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COMMUNICATION

Adsorption of water on graphene/Ru(0001)—an experimental ultra-high vacuum study

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Data for water adsorption on epitaxial graphene grown on Ru(0001) at ultra-high vacuum (clean conditions) are discussed. Accordingly, water adsorption, was not affected by the support. The interaction is not strictly hydrophobic. We propose simple rules based on ultra-high vacuum kinetics to classify the water-graphene-support interactions.

Hydrophobic surfaces are of recent and continuing interest in a variety of different disciplines due to numerous applications and unusual properties.^{1,2} For naturally occurring surfaces, micro/nano-scale hierarchical morphologies, for example, promote (super-)hydrophobicity (the so-called lotus effect). Therefore, a large number of studies concern various artificial nanostructured surfaces. Interestingly, for example, plant surfaces have been directly replicated.³ Simpler model systems such as hydrophobic single crystals are known, but typically surface functionalization is required. For example, non-wetting ice crystallites can be formed on Pt single crystals when covered first with a complete monolayer of water ice.⁴ Or, hydrogen-terminated Pt and Ni surfaces show hydrophobic properties^{5,6} as well as hydroxyl-terminated Si surfaces.⁷ Intrinsically, hydrophobic single crystal model surfaces are rare. The only systems appear to be surfaces of Au, Ag, Cu, and Sb^{4,8-10} with perhaps Gold⁴ and Antimony⁹ as the only convincing examples. Highly ordered pyrolytic graphite (HOPG) is used as a reference system of graphene, it appears to deviate from simple predictions for a hydrophobic system.¹¹⁻¹³ For example, based on a comparison of experiments conducted under ultra-high vacuum (UHV) and at ambient pressure, it was concluded in an earlier reference¹² that only contaminated HOPG may truly be hydrophobic, but UHV-cleaned samples were not. In addition, in a different study,¹³ deviations from zero-order kinetics were observed under UHV,¹³ whereas in recent work, using atomic force microscopy (AFM) at ambient pressure, water nanodroplets on hydrophobic HOPG were reported.¹⁴ Similar experimental kinetics data for UHV-cleaned graphene that probe the intrinsic properties of graphene are, to the best of our knowledge, still not available, although numerous theoretical and ambient pressure studies are published.¹⁵⁻¹⁷ For example, using apparently the same experimental and theoretical

techniques, the conclusions range from total "wetting transparency of graphene"¹⁶ to "not entirely transparent to wetting"¹⁵ to "negligible effect of the support."¹⁷ The cleanliness or defect densities of the graphene samples studied are unknown to us. However, all of these studies have apparently one feature in common: graphene was (mostly) characterized at ambient pressure conditions (i.e., in air).

In this communication, the missing experimental data for epitaxial graphene grown in UHV on Ru(0001), using a simple surface science technique, is discussed. In a UHV kinetics experiment using thermal desorption spectroscopy (TDS) at low temperatures, water is adsorbed onto the sample mounted in a UHV chamber. Subsequently, the surface temperature is raised and desorbing water is simultaneously detected with a mass spectrometer. Water was dosed by backfilling and using a UHV molecular beam scattering system. (See Supplemental Section for experimental details.)

According to our experiments, under UHV conditions, water adsorption kinetics and wettability on a clean ruthenium support¹⁸ and on graphene/ruthenium are very different. Thus, graphene is not transparent to wetting when deposited on metallic Ru(0001), i.e., the Ru support had no obvious effect on water adsorption at UHV on graphene/Ru, which is consistent with ref.¹⁷

The water adsorption kinetics show many features consistent with zero-order kinetics, which is usually a strong indication for hydrophobic interactions. However, deviations from zero-order kinetics are evident when considering the shape of the desorption curves. Thus, the water—graphene/Ru(0001) interaction is probably not perfectly hydrophobic at UHV.

Other supports for epitaxial graphene may show different effects at UHV. However, ruthenium can serve as a prototype of a metallic support. In addition, ruthenium has a number of advantages for a model study for growing graphene (see Supplemental document). Commercial samples (mostly used so far) such as graphene on copper foil or glass supports need to be exposed to the ambient and cannot be easily UHV cleaned. Removing amorphous carbon from these samples without destroying the graphene layer would be very difficult (impossible).

Water desorption at UHV is typically discussed in regard to sub-monolayer and multilayer formation with amorphous or crystalline water layers formed at large exposures.¹⁹⁻²¹ In TDS, hydrophilic systems usually show both a monolayer structure and condensation peak. Often in addition a crystallization peak is observed.^{2, 19-21} In contrast, for hydrophobic surfaces, only one water desorption peak is detected that may obey zero-order kinetics.^{2, 4, 9} In this case, a monolayer feature is missing in TDS. For a hydrophobic system, it is commonly assumed that zero-order kinetics is evident even in the sub-monolayer coverage range. Traditionally, the conditions for zero-order kinetics are fulfilled when an inexhaustible reservoir is available, (i.e., water evaporation from an ocean). In case of a hydrophobic system, the "droplets" (or 3D clusters in surface science terms) formed on the non-wetting surface would be that reservoir.²² Water starts to desorb (evaporate) along the outer surface of these droplets, feed by the interior. Thus, a two phase system may form. Therefore, our proposal is that a simple technique such as UHV TDS can be used to distinguish between hydrophobic and hydrophilic surfaces: **multiple TDS peaks (hydrophilic) compared to one TDS peak (hydrophobic)**. Many surfaces studied in surface science exhibit that behavior (Table 1).

Hydrophobic systems				
System	Hydrophobic	0 th order	TDS peaks	Ref.
Au(111)	Yes	Yes	1	4
Antimony(111)	Yes	Yes	1	9
Cu(111)	Yes	Yes	1	10
O ₂ -Au(111)	Yes	Yes	1	23
D ₂ -Ni(111)	Yes	Yes	1	6
D ₂ -Pt(533)	Yes	Yes	1	24
Octane-Pt(111)	Yes	Yes	1	5
Water-Pt(111)	Yes	Yes	1	25
Hydrophilic systems				
Ru(0001)	No	No	3	26
JSC-A1	No	No	5	27
TiO ₂ (110)	No	No	3	28
Pt(111)	No	No	2	25

Table 1. UHV kinetics experiments with water

However, this raises the question of whether assignment of hydrophobicity strictly requires zero-order kinetics. According to a recent AFM study,¹⁴ in which water nanodroplets were observed on HOPG, it appears that HOPG is hydrophobic under ambient conditions. However, conflicting evidence about the desorption order has been presented—zero-order¹² and nonzero-order desorption¹³ were observed at UHV. In most UHV kinetics studied in which zero-order desorption was evident, a hydrophobic interaction was concluded (Table 1). Therefore, we propose a "refined" criterion: **zero-order kinetics and only one TDS peak (strictly hydrophobic), deviations from zero-order kinetics but only one TDS peak (probably not perfectly hydrophobic), and multiple TDS peaks (strictly hydrophilic)**. This criterion is consistent with many model surfaces studied (Table 1). Note, however, that technical problems (pumping speed of the vacuum system or readsorption of water) may also cause apparent deviations from the expected desorption order. Although TDS is a simple technique, the devil is in the details. Therefore, water was dosed onto the sample by backfilling, as is commonly done,^{19, 20} and by using a molecular beam.^{9, 28} The latter setup avoids readsorption, sample

holder effects, and pumping speed limitations. In addition, studying atomically clean surfaces generally requires conducting the experiments under UHV in order to characterize the intrinsic properties of the model system. Even in UHV, HOPG and other graphitic systems are known to be covered with oxygen-containing residuals/functionalities with high decomposition temperatures.²⁹ Therefore, even for UHV experiments sample cleaning is required—degassing/flashing the sample to high temperatures. Note that, in our experiments graphene/Ru(0001) samples exposed to ambient pressure for more than 30 min could not be restored.³⁰

An epitaxial layer of graphene on Ru(0001) was obtained by decomposition of deuterated benzene under UHV, as described in detail elsewhere.³⁰ Monitoring the D₂ signal while forming graphene allowed for estimating the defect density of the graphene layer which was below 2% (Fig. S1).³⁰ This preparation procedure makes formation of double layer graphene virtually impossible. The sample was repeatedly annealed at UHV (base pressure 1x10⁻¹⁰ mbar) at 1300 K in order to remove functionalities. The sample was characterized in UHV by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and TDS (Supplemental section). Collecting Raman spectra would require air exposure of the samples. Several fresh epitaxial graphene layers were studied. For further experimental details refer to the Supplemental section.

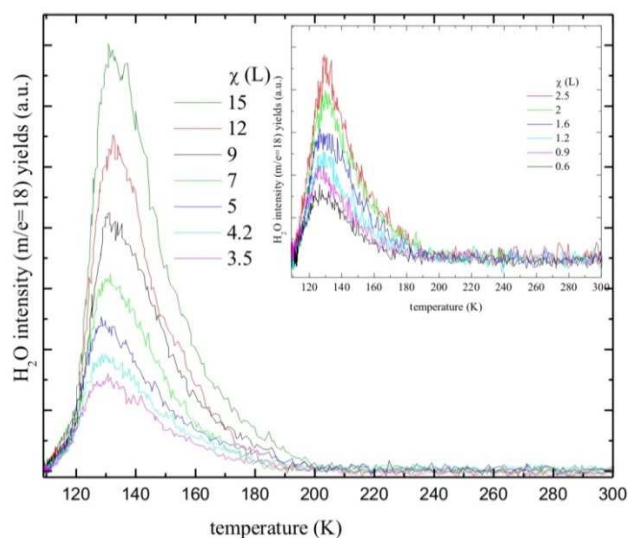


Figure 1. UHV thermal desorption data of water on graphene/Ru(0001) as a function of water exposure

Results of UHV TDS experiments of water on graphene/Ru(0001) are depicted in Fig. 1. The set of TDS curves corresponds to different exposures of water, i.e., to different initial water concentrations, χ . (1 sec of exposure at 1x10⁻⁶ torr equals one Langmuir, 1 L).

Water desorbs within 120–180 K, i.e., at low temperatures. Dissociative water adsorption, for example, would result in much higher desorption temperatures.¹⁹⁻²¹

Only one TDS peak is evident, which shifts slightly to greater temperatures with increasing exposure. Hydrophobic surfaces usually exhibit only one TDS structure (Table 1). The single peak observed in Fig. 1 did not saturate, which is consistent with the sublimation of ice. In fact, plotting the integrated TDS peak area versus exposure (Fig. S8), generated a single straight line. Therefore, water condensed with constant adsorption probability.

Note that the TDS curves for water desorption from Ru(0001), a system which was extensively studied in surface science,^{18, 31} are differently to those for graphene/Ru(0001). For example, at least two TDS peaks are observed for the water/Ru(0001) surface,^{18, 31} which appears to be "hydrophilic," forming a traditional monolayer/bilayer structure of water. Therefore, graphene/Ru(0001) does not mirror the water desorption kinetics of Ru(0001). Graphene is not transparent to water wetting on Ru(0001).

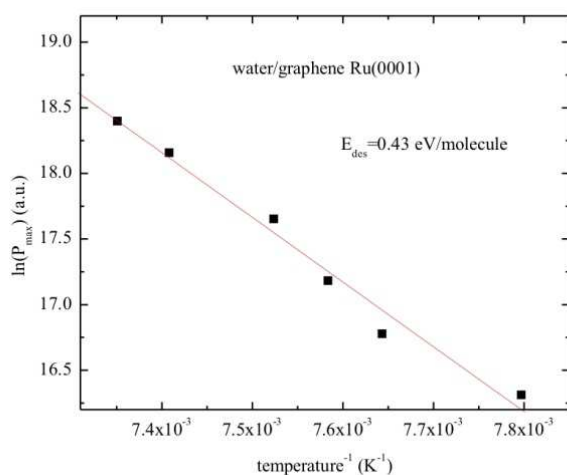


Figure 2. Kinetics parameter for water on graphene/Ru(0001)

The low temperature edges of all TDS curves (Fig. 1) align approximately. Thus, the desorption rate is initially independent of initial concentration, consistent with condensation of water and near zero-order kinetics. Analyzing the low temperature increase and assuming zero-order kinetics of the desorption rate, based on Fig. 2 and equations in the Supplemental document, resulted in a binding energy of 0.43 eV/molecule, which is similar to the heat of condensation of water (0.49 eV/molecule).¹¹ This further confirms that water condensation was observed in the TDS data. One TDS peak was observed and it matched the binding energy of condensed water. No further monolayer desorption features ("wetting structures") were observed in the TDS data (Fig. 1). The TDS maximum shifted simply because it takes longer to desorb the water when the initial concentration is increased.

Perhaps unexpectedly, the high temperature edges of the TDS curves (Fig. 1) did not drop abruptly to zero, as would be expected in the simplest case for zero-order kinetics. Because a delayed decay of the signal could also be caused by readsorption and/or pumping speed limitations, the UHV backfilling TDS

experiments were repeated by dosing water with a molecular beam scattering system. However, also in that case, a slow decrease was observed (Fig. S7) in the desorption rate. Earlier TDS data for a hydrophobic Antimony(111) surface studied with the same setup can be found in Fig. 3 in ref.⁹ In that case, a sharp drop of the signal was evident for the high temperature edges of the TDS curves.⁹ Therefore, we conclude that the high temperature TDS feature is intrinsic to graphene/Ru(0001) and indicated a deviation from exact zero-order kinetics.

Non-zero order condensation kinetics have been reported before for the water/HOPG surface and were attributed to hydrogen interactions in the water clusters.¹³ Desorption rates that become coverage-dependent below a critical water concentration were also reported for water adsorption on HOPG.¹² Therefore, deviations from exact zero-order kinetics or coverage-dependent kinetics are probably not completely unexpected for water adsorption on graphitic systems. The coverage-dependent kinetics could explain the high temperature "tails" of the TDS curves. A possible atomistic explanation was suggested for HOPG,^{12, 22} such that the coverage-dependence may be associated with an initial formation of two-dimensional (2D) water clusters acting as nucleation sites for subsequently formed three-dimensional (3D) water clusters. The water desorption kinetics were initially coverage-independent, resulting in the same initial desorption rate (same slope of low temperature edges), independent of the initial coverage. (Note that the binding energy agrees with water condensation, as discussed earlier.) This is the high water–low temperature coverage range where water desorbs from 3D clusters. Below a critical water coverage, however the desorption rate may become coverage-dependent, thereby smoothing the decrease of the desorption rate and resulting in the high temperature–low coverage tail of the TDS curves. Formally this may be described as quasi-zero-order kinetics. Diffusion of water and the dynamics of the adlayer as the temperature increases may also affect the desorption rate. Low temperature STM or HREELS studies may be able to confirm this hypothesis. Intercalation of water may theoretically also explain coverage-dependent water adsorption kinetics. (Delayed desorption of intercalated water.) However, we rule out this explanation since it may require double/multilayer graphene which is not present. Secondly, the TDS data would not be reproducible, because the morphology of the system would depend on the water exposure and/or sample history.³²

Very diverse conclusions can also be found in theoretical studies.³³ For molecular dynamics (MD) simulations predict a wetting transparency of graphene, see ref.¹⁶; for very similar MD simulations predicting that graphene is not entirely transparent to wetting see ref.¹⁵ A few DFT (density functional theory) calculations for water on graphene appeared in the literature (see e.g. ref.³⁴⁻³⁶), but the questions about transparency and wettability were so far not directly addressed. We hope that our UHV model study will stimulate more theoretical works.

Conclusions

As a pragmatic approach, in order to determine whether or not a surface is intrinsically hydrophobic, transparent, etc., the cleanest sample possible should be

characterized. In this project, UHV kinetics data were collected for the first time (as we believe) for water on graphene/Ru(0001). Water adsorption on graphene, grown on metallic Ru(0001), was not directly affected by the support. Graphene is not "transparent" to water wetting on Ru(0001). The desorption kinetics show many features of water condensation and a hydrophobic interaction, including low desorption temperature, a single peak evidenced by TDS, and alignment of the low temperature edges, except that the adsorption/desorption became coverage-dependent below a critical water concentration. Therefore, the water graphene/Ru(0001) interaction even at UHV was probably not strictly hydrophobic. Qualitatively, the results are in agreement with ref.¹⁷, in which an enclosed-environment SEM was utilized.

Notes and references

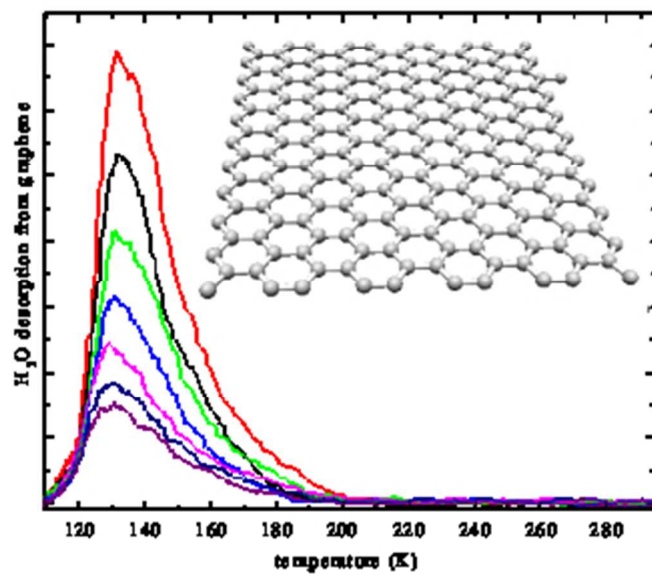
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Electronic Supplementary Information (ESI) available: [experimental setup, sample characterization, additional data, brief literature survey]. See DOI: 10.1039/c000000x/

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Kinetics of water adsorption on graphene at ultra-high vacuum
38x29mm (300 x 300 DPI)