

Water adsorption on graphene/Pt(111) at room temperature: A vibrational investigation

Cite as: AIP Advances 1, 042130 (2011); <https://doi.org/10.1063/1.3660325>

Submitted: 31 May 2011 • Accepted: 05 October 2011 • Published Online: 02 November 2011

A. Politano, A. R. Marino, V. Formoso, et al.



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[First-principles studies of water adsorption on graphene: The role of the substrate](#)

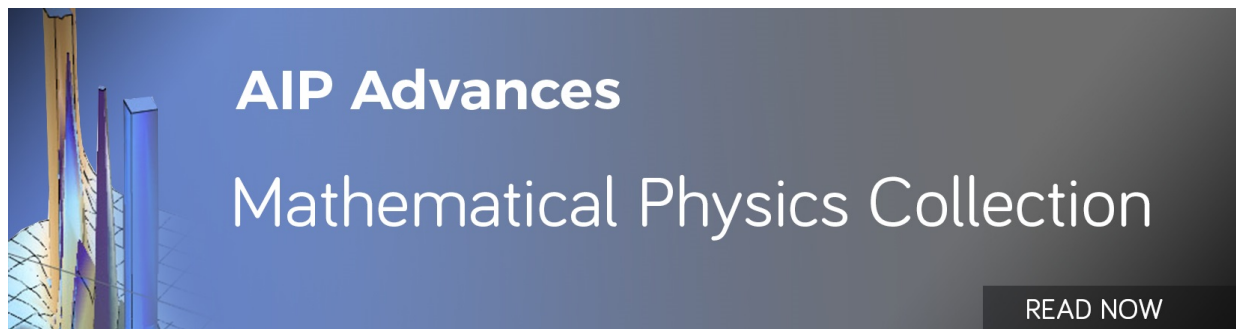
Applied Physics Letters **93**, 202110 (2008); <https://doi.org/10.1063/1.3033202>

[Epitaxial growth and structural property of graphene on Pt\(111\)](#)

Applied Physics Letters **98**, 033101 (2011); <https://doi.org/10.1063/1.3543624>

[A consistent and accurate ab initio parametrization of density functional dispersion correction \(DFT-D\) for the 94 elements H-Pu](#)

The Journal of Chemical Physics **132**, 154104 (2010); <https://doi.org/10.1063/1.3382344>

A banner for the AIP Advances Mathematical Physics Collection. It features a blue background with a 3D bar chart on the left. The text 'AIP Advances' is in white, and 'Mathematical Physics Collection' is in a larger white font. A 'READ NOW' button is in the bottom right corner.

AIP Advances
Mathematical Physics Collection
READ NOW

Water adsorption on graphene/Pt(111) at room temperature: A vibrational investigation

A. Politano,¹ A. R. Marino,¹ V. Formoso,^{1,2} and G. Chiarello^{1,2}

¹Dipartimento di Fisica, Università degli Studi della Calabria, 87036 Rende (CS) Italy

²Consorzio Interuniversitario per le Scienze Fisiche della Materia, CNISM, via della Vasca Navale, 84 Roma, Italy

(Received 31 May 2011; accepted 5 October 2011; published online 2 November 2011)

Water interaction with quasi-freestanding graphene deposited on Pt(111) has been investigated by using vibrational spectroscopy. Loss measurements show that water molecules dosed at room temperature can dissociate giving rise to C-H bonds. The formation of the C-H bonds strongly attenuates the optical phonons of the graphene sheet. On the other hand, at 100 K water has been found to adsorb only in molecular state. Present findings should be taken into account in engineering graphene-based devices which should work at atmospheric pressure and at room temperature. *Copyright 2011 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [doi:[10.1063/1.3660325](https://doi.org/10.1063/1.3660325)]

I. INTRODUCTION

The unusual properties of graphene are attracting a great attention as it represents a promising material for potential applications in electronics and photonics.^{1,2} The chemical modification of graphene is fundamental for tailoring its physical and chemical properties.³⁻⁷ In particular, the interaction of water with graphene is receiving much interest.⁸⁻¹⁵

Water molecules adsorbed on graphene act as dopants without remarkable changes in electron mobility.^{16,17} However, recently, it has been reported that water adsorption could change photoemission spectra of air-exposed graphene samples.¹⁸ Moreover, a tunable band gap of about 0.2 eV can be opened by controlled adsorption of water molecules.⁹ The hydrolysis products could be used for functionalizing graphene in order to create graphene field-effect transistors.^{19,20} However, a detailed understanding of the microscopic mechanisms ruling H₂O interaction with graphene is hitherto missing. In fact, the adsorption of water on surfaces involves a complex combination of electrostatic, van der Waals, and hydrogen bonding interactions.²¹⁻²⁶

Herein we report on high-resolution electron energy loss spectroscopy (HREELS) measurements on water adsorption on quasi-freestanding monolayer graphene (MLG) grown on Pt(111). HREEL experiments indicate that water molecules dosed at room temperature onto the graphene sheet can dissociate giving rise to C-H vibrational bands. The presence of the C-H bonds strongly attenuates the optical phonons of MLG. On the other hand, only vibrations of molecular water are present in the HREEL spectrum recorded at 100 K.

II. EXPERIMENTAL

Experiments were carried out in an ultra-high vacuum (UHV) chamber, which is divided into a main chamber and a preparation chamber, respectively, separated by a gate valve. The sample was a single crystal of Pt(111). The substrate was cleaned by repeated cycles of ion sputtering and annealing at 1300 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) measurements, respectively.^{27,28} MLG has been obtained by dosing ethylene onto the clean Pt(111) substrate at 1150 K. Thus, the graphene sheet is intrinsically thermally stable up to such preparation temperature, as shown in Ref. 29.



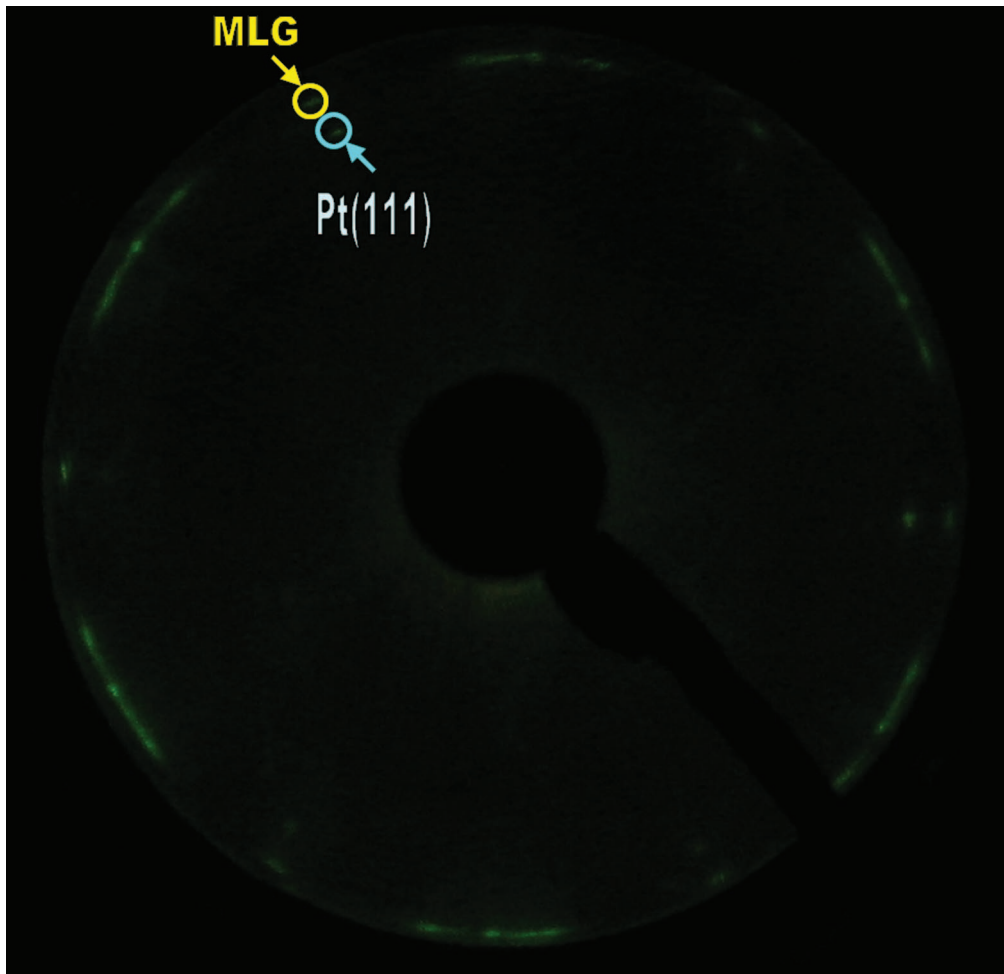


FIG. 1. LEED pattern of graphene on Pt(111), recorded at $E_p = 74.3$ eV and for a sample temperature of 100 K.

As demonstrated by in-situ low-energy electron microscopy,³⁰ no nucleation and growth of additional graphene sheets beyond the monolayer is possible on Pt(111).³⁰⁻³⁸

The attained LEED pattern (shown in Figure 1) is essentially similar to that one reported in Ref. 32. The ring pattern indicates the existence of different domains. Nonetheless, preferred orientations aligned with the substrate (R_0) are clearly distinguished. Despite the presence of other domains, the predominance of R_0 in the whole sample has been clearly inferred by the analysis of phonon dispersion measurements performed along the $\bar{\Gamma}$ - \bar{K} and the $\bar{\Gamma}$ - \bar{M} directions.

The presence of well-resolved spots in the LEED pattern is a clear fingerprint of the order of the MLG over-structure, also evidenced by the high electron reflectivity of the attained surface (even higher with respect to the bare Pt substrate).

Furthermore, the characterization of the MLG was carried out by measuring lattice vibrations which are a fingerprint of graphene formation,³⁹ as shown in Figure 2. The presence of well-resolved ZA (out-of-plane acoustic), ZO (out-of-plane optical), LA (longitudinal acoustic), LO (longitudinal optical) and TO (transverse optical) phonons ensures of the good order and crystalline quality of the graphene sheet.

The energy resolution of the HREEL spectrometer was degraded to 4 meV so as to increase the signal-to-noise ratio of loss peaks. The incidence angle has been set to 55° with respect to the sample normal.

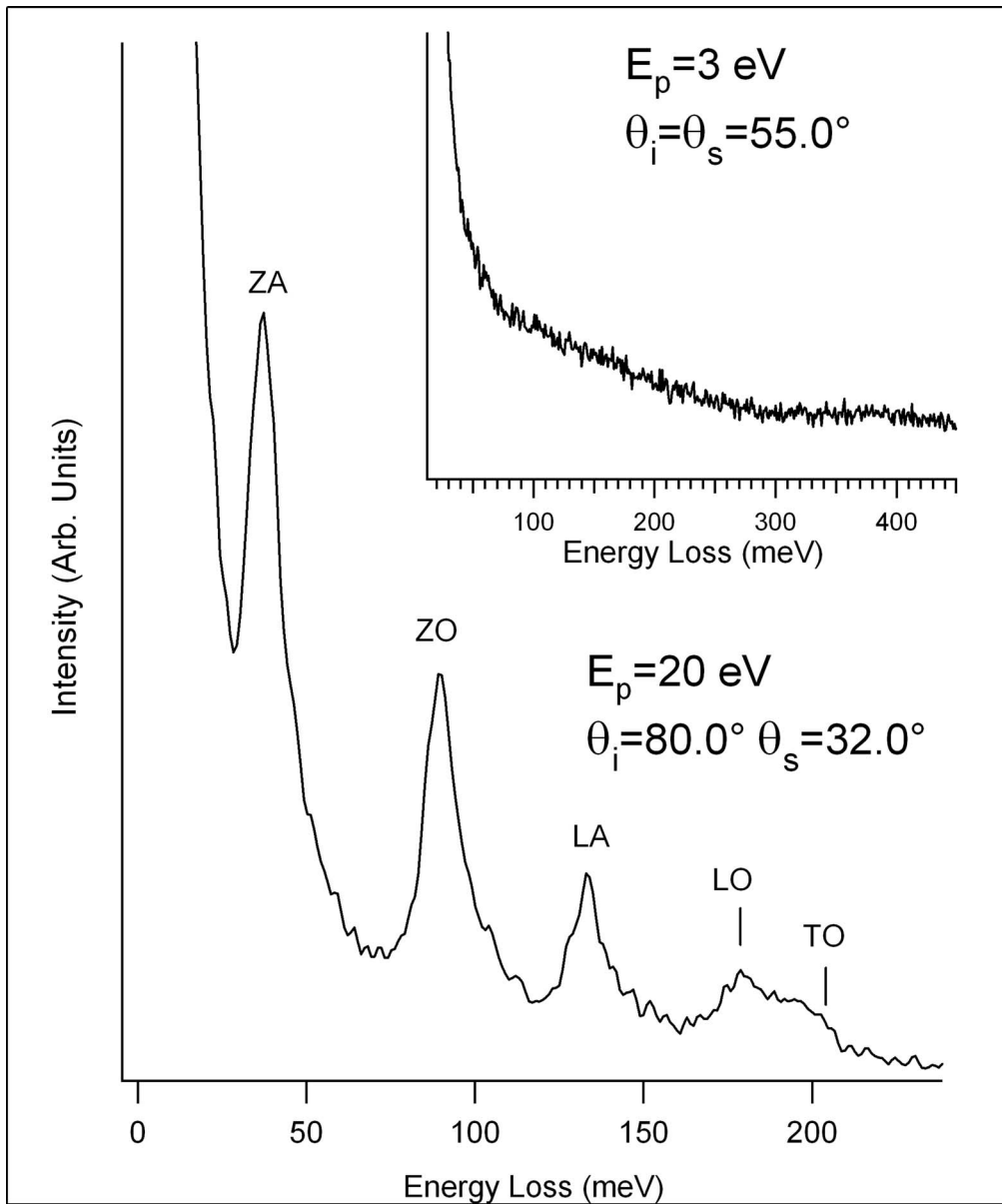


FIG. 2. HREEL spectrum of the MLG/Pt(111) for an impinging energy of 20 eV. The incidence angle is 80.0° while the scattering angle is 32.0° (impact scattering conditions). The inset shows the HREEL spectrum recorded for an impinging energy of 3 eV in the specular geometry with incidence angle of 55.0° (dipole scattering conditions). It is worth noticing that in scattering geometries near the specular conditions, the phonon modes of the graphene lattice cannot be detected, in agreement with results in Ref. 40. On the other hand, the lack of vibrational bands in dipole scattering conditions (spectrum in the inset) ensures of the absence of contaminants or adsorbed functional groups on the bare graphene surface. Similar results have been reported in Ref. 41.

The analysis of both LEED pattern and phonon modes show, in agreement with previous results,^{32,37,42,43} a negligible interaction between MLG and the underlying Pt substrate. Accordingly, MLG may be considered as a quasi-freestanding sheet on Pt(111).

III. RESULTS AND DISCUSSION

Figure 3 shows that the HREEL spectrum attained after exposing the pristine MLG (spectrum a) to 10^5 L (1 L = $1.33 \cdot 10^{-6}$ mbar · s) of water molecules at room temperature (spectrum b) in

the preparation chamber. Vibrational bands centered at 91, 180, and 360 meV were recorded. Interestingly, the latter two peaks indicate the occurrence of water dissociation as they are well known to be unambiguous fingerprint of the formation of C-H bonds.⁴⁴ They are assigned to the bending and stretching vibrations of C-H, respectively. More in details, the energy of the C-H stretching indicates the formation of a sp^3 bond. In fact, such mode is expected around 375–380 and 360–365 meV for the sp^2 and sp^3 hybridization, respectively.⁴⁵

The absence of vibrational modes of OH groups at 415–450 meV^{47,48} indicates that their adsorption energy is positive in the presence of co-adsorbed H atoms on the MLG sheet, i.e. such species are not stable at 300 K.

The intensity of vibrational features significantly increased in off-specular scattering geometry (spectrum c of the same Figure). This is a consequence of the weak oscillating dipole of chemisorbed H atoms⁴⁹ against the graphene sheet.

The low energy of the impinging electron beam E_p , i.e. 4 eV, ensures of the absence of electron beam-induced effects. As a matter of fact, dissociation of adsorbed water molecules on graphene by electron irradiation in Ref. 50 has been attained only for very high primary beam energies ($E_p = 5000$ eV).

For the sake of completeness, it is worth mentioning that losses at 50 meV (in spectrum c) and 91 meV (in spectrum b) of Figure 3 could be assigned to phonon modes of the single-side hydrogenated surface.⁴⁶ Such lattice vibrations strongly disperse as a function of the scattering angle, that is the parallel momentum transfer (see Ref. 46 for more details on their dispersion relation).

From the intensity of C-H stretch in HREEL spectra, we can estimate the H coverage to be 0.08 ± 0.04 ML.

Due to the high dissociation barrier for water molecules, we are led to suggest that water dissociation should occur on defects of the graphene lattice. As for most other materials, defects are unavoidable during the preparation of graphene. Obviously, defects exist even in the presence of well-resolved and sharp phonons (Figure 2), which indicate a very good crystalline quality, essential for preserving the unusual and peculiar properties of graphene.⁴⁵

Likewise, it has been demonstrated that water can dissociate at vacancy defects on graphite following many possible reaction pathways,^{46–48} some of which have activation barriers lower than half the value for the dissociation of bulk water. However, we could not exclude that the dissociation could be driven by the catalytic activity of the underlying Pt substrate. As an example, the role of the substrate on water adsorption on graphene has been put in evidence in Ref. 20. Moreover, strong effects from the growth method itself are possible.^{51–55} Water reactivity strongly depends on both the substrate underneath the graphene sheet as well as the amount and type of defects. We want to point out that our experiments have been performed with a particular type of graphene (quasi-freestanding epitaxial MLG) and under specific conditions. Thus, further experimental efforts are needed in order to establish whether results presented herein could be extended to all kinds of graphene samples.

Adsorbates desorb from MLG upon annealing at 450 K, as evidenced by the lack of vibrational modes in the annealed surface (spectrum d of Figure 3).

In Figure 4 we show the effects of H_2O exposure on the optical phonon modes of MLG. The pristine graphene (middle spectrum) is characterized by the presence of out-of-plane (ZO) and longitudinal (LO) optical phonons at 104 and 202 meV, respectively. After water adsorption and dissociation, the intensity of these modes strongly decreased (topmost spectrum of Figure 4). The band at 175–180 meV is due to the C-H stretching mode.

It is worthwhile mentioning that photoemission spectroscopy (PES) experiments on an air-exposed MLG/Au/Ni(111) sample¹⁸ reported a strong reduction of the intensity from the graphene π bands. The intensity decrease was tentatively assigned to adsorbate water from the atmosphere.

With the aim of investigating the possible occurrence of water dissociation at lower sample temperature (100 K), the initial stages of water adsorption on graphene were probed. We found that at 100 K water is adsorbed molecularly without trace of any dissociation (bottom spectrum of Figure 5). In fact, the HREEL spectrum shows clear fingerprint of molecular water (Figure 5). In particular, vibrational bands may be divided into four major categories (see Ref. 49 for a review): frustrated

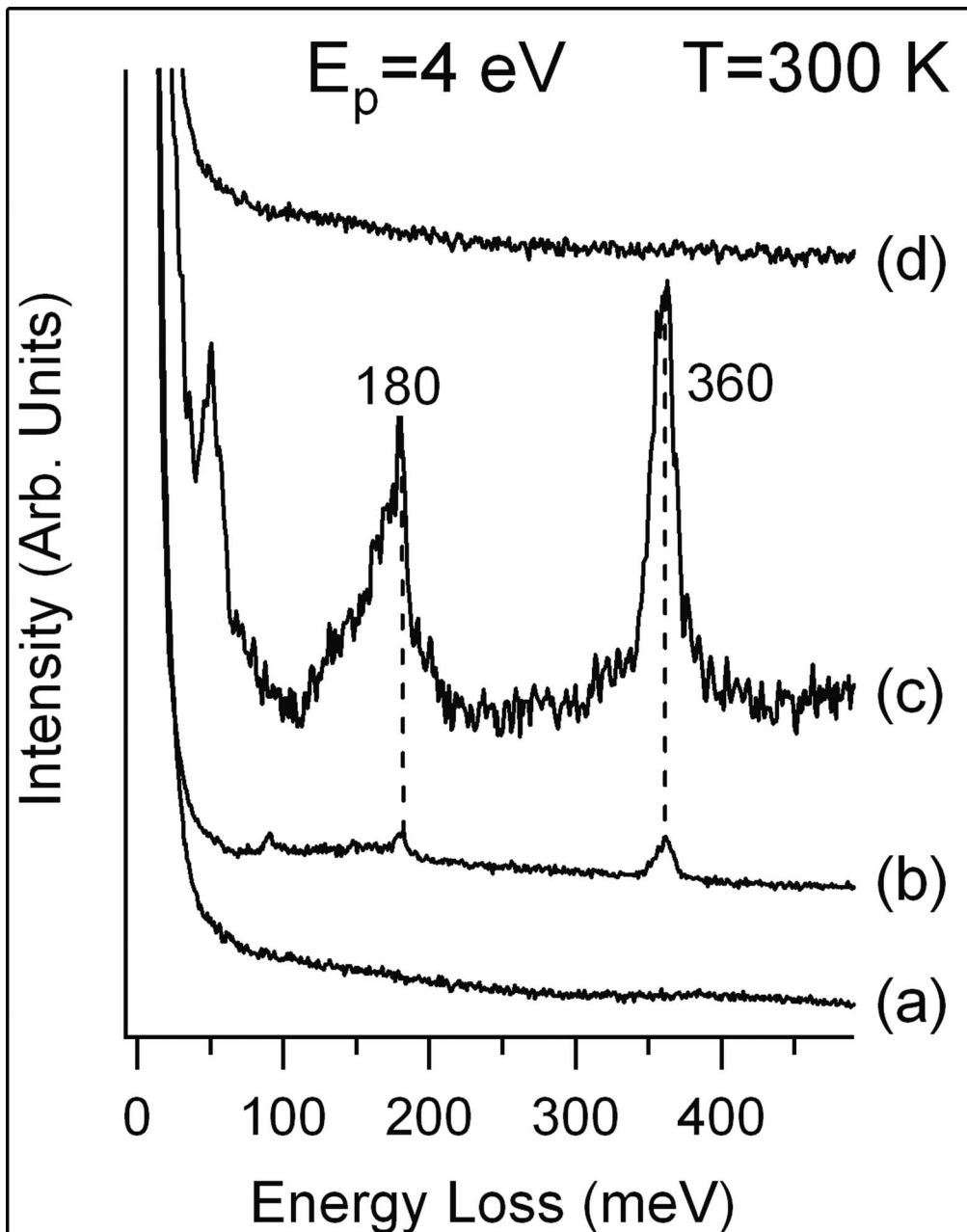


FIG. 3. HREEL spectra acquired in the specular geometry (incidence angle 55° with respect to the sample normal) for (a) MLG/Pt(111), successively exposed to 10^5 L of H_2O at 300 K (spectrum b) and annealed at 450 K (spectrum d). The spectrum (c) has been recorded for the same surface of the spectrum (b) but for an off-specular geometry (scattering angle 49°). The beam energy E_p is 4 eV. All measurements have been performed at room temperature and all spectra were normalized to the intensity of the elastic peak. The different signal-to-noise ratio in spectra b and c is due to the reduction of the intensity of the incident beam by 96% when going from the specular conditions (scattering angle 55°) to -6° off-specular (scattering angle 49°). The slight asymmetry of the band at 180 meV is due to the presence of spectral contributions from phonon modes of single-side hydrogenated graphene.⁴⁶

translations at 30 meV; frustrated rotations, i.e. librations at 100-110 meV; H_2O deformations, i.e. the scissoring band centered around 200 meV; and O-H stretching modes around 400 meV. The desorption of molecular water occurs at 140 K without evidence of any water dissociation (topmost spectrum of Figure 5).

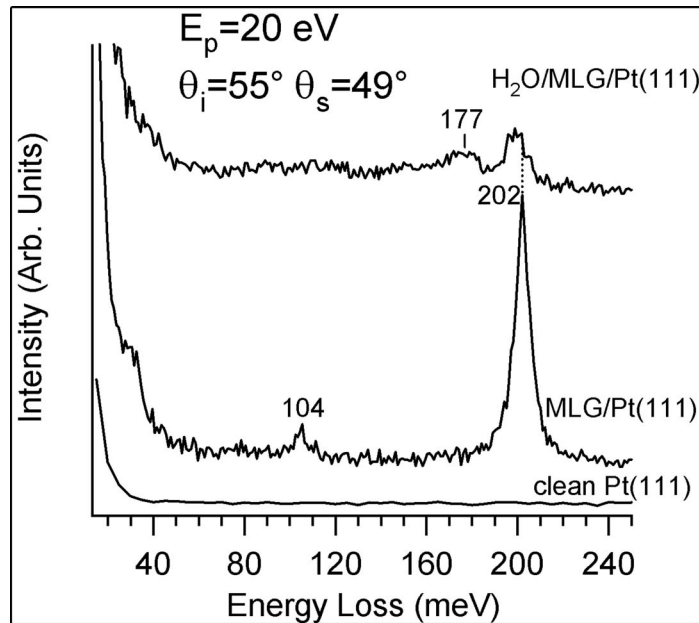


FIG. 4. HREEL spectrum of the clean Pt(111) substrate (bottom spectrum) and for the MLG/Pt(111) (middle spectrum) and the $\text{H}_2\text{O}/\text{MLG}/\text{Pt}(111)$ (topmost spectrum) surfaces. Optical phonon modes could be detected only for impact scattering conditions, i.e. off-specular geometries. The primary energy E_p is 20 eV. All measurements have been performed at room temperature.

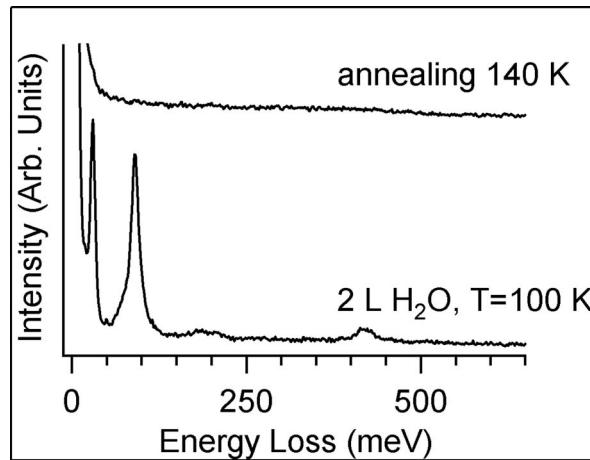


FIG. 5. HREEL spectrum of MLG/Pt(111) exposed to 2 L of water molecules at 100 K (bottom spectrum). Successively, the sample was annealed at 140 K (topmost spectrum).

IV. CONCLUSIONS

In summary, we have shown that water exposure at room temperature of MLG/Pt(111) could lead to the formation of C-H bonds. Such finding gives a response to previous results of Ref. 18. Dehydrogenation is possible upon annealing at 450 K. On the other hand, no dissociation was observed at 100 K.

Due to its peculiar properties, graphene represents a promising candidate for potential technological applications (sensors, plasmonic devices, protecting coatings, energy storage, THz electronics etc.). With this in mind, we want to point out that water-induced hydrogenation of graphene should be taken into account in engineering graphene-based devices which should work at atmospheric

pressure and at room temperature. Water dissociation could also afford interesting pathways to produce hydrogen.

- ¹ K. Novoselov, "Graphene: Mind the gap". *Nat. Mater.* **6**, 720-721 (2007).
- ² V. W. Brar, S. Wickenburg, M. Panlasigui, C. H. Park, T. O. Wehling, Y. Zhang, R. Decker, Ç. Girit, A. V. Balatsky, S. G. Louie, A. Zettl, and M. F. Crommie, "Observation of Carrier-Density-Dependent Many-Body Effects in Graphene via Tunneling Spectroscopy". *Phys. Rev. Lett.* **104**, 036805 (2010).
- ³ R. A. Nistor, D. M. Newns, and G. J. Martyna, "The Role of Chemistry in Graphene Doping for Carbon-Based Electronics". *ACS Nano* **5**, 3096-3103 (2011).
- ⁴ B. Huang, H. J. Xiang, and S.-H. Wei, "Controlling doping in graphene through a SiC substrate: A first-principles study". *Phys. Rev. B* **83**, 161405 (2011).
- ⁵ E. Beheshti, A. Nojeh, and P. Servati, "A first-principles study of calcium-decorated, boron-doped graphene for high capacity hydrogen storage". *Carbon* **49**, 1561-1567 (2011).
- ⁶ Y. Gao and Z. Yuan, "Anisotropic low-energy plasmon excitations in doped graphene: An ab initio study". *Solid State Commun.* **151**, 1009-1013 (2011).
- ⁷ H. Gao, L. Wang, J. Zhao, F. Ding, and J. Lu, "Band Gap Tuning of Hydrogenated Graphene: H Coverage and Configuration Dependence". *J. Phys. Chem. C* **115**, 3236-3242 (2011).
- ⁸ A. Ambrosetti and P. L. Silvestrelli, "Adsorption of Rare-Gas Atoms and Water on Graphite and Graphene by van der Waals-Corrected Density Functional Theory". *J. Phys. Chem. C* **115**, 3695-3702 (2011).
- ⁹ F. Yavari, C. Kritzing, C. Gaire, L. Song, H. Gulapalli, T. Borca-Tasciuc, P. M. Ajayan, and N. Koratkar, "Tunable Bandgap in Graphene by the Controlled Adsorption of Water Molecules". *Small* **6**, 2535-2538 (2010).
- ¹⁰ M. E. Suk and N. R. Aluru, "Water Transport through Ultrathin Graphene". *J. Phys. Chem. Lett.* **1**, 1590-1594 (2010).
- ¹¹ A. P. Seitsonen, A. M. Saitta, T. Wassmann, M. Lazzeri, and F. Mauri, "Structure and stability of graphene nanoribbons in oxygen, carbon dioxide, water, and ammonia". *Phys. Rev. B* **82**, 115425 (2010).
- ¹² J. H. Park and N. R. Aluru, "Ordering-Induced Fast Diffusion of Nanoscale Water Film on Graphene". *J. Phys. Chem. C* **114**, 2595-2599 (2010).
- ¹³ M. C. Gordillo and J. Martí, "Effect of Surface Roughness on the Static and Dynamic Properties of Water Adsorbed on Graphene". *J. Phys. Chem. B* **114**, 4583-4589 (2010).
- ¹⁴ M. C. Gordillo and J. Martí, "Water on graphene surfaces". *J. Phys.: Condens. Matter* **22**, 284111 (2010).
- ¹⁵ G. A. Kimmel, J. Matthiesen, M. Baer, C. J. Mundy, N. G. Petrik, R. S. Smith, Z. Dohnálek, and B. D. Kay, "No confinement needed: Observation of a metastable hydrophobic wetting two-layer ice on graphene". *J. Am. Chem. Soc.* **131**, 12838-12844 (2009).
- ¹⁶ K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field in atomically thin carbon films". *Science* **306**, 666-669 (2004).
- ¹⁷ F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, and K. S. Novoselov, "Detection of individual gas molecules adsorbed on graphene". *Nat. Mater.* **6**, 652-655 (2007).
- ¹⁸ D. Marchenko, A. Varykhalov, A. Rybkin, A. M. Shikin, and O. Rader, "Atmospheric stability and doping protection of noble-metal intercalated graphene on Ni(111)". *Appl. Phys. Lett.* **98**, 122111 (2011).
- ¹⁹ J. P. Robinson, H. Schomerus, L. Oroszlány, and V. I. Fal'ko, "Adsorbate-Limited Conductivity of Graphene". *Phys. Rev. Lett.* **101**, 196803 (2008).
- ²⁰ T. O. Wehling, A. I. Lichtenstein, and M. I. Katsnelson, "First-principles studies of water adsorption on graphene: The role of the substrate". *Appl. Phys. Lett.* **93**, 202110 (2008).
- ²¹ S. Meng and S. Gao, "Formation and interaction of hydrated alkali metal ions at the graphite-water interface". *J. Chem. Phys.* **125**, 014708 (2006).
- ²² S. Meng, E. G. Wang, C. Frischkorn, M. Wolf, and S. Gao, "Consistent picture for the wetting structure of water/Ru(0001)". *Chem. Phys. Lett.* **402**, 384-388 (2005).
- ²³ S. Meng, E. G. Wang, and S. Gao, "Water adsorption on metal surfaces: A general picture from density functional theory studies". *Phys. Rev. B* **69**, 195404 (2004).
- ²⁴ S. Meng, L. F. Xu, E. G. Wang, and S. Gao, "Vibrational Recognition of Hydrogen-Bonded Water Networks on a Metal Surface". *Phys. Rev. Lett.* **89**, 176104 (2002).
- ²⁵ Y. Yang, S. Meng, and E. G. Wang, "Water adsorption on a NaCl (001) surface: A density functional theory study". *Phys. Rev. B* **74**, 245409 (2006).
- ²⁶ Y. Yu, Q. Guo, S. Liu, E. G. Wang, and P. J. Möller, "Partial dissociation of water on a MgO(100) film". *Phys. Rev. B* **68**, 115414 (2003).
- ²⁷ A. Politano, R. G. Agostino, E. Colavita, V. Formoso, and G. Chiarello, "Purely quadratic dispersion of surface plasmon in Ag/Ni(111): the influence of electron confinement". *Phys. Status Solidi Rapid Res. Lett. (RRL)* **2**, 86-88 (2008).
- ²⁸ A. Politano, V. Formoso, and G. Chiarello, "Alkali adsorption on Ni(111) and their coadsorption with CO and O". *Appl. Surf. Sci.* **254**, 6854-6859 (2008).
- ²⁹ H. Zhang, Q. Fu, Y. Cui, D. Tan, and X. Bao, "Growth mechanism of graphene on Ru(0001) and O₂ adsorption on the graphene/Ru(0001) surface". *J. Phys. Chem. C* **113**, 8296-8301 (2009).
- ³⁰ P. Sutter, J. T. Sadowski, and E. Sutter, "Graphene on Pt(111): Growth and substrate interaction". *Phys. Rev. B* **80**, 245411 (2009).
- ³¹ T. Fujita, W. Kobayashi, and C. Oshima, "Novel structures of carbon layers on a Pt(111) surface". *Surf. Interface Anal.* **37**, 120-123 (2005).
- ³² M. Gao, Y. Pan, L. Huang, H. Hu, L. Z. Zhang, H. M. Guo, S. X. Du, and H. J. Gao, "Epitaxial growth and structural property of graphene on Pt(111)". *Appl. Phys. Lett.* **98**, 033101 (2011).

- ³³ B. J. Kang, J. H. Mun, C. Y. Hwang, and B. J. Cho, "Monolayer graphene growth on sputtered thin film platinum". *J. Appl. Phys.* **106**, 104309 (2009).
- ³⁴ G. Otero, C. Gonzalez, A. L. Pinardi, P. Merino, S. Gardonio, S. Lizzit, M. Blanco-Rey, K. Van de Ruit, C. F. J. Flipse, J. Méndez, P. L. de Andrés, and J. A. Martín-Gago, "Ordered Vacancy Network Induced by the Growth of Epitaxial Graphene on Pt(111)". *Phys. Rev. Lett.* **105**, 216102 (2010).
- ³⁵ A. Politano, A. R. Marino, V. Formoso, D. Fariás, R. Miranda, and G. Chiarello, "Evidence for acoustic-like plasmons on epitaxial graphene on Pt(111)". *Phys. Rev. B* **84**, 033401 (2011).
- ³⁶ N. A. Vinogradov, K. Schulte, M. L. Ng, A. Mikkelsen, E. Lundgren, N. Mårtensson, and A. B. Preobrajenski, "Impact of Atomic Oxygen on the Structure of Graphene Formed on Ir(111) and Pt(111)". *J. Phys. Chem. C* **115**, 9568–9577 (2011).
- ³⁷ Y. Yamada, C. Sugawara, Y. Satake, Y. Yokoyama, R. Okada, T. Nakayama, M. Sasaki, T. Kondo, J. Oh, J. Nakamura, and W. W. Hayes, "He/Ar-atom scattering from molecular monolayers: C₆₀/Pt(111) and graphene/Pt(111)". *J. Phys.: Condens. Matter* **22**, 304010 (2010).
- ³⁸ A. Politano, A. R. Marino, V. Formoso, and G. Chiarello, "Evidence of Kohn anomalies in quasi-freestanding graphene on Pt(111)". Carbon doi:10.1016/j.carbon.2011.1009.1028 (2011).
- ³⁹ L. J. Karssemeijer and A. Fasolino, "Phonons of graphene and graphitic materials derived from the empirical potential LCBOPII". *Surf. Sci.* **605**, 1611-1615 (2011).
- ⁴⁰ H. Yanagisawa, T. Tanaka, Y. Ishida, M. Matsue, E. Rokuta, S. Otani, and C. Oshima, "Analysis of phonons in graphene sheets by means of HREELS measurement and ab initio calculation". *Surf. Interface Anal.* **37**, 133-136 (2005).
- ⁴¹ A. Politano, A. R. Marino, V. Formoso, and G. Chiarello, "Hydrogen bonding at the water/quasi-freestanding graphene interface". *Carbon* **49**, 5180-5184 (2011).
- ⁴² A. B. Preobrajenski, M. L. Ng, A. S. Vinogradov, and N. Mårtensson, "Controlling graphene corrugation on lattice-mismatched substrates". *Phys. Rev. B* **78**, 073401 (2008).
- ⁴³ J. Wintterlin and M. L. Bocquet, "Graphene on metal surfaces". *Surf. Sci.* **603**, 1841-1852 (2009).
- ⁴⁴ B. D. Thoms and J. E. Butler, "HREELS scattering mechanism from diamond surfaces". *Phys. Rev. B* **50**, 17450-17455 (1994).
- ⁴⁵ A. Horn, J. Biener, A. Schenk, C. Lutterloh, and J. Küppers, "H/D exchange reaction at graphitic CH groups by thermal H(D) atoms". *Surf. Sci.* **331-333**, 178-182 (1995).
- ⁴⁶ E. Cadelano, P. L. Palla, S. Giordano, and L. Colombo, "Elastic properties of hydrogenated graphene". *Phys. Rev. B* **82**, 235414 (2010).
- ⁴⁷ A. Politano, V. Formoso, and G. Chiarello, "Chemical Reactions at Clean and Alkali-Doped Mismatched Metal/Metal Interfaces". *J. Phys. Chem. C* **113**, 316-320 (2009).
- ⁴⁸ A. Politano and G. Chiarello, "Enhancement of hydrolysis in alkali ultrathin layers on metal substrates in the presence of electron confinement". *Chem. Phys. Lett.* **494**, 84-87 (2010).
- ⁴⁹ G. Lee and E. W. Plummer, "High-resolution electron energy loss spectroscopy study on chemisorption of hydrogen on Cu(111)". *Surf. Sci.* **498**, 229-236 (2002).
- ⁵⁰ J. D. Jones, K. K. Mahajan, W. H. Williams, P. A. Ecton, Y. Mo, and J. M. Perez, "Formation of graphane and partially hydrogenated graphene by electron irradiation of adsorbates on graphene". *Carbon* **48**, 2335-2340 (2010).
- ⁵¹ K. F. McCarty, P. J. Feibelman, E. Loginova, and N. C. Bartelt, "Kinetics and thermodynamics of carbon segregation and graphene growth on Ru(0001)". *Carbon* **47**, 1806-1813 (2009).
- ⁵² E. Loginova, N. C. Bartelt, P. J. Feibelmarr, and K. F. McCarty, "Factors influencing graphene growth on metal surfaces". *New J. Phys.* **11**, 063046 (2009).
- ⁵³ J. Coraux, A. T. N'Diaye, M. Engler, C. Busse, D. Wall, N. Buckanie, F. J. Meyer Zu Heringdorf, R. van Gastel, B. Poelsema, and T. Michely, "Growth of graphene on Ir(111)". *New J. Phys.* **11**, 023006 (2009).
- ⁵⁴ E. Loginova, N. C. Bartelt, P. J. Feibelman, and K. F. McCarty, "Evidence for graphene growth by C cluster attachment". *New J. Phys.* **10**, 093026 (2008).
- ⁵⁵ L. S. Caputi, G. Chiarello, and L. Papagno, "Carbonaceous layers on Ni (110) and (100) studied by AES and EELS". *Surf. Sci.* **162**, 259-263 (1985).