics: Conference Series **554** (2014) 012009 doi:10.1088/1742-6596/554/1/012009

Hydrogen on graphene investigated by inelastic neutron scattering

C Cavallari [1,2], D Pontiroli[2], M Jiménez-Ruiz[1], A Ivanov [1], M Mazzani [2], M Gaboardi [2], M Aramini [2], M Brunelli[1], M Riccò [2] and S Rols [1,3]

[1] Institut Laue Langevin, 6 rue J. Horowitz, 38042 Grenoble, France
[2] Dipartimento di Fisica e Scienze della Terra, Università degli Studi di Parma Parco Area delle Scienze 7/A, 43124 Parma, Italia

Email: rols@ill.fr, cavallari@ill.fr

Abstract. Inelastic neutron scattering experiments and *ab-initio* calculations have been used to investigate the vibrational modes, in a wide energy region between 0 and 200 meV, of hydrogenated graphene produced by chemical method. The results show the presence of atomic hydrogen chemisorbed at the graphene surface. At 10 K, the measured high energy density of states is remarkably similar to that of hydrogenated ball-milled graphite, in which hydrogen is most likely bonded to C atoms at the edges. In fact, in both hydrogenated graphene and hydrogenated ball-milled graphite, the high frequency modes (100-200 meV) show strong similarities with the C-H bending modes of the coronene molecule, in which hydrogen is bonded at the edges. This hypothesis has been supported by *ab-initio* calculations.

1. Introduction

The hydrogen interaction with graphene is attracting considerable attention from both fundamental and applicative implications. The physico-chemical understanding of the peculiar state of hydrogen at the graphene surface is highly relevant in many different fields, ranging from interstellar chemistry to the possibility of tailoring its electric and magnetic properties, just to mention few examples.

Most of the recent efforts regarding H adsorption have been stimulated by the prospect of using graphene-based compounds as hydrogen storage media. In the recent years, the massive production of graphene exploiting the thermal exfoliation of graphite oxide has opened the route towards new practical applications of graphene e.g in the field of hydrogen storage. From the fundamental point of view, the gram scale graphene synthesis allowed experimental investigation using bulk techniques that usually require large amount of samples [1].

So far, the interaction between hydrogen and graphene has been studied extensively especially from the theoretical point of view.

[3] To whom any correspondence should be addressed

From the experimental point of view, atomic hydrogen was found to passivate some fractions of dangling bonds [2]. However, a variety of C-H chemical bonds occur in different carbon materials and a general tendency for H to saturate π-bonds on the plane, converting sp^2 to sp^3 carbon was also observed [3].

The precise mechanism of H adsorption is still unknown and according to experiments, the H state at the graphene surface, as well as the stability of H aggregates, strongly depend on the chemical state of the surface and it is therefore extremely sensitive to the graphene synthesis, manipulation and history.

In this paper we present a study of the hydrogen dynamics at the graphene surface, with inelastic neutron scattering (INS) and DFT molecular dynamics (MD) simulations. Graphene samples were synthesized by thermal exfoliation of graphite oxide (TEGO) and then exposed to hydrogen flux at 1073 K. Graphene (TEGO) and nanographite (ball-milled graphite) have been investigated in both the pristine conditions and after hydrogenation, in order to evidence, in particular, the peculiarities of hydrogen at the graphene surface.

Sample synthesis and preparation, neutron experiments and computation methods are described in Section 2. The discussion of the results and the conclusion are given in Section 3 and Section 4, respectively.

2. Experimental procedure

2.1. Synthesis and preparation

Graphene samples under investigation were produced by thermal exfoliation of graphite oxide [4].

Commercial highly pure graphite powder (RW-A grade, purchased from SGL Carbon group) was oxidized following the Brodie method, to obtain graphite oxide (GO). The reduction of GO is reached by thermal exfoliation at 1320 K, under vacuum for 30 min. TEGO samples have been previously characterized with Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Selected-Area Electron Diffraction (SAED). The complete characterization has been reported in [3] and [1] and clearly demonstrated that the samples contain both single and few layers structures of sp^2 carbon [5]. Nanographite was obtained by mechanical ball-milling of graphite in strict oxygen and moisture free conditions. Highly pure commercial graphite was measured as a reference.

Hydrogenated samples were obtained by thermal treatment of pristine TEGO in a hydrogen flux of 110 ml/min, keeping the maximum temperature of 1073 K for one hour. Hydrogenated TEGO (H-Graphene) was the principal subject of our investigations.

All the synthesis steps, preparation and hydrogenation process, as well as the subsequent sample handling and storage were done in argon atmosphere (oxygen and moisture levels below 1 ppm), in order to prevent any possible contamination of the samples with air.

2.2. Inelastic Neutron Scattering

In order to probe the local hydrogen environment, we have performed inelastic neutron scattering (INS) experiments. Vibrational spectroscopy based on INS is a very powerful method to provide information about the dynamical properties of matter and offers several advantages, in particular the very high sensitivity to modes involving hydrogen motion and the absence of symmetry selection rules. Hydrogen has a very strong incoherent cross section, which is more than one order of magnitude larger than the total scattering cross section of carbon. In the case of inelastic scattering for hydrogenated compounds, all scattering can be assumed incoherent and the double differential cross section is then directly related to the vibrational density of states and can be written as [6]:

$$\left.\frac{\partial^2\sigma}{d\Omega dE}\right|_{inc} = \frac{N}{8\pi}\frac{k_f}{k_i}\langle n(\omega)+\frac{1}{2}\pm\frac{1}{2}\rangle\frac{Q^2}{\omega}\sum_{j=1}^{3N-6}\delta(\omega-\omega_j(\vec{q}))\times\sum_{i=1}^{N}\frac{\sigma_i}{M_i}\left|\widehat{Q}\cdot\widehat{e_{ij}}\right|^2 e^{-2W(\vec{Q})_i}$$

where k_i and k_f are the incident and scattered neutron wave vector, $\vec{Q}$ is the momentum transfer, $n(\omega)$ is the temperature dependent Bose population factor, $e^{-2W(\vec{Q})}$ is the Debye-Waller factor.

Inelastic Neutron Scattering experiments were performed using two complementary techniques, Time-of-Flight spectroscopy and filter-analyzer neutron spectroscopy. The combined use of these techniques allowed us to measure the vibrational density of states in a very wide energy region, ranging from 0 meV up to hundreds of meV. We used the hot neutron spectrometer IN1-BeF, at the Institut Laue Langevin (Grenoble, France), with the Beryllium filter option: a block of polycrystalline Be, cooled to 20 K, scatters out all neutrons having final energy higher than 3.5 meV. A Cu(220) monochromator was used, limiting the neutron energy in the low part of the spectrum at 35 meV and providing an energy resolution of approximately 4% in the energy range probed (up to 200 meV). The samples were held at 10 K using a standard Orange cryostat.

In the extent that k_f is much smaller than k_i, that is the case of the Beryllium filter analyzer spectrometer IN1BeF, the observed intensity in a low-temperature experiment is directly proportional to the phonon density of states.

The inelastic neutron scattering at lower energies was performed using the Fermi chopper thermal neutron time-of-flight spectrometer IN4C, also at the Institut Laue Langevin.

From time-of-flight data, the Generalized vibrational Density of States (GDOS) can be derived in an extensive (0-200 meV) energy scale using a relatively large neutron incident wavelength (in this work we used λ=2.4 Å) in up-scattering mode (neutron energy gain) and relatively high temperature (320 K). GDOS were obtained from time-of-flight data after proper treatment, corrections and normalization to the mass of the samples, as described in the ref [7].

In both experiments the samples (about 0.5 g) were sealed inside standard Al flat container with an Indium O-ring. Cell-filling and sample-handling for the neutron experiments were carried out inside a glove-box under pure argon atmosphere.

The simulations of poly-aromatic hydrocarbons with chemical formula $C_{6n^2}H_{6n}$ with n=2, 3 and 4 were performed by taking a one-layer model of (0001) graphite basal plane with H covalently bonded at the external edges. Ab-initio molecular dynamics trajectories were produced using the frozen-core all-electron plane wave (PAW) method, as implemented in the Vienna *ab initio* DFT code VASP [8] with the GGA-PBE approximation [9]. Fully relaxed structures were used as input for the trajectory productions in the MD runs. A 2 ps thermal equilibration step was performed initially at 300 K in the NVT ensemble (time step 1.0 fs) using the Berendsen thermostat with a velocity scaling each 2 steps. The equilibration runs were followed by a production run of 10 ps performed also in the NVT ensemble and using the Nose thermostat, with a coupling constant of 96 THz. We used the nMOLDYN program [10] to compute the GDOS as the time-Fourier transform of the velocity autocorrelation function (VACF), from the coordinates of the atoms at each step of the *ab-initio* molecular dynamics (MD) trajectories. The computation of the VACF using an incoherent weight allows extraction of the GDOS of the H atoms directly. Finally, the simulated GDOS were convoluted with a Gaussian function, to take into account the instrumental resolution.

3. Discussion and Results

As preliminary characterization, the GDOS of graphite, nanographite and graphene are reported in Figure 1a. The GDOS of graphite shows the well-known distinct and well-defined features corresponding to flat regions of the dispersion curves [11]. The reduced dimensions of the grains in nanographite and graphene have strong effects on the dynamical properties: peaks in the density of states progressively broaden, with an increased proportion in the low frequency part of the spectrum. This reveals the decrease in dimensionality of the system by introduction of turbostratic disorder, up to a complete loss of out of plane coherence in defective graphene.

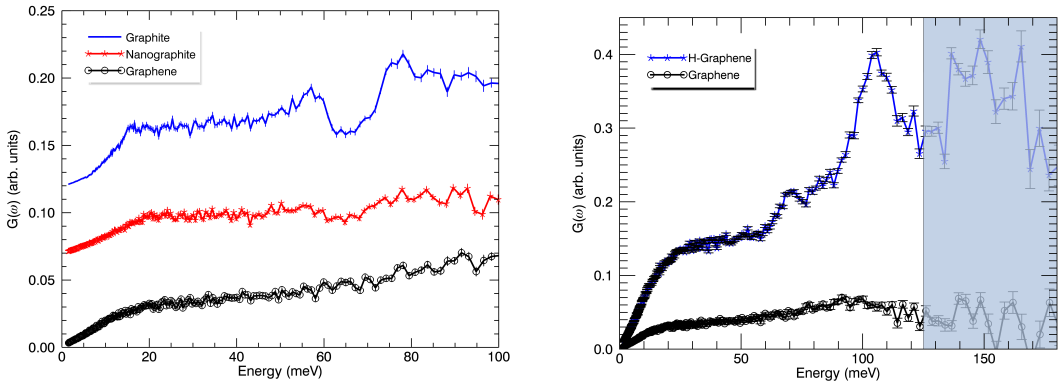
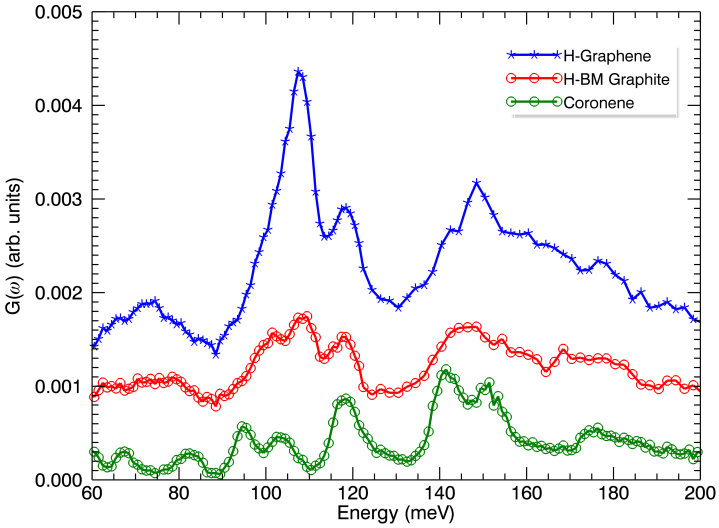


Figure 1a (left) Generalized Density of States (GDOS) measured at 320K and 2.4Å of graphite (solid blue line, in the upper part of the figure), ball-milled graphite (nanographite, in red stars, in the middle) and as-prepared TEGO (black circle, in the bottom part of the figure). Figure 1b (right) Generalized Density of States (GDOS) measured in the same conditions of as-prepared TEGO (black circles) and H-TEGO (blue stars). In H-TEGO features at high frequencies are mainly due to internal vibration of H. The low frequency region shows a featureless intensity, assigned to lattice vibration of reduced coherence extension, originating from phonons in defective graphene. Data in the high frequency part of the spectrum have been overshadowed because the low thermal population of these modes at 320 K does not allow to rigorously discuss to features observed in up-scattering mode.

Figure 1b shows the effect of the hydrogenation. The enhancement in intensity observed in the GDOS after hydrogenation of TEGO denotes an increased quantity of hydrogen. It is possible to distinguish two different frequency domains, distributed over a broad energy region. In the low frequency region of the spectra ([0, 50 meV]) no sharp features are observed. A linear increase of the GDOS is observed up to 20 meV, and upon this value it becomes flat. This range mostly features out–of–plane modes of the graphene surface. The constant shape but increased intensity of the GDOS in this range from as prepared TEGO to H–TEGO reflects that the hydrogen atoms follow adiabatically the plane motion for these modes, so-called riding modes.

By contrast, additional bands, located around 70, 100 and 150 meV are observed in the high frequency region of H-TEGO. These features are completely compatible with the C-H bending modes in polycyclic aromatic hydrocarbons, as in coronene or corannulene [12,13], witnessing the effectiveness of defects in dissociating the molecule of hydrogen and trapping atomic hydrogen in covalent bonds. The very low thermal population of the high energy modes at the temperature we performed the experiment (320 K) in up-scattering mode does not allow to rigorously discuss to features observed, in particular the band located around 150 meV.



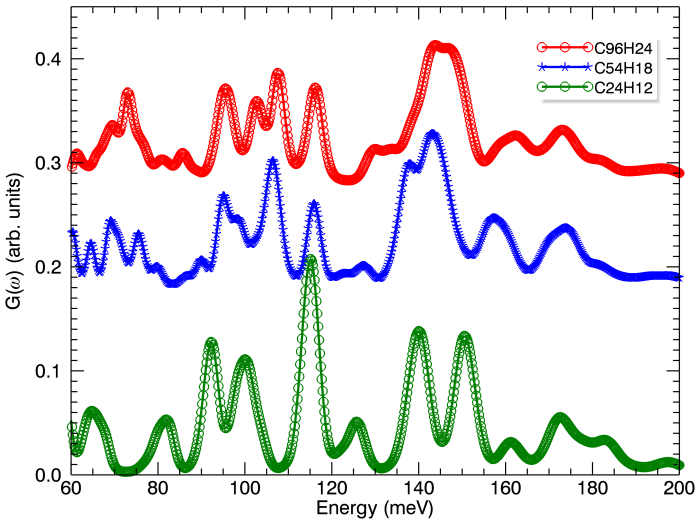


Figure 2 (top): Inelastic scattering spectra of H-graphene (blue stars) and H-BM graphite (hydrogenated nanographite in red circles) measured at 10K using the high resolution Be-filter hot neutron spectrometer IN1.

Figure 3 (bottom): Simulated INS spectra of coronene and larger hydrogenated aromatic molecules of the type $C_{6n^2}H_{6n}$ (in this work, n=2, 3, 4 have been considered. The case n=2 corresponds to coronene).

To get a deeper insight into the nature of the C-H vibrational bands of hydrogenated graphene, high resolution spectra of the same sample, together with hydrogenated nanographite and coronene were obtained using the IN1Be filter spectrometer and are shown in Figure 2. The internal complex structures of the H-graphene vibrational bands already observed in the TOF spectra, especially those of the peak located around 110 meV, are now better resolved.

It is possible to highlight important similarities between the spectra of H-nanographite and H-graphene, especially concerning the position in frequency of the peaks, which can be attributed to common dynamical features. In particular, the spectra can be decomposed into three zones: the first below 90 meV features a broad peak at ~ 70 meV, the second between 90 and 130 meV features a complex structure formed of several peaks with a dominant contribution at ~107 meV and a secondary maximum at ~117 meV, the third above 130 meV is composed of a broad asymmetric band with

maxima located at ~ 145 meV. Similar features are found in the coronene data, although the molecular nature of the latter being responsible for the clearer definition of the bands. In particular, the peak at ~105 meV is well reproduced.

Calculations for coronene $C_{24}H_{12}$ and two larger hydrogenated graphene fragments $C_{6n^2}H_{6n}$ with n=2 and 3 are presented in Figure 3. A very good agreement between the simulated and experimental GDOS is obtained for coronene. When increasing the size of the hydrogenated aromatic molecules from $C_{24}H_{12}$ to $C_{96}H_{24}$, one observes a progressive evolution of the coronene molecular spectrum towards a more complex spectrum, with lattice-like character: the well defined peaks merge into frequency zones, featuring complex structures and gaps. The three zones description of the data can be applied to the $C_{96}H_{24}$ simulated GDOS, and the overall shape of the latter can account for most of the features observed in the H-nanographite spectrum. This observation suggests that H atoms are located at the edges of the nanodomain regions of the H-nanographite sample, and that single H saturation per edge C atoms applies.

By contrast, our simulations fail to reproduce the main feature of the H-TEGO GDOS, e.g. no dominant peak at 107 meV is calculated. This means that a model in which H atoms are located only at the external borders of the graphene flake does not describe the bending mode region of the H-graphene spectrum in a complete way. Compared to nanographite, thermal exfoliated graphite oxide is well known to have a much more extended surface area and to be characterized by in-plane defects, produced during the synthesis process. The extra dynamical features in H-graphene, which appear as over-intensity located in particular at the 107 meV band, can be attributed to H covalently bonded to in-plane defects.

4. Conclusions

In this paper, we have presented the results of the first investigation of the local hydrogen environment in hydrogenated graphene, produced by chemical methods, using neutron spectroscopy and DFT simulations.

Our work evidences the effectiveness of defects in dissociating the hydrogen molecules and trapping atomic hydrogen with covalent bonds.

We found that the frequencies of the C-H bending modes in the neutron spectra are strongly comparable to the ones of polycyclic aromatic molecules as coronene, in which H is located at the external edges. We isolated a contribution at 107 meV that we associate with H atoms bonded at the surface of the graphene plane.

INS, in combination with DFT calculations, constitutes a unique way to efficiently probe the H states at the graphene surface and has allowed for unraveling its specific configurations at a local scale even in a very complex carbon matrix.

Authors thank ILL for neutron beam-time allocations and ILL C-Lab for simulation support.

References

[1] Gaboardi M, Bliersbach A, Bertoni G, Aramini M, Vlahopoulou G, Pontiroli D, Mauron Ph, Magnani G, Salviati G, Zuttel A and Riccò M 2014 *J. Chem. Mat. A* **2** 1039

[2] Horneaker L, Rauls E, Xu W, Sljivancanin Z, Otero R, Stensgaard I, Lægsgaard E, Hammer B and Besenbacher F 2006 *Phys. Rev. Lett* **97** 186102

[3] Riccò M., Pontiroli D., Mazzani M., Choucair M., Stride J.A. and Yazyev O.V. 2011 *NanoLett.* **11 (11)**,4919-4922

[4] Park S and Ruoff R S 2009 *Nat. Nanotechnol.* **4** 217

[5] Hernandez Y, Nicolosi V, Lotya M, Blighe F M, Sun Z, De S, McGovern I T, Holland B, Byrne M, Gun'Ko Y K, Boland J J, Niraj P, Duesberg G, Krishnamurthy S, Goodhue R, Hutchison J, Scardaci V, Ferrari A C and Coleman J N 2008 *Nat. Nanotechnol.* **3** 563

[6] Lovesey S W 1984 *Theory of Neutron Scattering from Condensed Matter* (Oxford: Clarendon Press)

[7] Bousige C, Rols S, Cambedouzou J, Verberck B, Pekker S, Kovats E, Durkò G, Jalsovsky

I, Pellegrini E and Launois P 2010 *Phys. Rev. B* **82** 195413
[8] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
[9] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[10] Hinsen K, Pellegrini E, Stachura S and Kneller G R 2012 *J. Comput. Chem.* **33** 2043
[11] Nicklow R, Wakabayashi N and Smith H G 1972 *Phys. Rev. B* **5** 4951
[12] Mitchell P C H, Ramirez-Cuesta A J, Parker S F, Tomkinson J and Thompsett D 2003 *J Phys Chem B* **107** 6838
[13] Le Parc R, Hermet P, Rols. S, Maurin D, Alvarez L, Ivanov A, Quimby J.M, Hanley C G, Scott LT and Bantignies J L 2012 *J Phys Chem C* **116** 25089