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1 Spontaneous Liquid Water Dissociation on Hybridised Boron
2 Nitride and Graphene atomic layers
3 from Ab Initio Molecular Dynamics Simulations

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8 Abstract

9
10 Two-dimensional materials such as graphene (G) and hexagonal boron nitride (BN)
11 have demonstrated potential applications in membrane science and in particular for
12 the harvest of blue energy. Although pure G and BN atomic layers are known to
13 remain inert towards neutral water, one may wonder about the aqueous reactivity of
14 hybridized monolayers formed by joining BN and G sheets in a planar fashion. Here,
15 we perform Ab Initio molecular dynamics of liquid water in contact with all possible
16 planar heterostructures. Remarkably, we could observe the spontaneous chemisorp-
17 tion and dissociation of interfacial water molecule into its self-ions, at one specific
18 and non-standard one-dimensional border. Our simulations predict that this type of
19 heterostructure is prone to ionize liquid water already in the absence of any electrical
20 gating.

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21 INTRODUCTION

22 Among the many materials being studied for chemical applications, two-dimensional
23 (2D) ideal materials like graphene (G hereafter) and hexagonal boron nitride (hBN; BN
24 hereafter) are some of the most versatile and interesting ones, thanks to their structural
25 similarity albeit differential properties and especially for BN to its promising applications in
26 blue energy - harvesting energy from salinity gradient in water [1, 2]. However less is known
27 about how doping in these twin materials alters their interactions with interfacial molecules.
28 Indeed, experimental routes to produce hybrid composites of BN and G have been pioneered
29 by Ci and coworkers [3] and recently summarized in a review [4]. Precisely several routes of
30 synthesis have emerged either from bulk copolymerisation [5] or from growing catalytically
31 on a variety of pure and alloy metal substrates, such as Cu [6–10], Ru [11–13], Rh [14], Ir
32 [15, 16], Pt[17] or Cu-Ni alloy [18]. The latter fabrication of metal-supported monolayers
33 are being obtained with high levels of control being reported on the nanometer scale thanks
34 to the Scanning Tunneling Microscopy (STM) probe and sometimes real-time Low Energy
35 Electron Microscopy (LEEM). In most of these studies, zigzag (ZZ) linking edges are prefer-
36 entially formed with respect to the armchair (AC) interface. Moreover in the ZZ edge there
37 is either a C-N interface or a C-B interface - defining donor and acceptor interface states
38 respectively -, the latter being found more favorable [15].

39 Beyond synthesis and characterisation, there is much less progress on the reactivity of the as
40 produced composite border. Using zero Kelvin DFT framework the dissociative reactivity
41 of a gaseous molecules such as di-oxygen [5, 19] and water [20] have been explored on a
42 variety of hybridised materials issued from G and BN. But the reacting molecules were
43 always treated as single frozen species, far from their true environment in the liquid water.
44 Indeed liquid water requires a full quantum treatment to properly include dynamical proton
45 transfers between H-bonding water molecules denoted as the Grotthuss mechanism.[21–23]
46 Closer to the task at hand, M. Sprik has shown in pioneering publications that the full
47 quantum treatment of interfacial water is necessary for correctly describing the proton state
48 at wet surfaces of oxide and clay materials. [24, 25] To our knowledge, a realistic simulation
49 of the interface between water solvent and in-plane BN-G heterostructures remains highly
50 promising albeit challenging. This is the major goal of our study.

51

52 From our comparative theoretical study of suspended G and BN monolayers immersed
53 into high pH ionized water [26], both materials are found electrified through the favorable
54 adsorption of the solvated hydroxide ion but in a contrasting manner that gives full support
55 to previous nanofluidics measurements and analysis [1, 27].
56 In this paper we undertake a screening of the possible border configurations when matching
57 BN and G monolayer materials in a planar fashion. On all borders we first compute the
58 dissociative adsorption of single water molecule in vacuum and corrected in a dielectric
59 solvent in order to hint at the most favorable ones. On a few selected ones we run extensive
60 Ab Initio Molecular Dynamics (AIMD) with an explicit interface with bulk water. On one
61 border an interfacial H₂O molecule is found to spontaneously chemisorb onto one boron
62 atom before dissociating by transferring a proton to the surrounding water. These reactive
63 events occur within the few ps of the simulation unveiling the unexpected high reactivity of
64 the hybrid composites.

65 **RESULTS AND DISCUSSION**

66 **Static DFT study**

67 As a start we considered all possible BN-G planar heterojunctions as candidates. The
68 five different junctions and their labelling are displayed in Fig.1, and the corresponding
69 simulation cells are displayed in Supplementary Figure 1. Note that each cell contains two
70 border regions due to periodic boundary conditions. In the interface the border hexagons
71 are necessarily a composite BCN one: for ZZ (AC) border there is an odd (even) number of
72 each material. As a result we have considered the borders ZZ(B) and ZZ(N) and AC that are
73 standard ones. For completeness we have also modelled the BinC and NinC junctions which
74 comprise one single atom of each material. Notably in these junctions the border regions
75 has an extended width of two hexagons while the border region is limited to one hexagon in
76 any of the ZZ and AC edge geometries. To our knowledge the BinC and NinC junction have
77 never been characterized experimentally and we denote them non-standard edges. For each
78 junction, several H₂O dissociative adsorption configurations are possible and inspired by the
79 previous studies [20, 26] we restrict them to the ones where i) the hydroxide is chemisorbed
80 on a boron atom, ii) the proton is chemisorbed on a carbon atom, iii) the co-adsorption

81 occurs within the same hexagon in a cis conformation. The ii) choice is motivated by the
82 exhaustive DFT study of Ref. [20] that shows C-H bonds are significantly stronger than
83 N-H bonds when dissociating water on B-doped G and C-doped BN single layers. In total,
84 17 adsorption configurations are compared on 5 junction geometries and their dissociative
85 adsorption energies are displayed in Fig. 2. The dissociative adsorption energies of H₂O
86 called E_{ads} on different edges were computed first in vacuum and second in implicit water
87 at $T = 0$ K. To do so, the value of E_{ads} is obtained by comparing the total energy of the
88 adsorbed ions on the surface $E_{ads/surf}$ with that of the flat pristine surface $E_{pristine}$ added
89 to that of the pristine water molecule E_{H_2O} i.e. $E_{ads} = E_{ads/surf} - (E_{pristine} + E_{H_2O})$. The
90 adsorption energy calculation scheme is illustrated in Supplementary Figure 2.

91 E_{ads} on pristine atomic layers of BN and G were also included for comparison and yielded
92 unfavorable dissociative adsorption energies above 2.5 eV (see Supplementary Table 1) in
93 good agreement with previous results [20]. Also our AIMD study of water/BN and water/G
94 interfaces with and without aqueous hydroxide ion gave no indication of water adsorption
95 into these pristine layers. Indeed we showed differential adsorption of aqueous OH⁻ at
96 these interfaces in quantitative agreement with the measured negative surface charge, hence
97 precluding co-adsorption of protons and consequently excluding water dissociation on the
98 pristine layers. [26] As a general trend already observed in our previous static DFT study
99 [28], the dissociative adsorption energies tend to be destabilized in implicit water versus in
100 vacuum (see the orange triangles in the plot Fig. 2 are mostly lying in the energy scale below
101 the blue circles). In some cases however the energy does not change too much when intro-
102 ducing a solvent correction. Our energetic results show that the non-standard edges - BinC
103 and NinC on the left side of the plot in Fig. 2 - are more reactive towards water dissociative
104 adsorption than the ZZ edges. AC configurations (right side) are globally the less reactive
105 ones. Precisely, Fig. 2 exhibits three adsorbed configurations with negative (favorable) dis-
106 sociative adsorption energies in the implicit water case: BinC Aa (-0.88 eV) and BinC Ba
107 (-0.88 eV), and NinC Aa (-0.57 eV). These results corroborate the chemical enhancement
108 effect of one-dimensional boundaries in 2D materials. Furthermore, the magnitude of the
109 favourable adsorption energies indicate a strong interaction between the adsorbates and the
110 surface, calling for more realistic dynamical quantum studies on the reactivity of H₂O at the
111 liquid water / planar heterojunction interface, that we detail below.

112 **Metastability of co-adsorbed hydroxide and proton by AIMD**

113 Hydrogen bonds are of primordial importance for the water solvent. Therefore implicit
114 solvation schemes can not fully satisfactorily describe the adsorption of H₂O fragments on
115 BN and G atomic layers. In fact, the water self-ions OH⁻ and H⁺ resulting from water
116 auto-dissociation are transient species in water because they are subjected to fast proton
117 transfers from H-bonded water molecules. In order to properly simulate such systems, one
118 must resort to computationally expensive *ab – initio* molecular dynamics (AIMD) simula-
119 tions in which water molecules are comprehensively described. We therefore computed 10
120 ps long unbiased AIMD trajectories of several adsorption configurations in contact with 195
121 water molecules equilibrated at 323 K (see Methods). An example of an AIMD simulation
122 cell without adsorbates is displayed in Fig. 3. Due to computational costs only 4 of the 17
123 configurations could be tested by AIMD. The dissociated configurations tested by AIMD
124 correspond to coloured (red and green) labels in Fig. 2: the 3 configurations identified as
125 favourable in implicit water by static DFT (BinC Aa, Ba and BinC Aa) and the most
126 unfavourable dissociation configuration among the ZZ edges: ZZ(N) Ab. This last edge
127 configuration corresponds to the experimentally observed junction geometry. In all 4 cases,
128 the co-adsorbed fragments OH⁻ and H⁺ were found metastable, as none of the adsorbed
129 fragments was desorbing during the 10 ps of the dynamics. More interestingly the most
130 unfavourable of the 4 configurations (ZZ(N) Ab) was also found metastable, despite a static
131 adsorption energy computed as high as +1.97 eV. Hence it is likely that all of the 17 config-
132 urations considered in the present work would be found metastable if tested similarly i.e. by
133 free AIMD simulations. This points out that the theoretical results originating solely from
134 static DFT results might convey a partial picture of the reactivity in water solvent. This
135 stresses even further the necessity of an explicit and quantum description of solvents like
136 water at the interface of 2D materials.

137 **Spontaneous Reaction**

138 It is crucial to stress that the timescale and the number of chemical objects that one
139 can simulate with AIMD do not allow for the observation of rare chemical events, so that
140 one can only hope to witness extremely easy reactions along an unbiased trajectory. The

141 observation of any spontaneous reaction is therefore a strong indication of the extremely
142 high reactivity of those surfaces. To better study the water dissociation mechanism, a water
143 interface with a pristine NinC junction i.e. free of fragments, was thermalized at 323 K
144 while preventing all water molecules to approach the surface below 2 Å. Upon release of the
145 latter constraint, a water molecule starting at a large distance of 2.8 Å from the surface (see
146 Fig. 4a, cyan line) i.e. within the interfacial solvent layer (see the inset of Fig. 4b, water
147 density peak at 3.3 Å), was found to chemisorb on a boron atom of the junction after $t = 1.2$
148 ps of free MD (see Fig. 4c, inset 2). The water adsorbates then rapidly dissociates into an
149 adsorbed hydroxide and an aqueous hydronium at $t = 1.3$ ps (see Fig. 4c, inset 3). Although
150 the ions dynamically recombine transiently at certain points of the 10 ps long trajectory,
151 the as created hydronium cation diffuses further away from the first solvation shell of the
152 fixed adsorbed OH^- . To identify the dissociation state from the atomic configurations, we
153 associate each hydrogen atom to the closest oxygen to it. The atoms with respectively one
154 and three associated hydrogen are then defined as corresponding to the hydroxide and the
155 hydronium. During the simulation the adsorbate is in a OH^- state only 94% of the time
156 and in a H_2O state 6% of the remaining time.

157 The distance from the surface of the oxygen that adsorbs and the distance between the
158 two water self-ions are respectively displayed in cyan and green in Fig. 4a. The chaotic
159 trajectory (green line) of the hydronium ion in water is simply the manifestation of its
160 intrinsic reactivity in water: it will transfer one proton to a neighboring water that will
161 become the hydronium species. This results into large diffusion jumps of the hydronium
162 cation and blinking effects when tracking it in the dynamical simulation (see the whole 10
163 ps trajectory in Supplementary Movie 1).

164 We therefore propose a reaction in three steps, as illustrated in Fig. 4c: diffusion of H_2O
165 near the junction, chemisorption onto a border boron atom and subsequent but immediate
166 dissociation. The last step indeed is seen to occur only once the adsorbed state reached, not
167 during the approach of H_2O to the surface.

168 Starting from a different atomic configuration, another trajectory simulating the same
169 reactive interface was computed for 21 ps. The chemisorption was once again observed -
170 at $t = 2.5$ ps-, corroborating the likeliness of this reaction (see Supplementary Figure 3).
171 Yet, although one proton of the adsorbates appears to be shared with a solvating water
172 molecule, no clear dissociation occurs, i.e. with diffusion of the excess proton further than

173 the first solvation layer. With the method described above to identify the water self-ions
174 from simulation, the adsorbate is in a OH^- state only 15% of the time and in a H_2O state
175 85% of the remaining time. Thus by comparing the two trajectories on the same junction
176 starting with different solvent configuration, it appears that the organization of the solvation
177 shell around the water adsorbate is playing a key role for its dissociation. This is expected
178 from the strong role of solvent reorganisation in the proton diffusion process [21, 22] but is
179 magnified here by sequential adsorption and dissociation processes. Further studies would
180 be necessary to better understand how the solvent re-organization is coupled to these two
181 events.

182 Taking into account periodic boundary conditions (PBC) of the simulation, the spontaneous
183 dissociative adsorption of H_2O occurs at least once every 1.5 nm which corresponds to
184 roughly 1/6 of the border boron sites being bonded to an oxygen atom. This estimate being
185 based on the observation of the reaction in a limited time - 10 ps long AIMD trajectory-,
186 we expect the actual occurrence to be much higher.

187 In the following, we aim at quantifying the reactivity of H_2O with the NinC junction
188 by determining the free energy of adsorption of a water molecule. This was derived from
189 the potential of mean force (PMF) obtained by umbrella sampling while moving the adsor-
190 bate away from the surface to the first interfacial layer of solvent by restraining the oxygen
191 distance of the interacting water to the surface (see Methods). Because of the very high
192 reactivity of the interface, preventing all other water molecules of the simulation cell from
193 approaching the surface at less than 2 Å was proven necessary to avoid spontaneous adsorp-
194 tion. This is similar to constraining coordination numbers for the computation of pKa's to
195 avoid unwanted re-protonation of the acid.[29, 30] The resulting free energy profile shown in
196 Fig. 4b displays a chemisorption well of - 43 meV located 1.6 Å away from the surface and
197 a barrier of 90 meV at 2 Å. The basin around 3 Å corresponds to the water density peak
198 of the first water layer at 3.3 Å from the surface. The minimum of this basin was taken
199 as reference energy for the PMF (see Fig. 4b, horizontal grey dotted line). Interestingly,
200 the barrier height corresponds solely to about $4 k_B T$, while a large number of potentially
201 reacting molecules are present close to the junction as H_2O is the solvent, which furthermore
202 displays a density peak in the vicinity of the surface.

203 How realistic are our predicted reactive junctions towards liquid water? Experimentally
204 the observed ZZ border is mostly the ZZ(B) one [8, 15] and not the one that we found

205 highly reactive i.e. NinC. Hence we tested a similar reactivity at the ZZ(B) border [8, 15]
206 by thermalizing, i.e. running MD at room temperature, a simulation cell consisting of
207 one H₂O adsorbed on the border boron atom in plain water by restraining the adsorbed
208 water molecule at 1.6 Å from the surface. Upon release of the latter restraint the water
209 molecule was found to spontaneously desorb within a few hundreds of femtoseconds, as
210 displayed in Supplementary Movie 2. Nevertheless, the adsorption configuration ZZ(B) Ba
211 was also identified as metastable i.e the OH et H co-fragments remain stable during free
212 MD (see previous section). Hence we postulate that the metastable adsorption state of the
213 water fragment could be reached from ions already separated in solution or via concerted
214 formation of the B-O bond and rupture of one O-H bond.
215 Nevertheless even if sharp 1D interfaces with NinC edge hexagons are not likely to be
216 observed in planar heterojunctions, we infer that these asymmetric hexagons can still be
217 present locally in a zero dimensionality of defects like G-doped BN and vice versa BN-doped
218 graphene materials. Thus we hope that our results can forster such experiments to undertake
219 a controlled reactivity study of environmental molecules on these composite BCN materials.

220 CONCLUSION

221 By means of ab initio calculations, we have evidenced a covalent chemistry on one water-
222 immersed BN-G planar heterostructure, chemistry that does not exist on pristine materials.
223 A large variety of border geometries were tested and the dissociative adsorption of H₂O to
224 form B-OH⁻ and C-H⁺ fragments was found energetically favorable in a few cases. One
225 junction geometry was identified as particularly reactive with spontaneous adsorption of
226 H₂O and subsequent dissociation into an adsorbed hydroxide and an aqueous hydronium.
227 This reactive junction comprises one row of BN hexagons with one C atom substituting B
228 and the next adjacent row of G hexagons with one N atom substituting C. Moreover such
229 asymmetric composite hexagons echoe substitutional doping in 2D materials and hence may
230 be also observed in patchy BN islands embedded in a graphene sheet and vice versa[5, 31].
231 The use of state-of-the-art techniques such as atomic force microscopy in water is an exquisite
232 tool of choice to seek experimental evidence for the water adsorption and dissociation at the
233 hBN-graphene junction. This unique tool requires an ultimate reduction of the noise and has
234 been developed recently [32, 33]. We hope that our prediction will trigger more reactivity

235 studies on chemically doped 2D materials.

236 **METHODS**

237 Both DFT and AIMD simulations were performed using orthorhombic cells containing a
238 hexagonal sheet consisting of 72 Carbon, 36 Boron and 36 Nitrogen atoms. To model the
239 junctions of the zigzag and armchair type, $14.77 \text{ \AA} \times 25.58 \text{ \AA}$ and $12.78 \text{ \AA} \times 29.55 \text{ \AA}$ single
240 layers were respectively used, separated by 15 \AA of vacuum for static DFT calculations and
241 21 \AA of explicit water for AIMD trajectories. The top views of the neutral Lewis structures
242 of the three investigated cells are displayed in Supplementary Fig. 1a-c. The first and the
243 second cell parameters are respectively parallel to the hybridised junction and perpendicular
244 to the surface. The hBN and graphene primitive lattice parameters \mathbf{a} (2.51 \AA and 2.47 \AA
245 respectively) evaluated within the present DFT framework exhibit a mismatch of 0.04 \AA , in
246 agreement with previous calculations using a similar method[28, 34]. The lattice parameter
247 of hBN was chosen to construct the cell, therefore inducing strain in the counterpart network.
248 Because of the lattice mismatch, only a large supercell containing thousands surface atoms
249 could prevent inducing strain in the layer. Static DFT calculations were performed using
250 the Vienna Ab Initio Simulation Package (VASP) in its version 5.4.1, with a 800 eV cutoff
251 of the plane-wave expansion of the wave functions. The electronic cores were described
252 by pseudo-potentials under the projector augmented wave method [35]. The framework of
253 the generalized gradient approximation (GGA) was used to evaluate exchange-correlation
254 energies, with the so-called optPBE functional developed by Klimeš, Bowler and Michaelides
255 [36]. The first Brillouin zone of the supercell was sampled at the gamma point. Solvation
256 energies in implicit water were evaluated within the approach implemented into VASP by
257 Mathew and Hennig [37]. In this scheme, the solvent is represented as a dielectric constant
258 which is a functional of the electronic density, continuously spanning values from 0 to 80,
259 the bulk water value asymptotically approached in regions where the electronic density is
260 lower than $\rho_{cut} = 0.0025 \text{ \AA}^3$. All atomic configurations which energy was used to derive
261 adsorption strengths were obtained after relaxing the structure to reach atomic forces below
262 0.05 eV/\AA . A typical VASP input for a static DFT calculation with implicit water is shown
263 in Supplementary Note 1.

264 AIMD was performed with the CP2K 5.1 code[38]. The forces were computed using density

265 functional theory (DFT) as implemented in the QuickStep module[39, 40]. Wavefunctions
266 were projected over DZVP-MOLOPT-SR-GTH basis sets [41] and planewaves expanded to
267 a 600 Ry energy cutoff. Geodecker-Teter-Hutter pseudopotentials were used to represent
268 electronic cores [42–44]. The Perdew, Burke and Ernzerhof (PBE) functional was used[45]
269 with the D3 dispersion correction scheme[46, 47]. In order to limit nuclear quantum effects
270 and to reduce the time step size needed for energy conservation in our Born-Oppenheimer
271 AIMD, the mass of all protons was substituted by that of deuterium. A time step of 0.5
272 fs was used for the dynamics. AIMD simulations were carried out in the NVT ensemble
273 at 323 K using Nose-Hoover thermostats [48, 49] with a time constant of 500 fs. The PBE
274 functional predicts a reasonable liquid water structure at this slightly increased temperature
275 condition. The 21 Å high simulation cell contained 195 H₂O, yielding a pressure $\langle P \rangle = 2 \pm$
276 3 MPa (see Supplementary Methods), and was built as follows. Using the Packmol software
277 [50], the water molecules were randomly placed inside a 16 Å high cell which was later
278 juxtaposed to the surface with a 2.5 Å vacuum separation between the hexagonal layer and
279 the liquid. The system was heated up to 600 K before cooling down to 323.15 K, followed by
280 a 3 ps equilibration. To test the metastability of the adsorbed state the two adsorbates were
281 added to the simulation cell and restrained close to the surface for 2.5 ps before removal of
282 the biases.

283 To obtain the potential of mean force of a water molecule close to the junction, the distance
284 of one particular water oxygen to the surface was restrained using a harmonic bias with a
285 force constant of 0.1 Ha/Bohr. This collective variable was defined as the oxygen distance
286 to the closest surface atom. The target of the restraint was progressively moved from
287 1.4 Å to 3.6 Å along successive trajectories of 5 ps which starting point corresponds to
288 0.05 to 1 ps of the previous run. The two oxygen-hydrogen bond of the target H₂O were
289 restrained by a harmonic potential centered at 1 Å with a force constant of 0.025 Ha/Bohr.
290 Simultaneously, harmonic biases with a force constant of 0.1 Ha/Bohr were applied to each
291 combination of another oxygen atom and any boron atom. The restraints were only applied
292 when the oxygen-boron distance would come close to 2 Å in order to prevent spontaneous
293 adsorptions. To define the collective variables and apply the biases, the open-source and
294 community developed PLUMED library[51] was used in its version 2.4[52] as implemented
295 in the CP2K 5.1 code. Typical CP2K and PLUMED input files used for biased dynamics
296 can be respectively found in Supplementary Note 2 and Supplementary Note 3. Further

297 details regarding the PLUMED bias can be found in Supplementary Methods. To derive
298 the free energy profile, the biased trajectories were analyzed using a home implementation
299 of the Weighted Histogram Analysis Method (WHAM) developed by Kumar *et al.* [53] as
300 formulated by Souailles and Roux in their extension of this protocol[54]. A bin size of 0.05 Å
301 was choose to compute the histograms. Evidence of convergence of the WHAM analysis used
302 to derive the PMF of Fig. 4b is displayed in Supplementary Figure 4. The final snapshot of
303 the trajectory with the H₂O restrained at 3.2 (3.0) Å from the surface was used as starting
304 point for the bias-free trajectory leading to spontaneous adsorption of a water molecule,
305 with (without) further dissociation. The water density profile displayed in inset in Fig. 4b
306 was evaluated over 30 ps of trajectory corresponding to the gathering of the two simulations
307 of the NinC junction in water. More detailed profiles are displayed in Supplementary Figure
308 5.

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431 **CONFLICTS OF INTEREST**

432 There are no conflicts of interest to declare.

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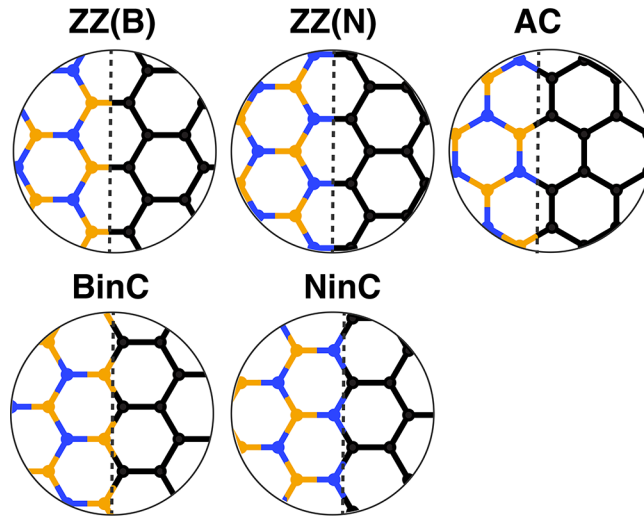


Figure 1. Possible junction geometries for the planar heterostructure and their **acronyms**. ZZ (AC) stands for zigzag (armchair) edges where the composite hexagons comprises 3 (4 or 2) atoms from BN and 3 (2 or 4) atoms from GR. For the zigzag boundaries, there is either a C-B interfacial bond called ZZ(B) or a C-N bond called ZZ(N). The junctions BinC and NinC correspond to a composite hexagon formed with one single atom B and N respectively from BN and the rest from GR. The junction line is schematically represented by a black dotted line while the boron, carbon and nitrogen atoms are respectively displayed in orange, black and blue.

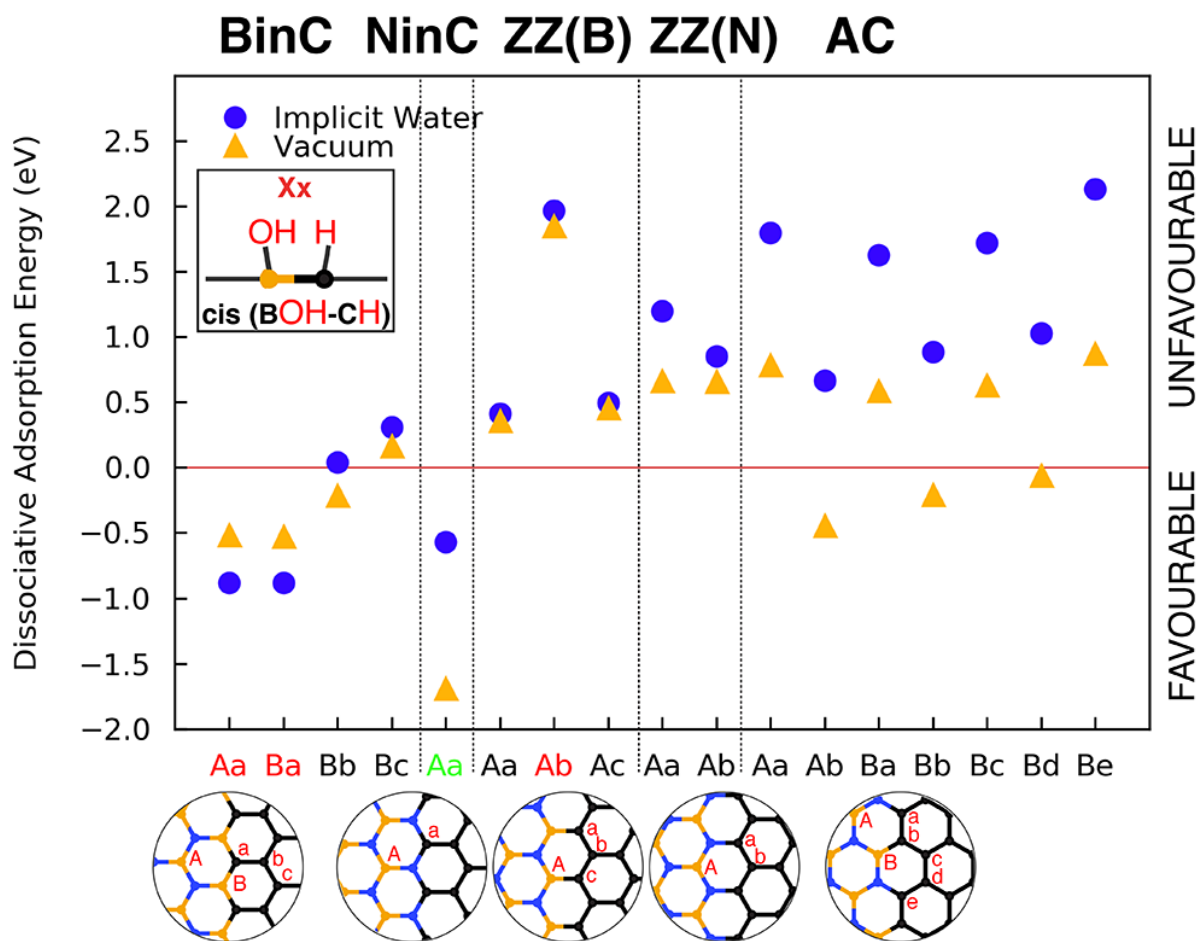


Figure 2. Static DFT H₂O Dissociative Adsorption Energies limited to OH fragment bonded to a boron atom while H fragment bonded to a carbon atom in the same composite hexagon of the heterostructure. Dissociative adsorption energies of H₂O in vacuum (orange triangles) and implicit water (blue circles) for various adsorption configurations on 5 distinct junction geometries defined in Fig. 1. Red uppercase letters label hydroxide adsorption sites while red lowercase letters indicate associated proton adsorption sites. Coloured labels indicate configuration which meta-stability was also tested in explicit water by ab-initio molecular dynamics. Spontaneous dissociative adsorption of H₂O was observed on the green labelled geometry.

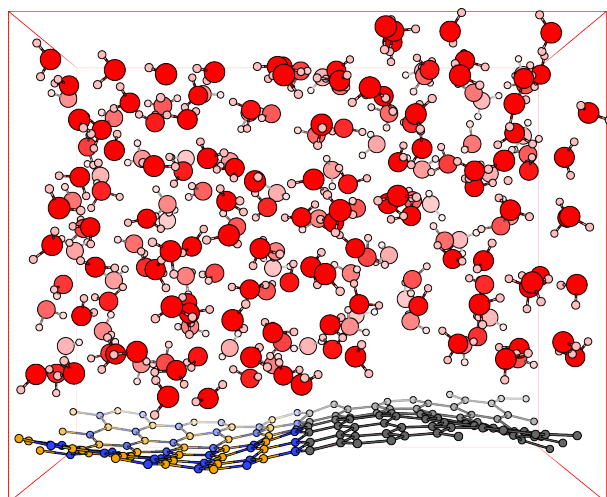


Figure 3. Ab Initio Molecular Dynamics Simulation Cell. Example of simulation cell with explicit water. The NinC junction geometry is represented along with 195 H₂O. Hydrogen, boron, carbon, nitrogen and oxygen atoms are respectively represented in pink, orange, grey, blue and red.

437 :

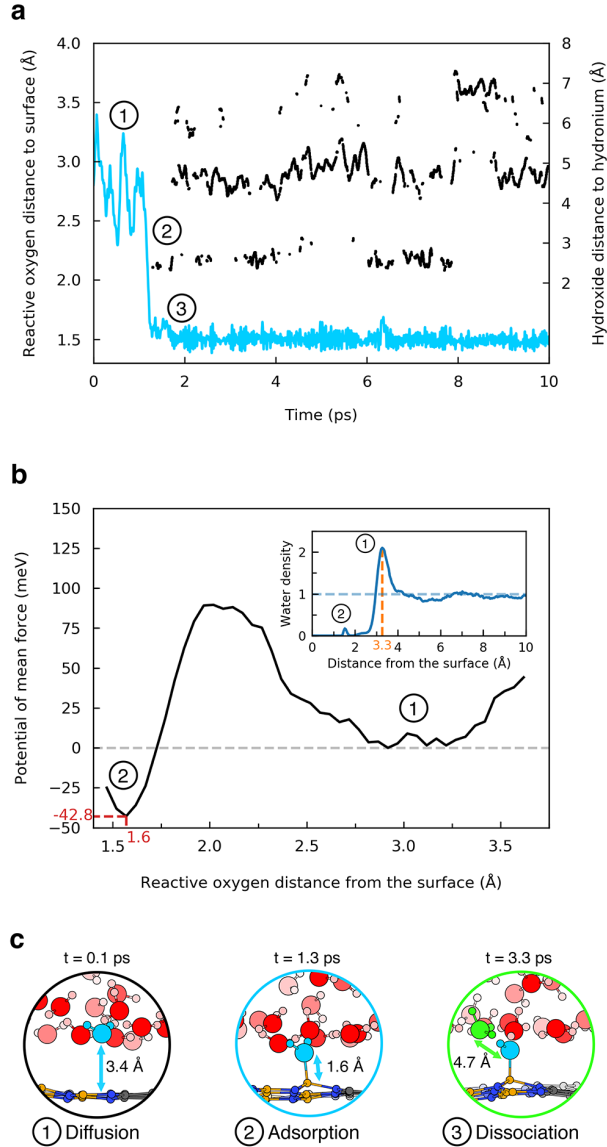


Figure 4. Spontaneous Dissociative Adsorption of Water. 10 ps long bias-free AIMD simulation of the Ni₄C junction in water leading to the observation of a water dissociative adsorption. **a)** The distance to the surface of the oxygen adsorbing on a boron atom and the distance between the dissociated OH⁻ and H₃O⁺ are respectively represented by a cyan line and black dots along the trajectory. **b)** Potential of mean force of a H₂O with respect to its distance to the surface (black line), with the energy reference represented by a grey dotted horizontal line. The energy and position of the chemisorption well is indicated in red. (inset: The water density with respect to the distance of the surface with the horizontal and vertical lines respectively indicating the bulk density value and the position of the interfacial layer. The density corresponds to an average over the whole cell.) **c)** Snapshots of the dynamics with associated times and distances. The reactive H₂O and OH⁻ are both represented in cyan. Circled numbers correspond to the ones in **a** and **b**.