Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information to:
"Spontaneous Liquid Water Dissociation on Hybridised Boron Nitride and Graphene atomic layers from Ab Initio Molecular Dynamics Simulations"

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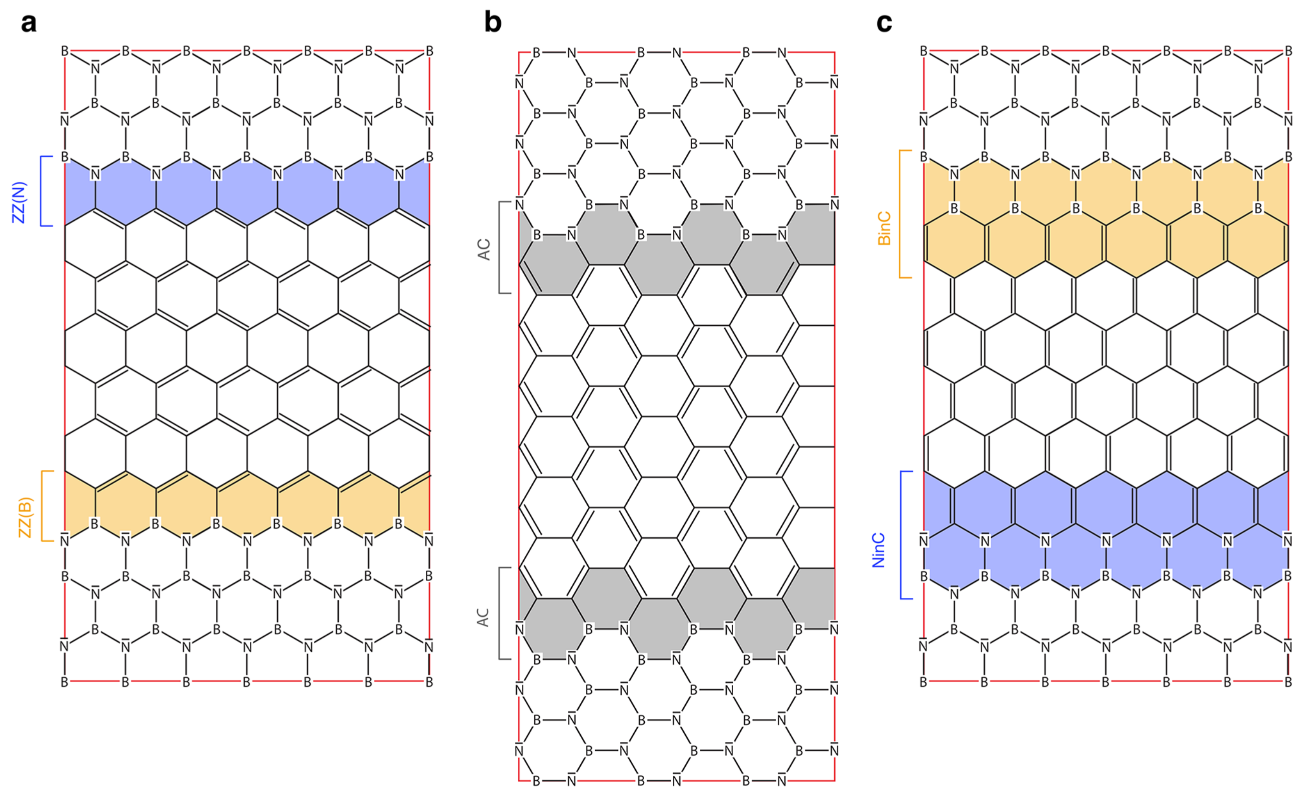
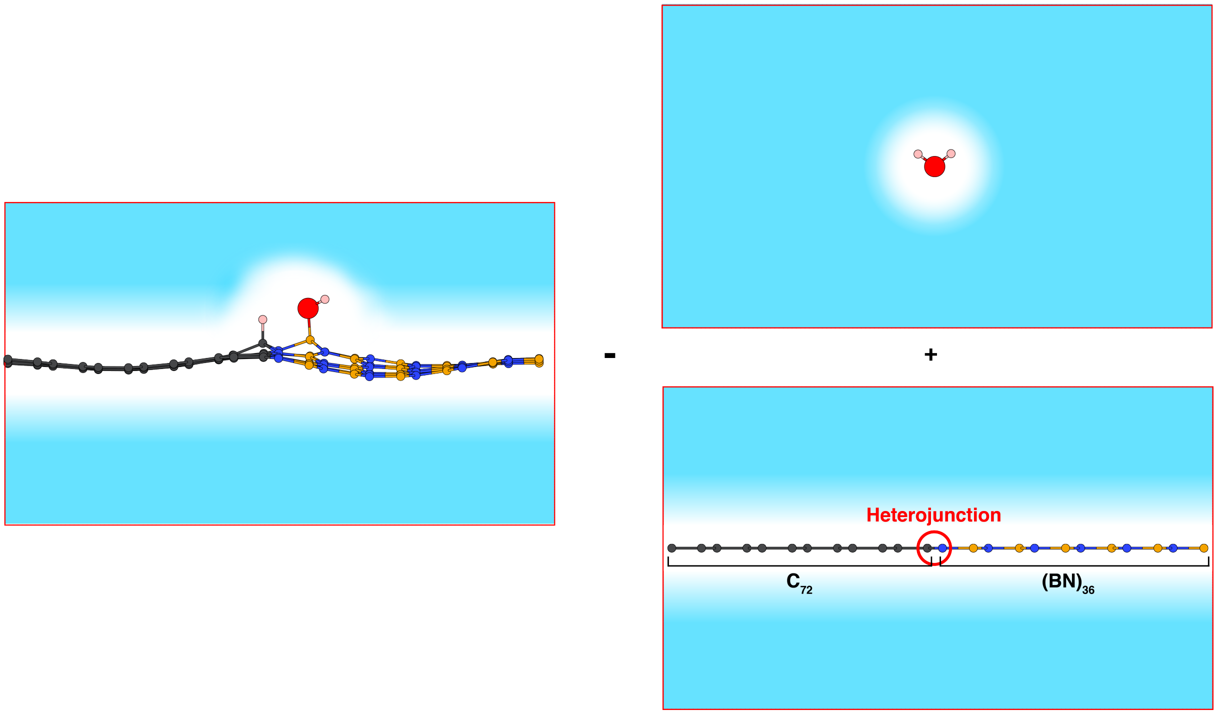
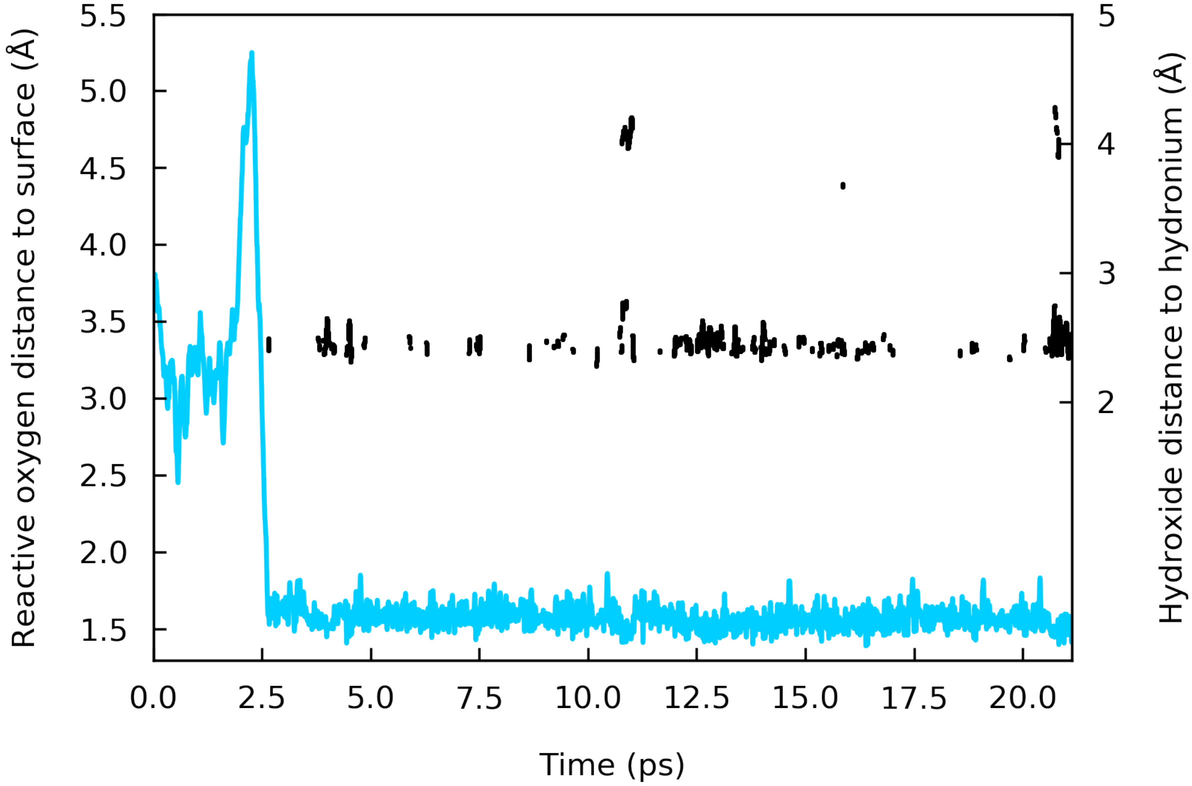
SUPPLEMENTARY FIGURES



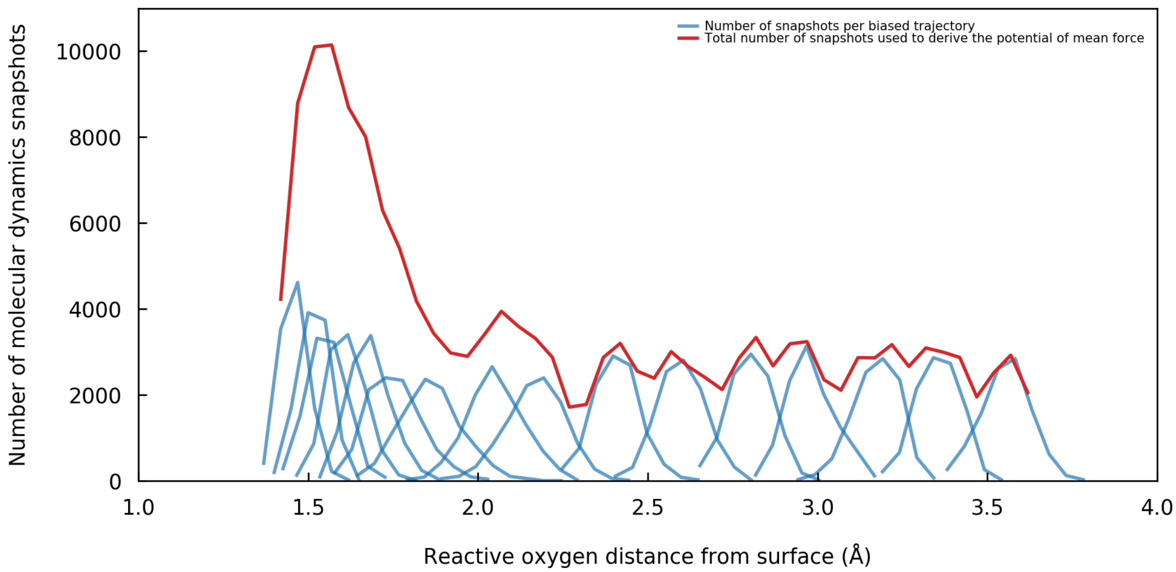
Supplementary Figure 1. Neutral Lewis structure of the simulation cells containing the two types of ZZ edges (a), the AC junction (b) and the two types of non-standard edges. Dimensions of the cells are 14.77 Å × 25.58 Å for the ZZ edges and 12.78 Å × 29.55 Å for the AC edges. The C-N, C-B and C-N/C-B junctions are respectively highlighted in blue, orange and grey while the limit of the cell is represented in red.



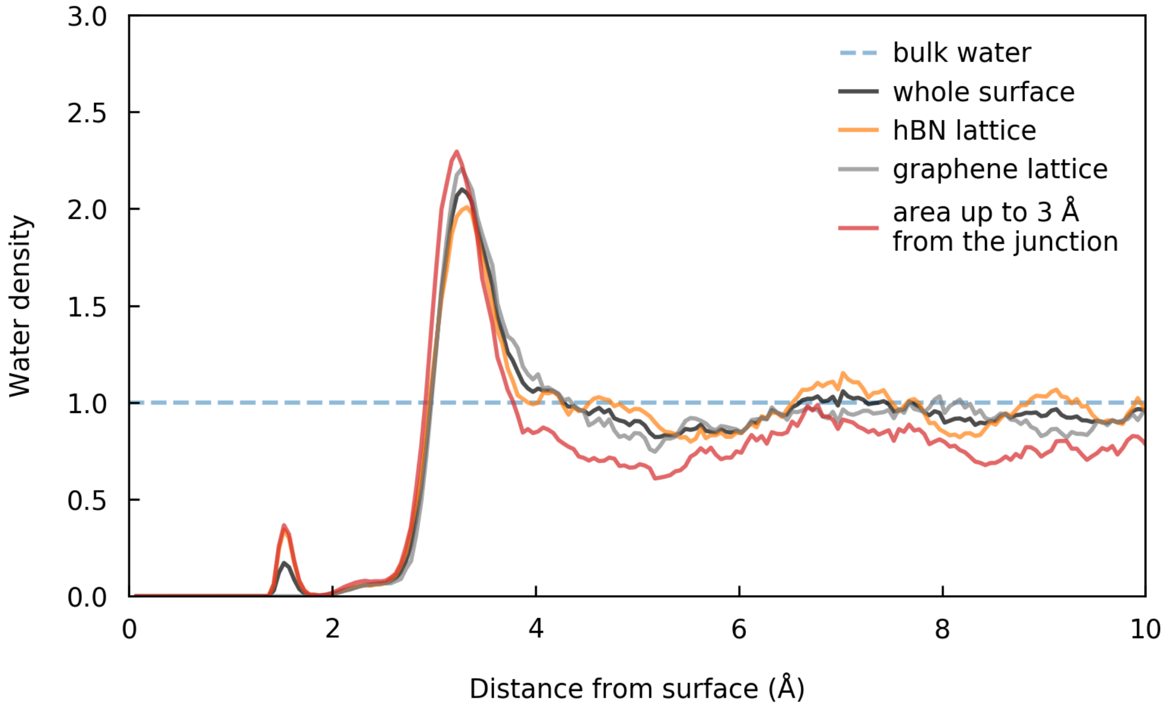
Supplementary Figure 2. **Adsorption Energies Calculation Scheme** Side views of simulations cells used to derive dissociative adsorption energies of H_2O at h-BN/graphene heterostructures in either vacuum or implicit water (represented in light blue). Surface with a hydroxide and a proton respectively chemisorbed on a boron and a carbon atom (left), pristine surface (bottom right) and single H_2O molecule (top right). Hydrogen, boron, carbon, nitrogen and oxygen atoms are respectively represented in pink, orange, grey, blue and red. The dissociative adsorption energy corresponds to the difference of the total energies of the right cell with the two left cells.



Supplementary Figure 3. Non-dissociative spontaneous adsorption of water. Distance between the reactive Oxygen atom and the surface (cyan) and between OH^- and H_3O^+ ions along a 20 ps long non-biased trajectory of the ZZ(N)/water interface. A water molecule spontaneously adsorbs on the surface but only dynamically dissociates.



Supplementary Figure 4. Evidence of convergence of the umbrella sampling. Histograms of the probed reactive oxygen distance from surface in terms of number of molecular dynamics snapshots for each biased trajectory (blue) and on overall (red).



Supplementary Figure 5. Water density profiles on top of the ZZ(N) heterostructure averaged over two trajectories of 10 and 21 ps. The density over the whole surface, the BN lattice, the graphene lattice and the junction are respectively represented in black, orange, grey and red. The junction region was arbitrarily defined as the area up to 3 Å away from the edge. The bulk density of liquid water is represented by a blue horizontal line as an indication.

Material	Configuration	E_{ads}^{vac}	E_{ads}^{sol}
BN	ortho	2.59	2.59
	para	3.34	3.01
Graphene	ortho	2.56	2.69
	para	2.92	3.00
	meta	3.46	3.57

Supplementary Table 1. Dissociative adsorption energy of H_2O on 60 atoms BN and graphene single layers in vacuum (E_{ads}^{vac}) and in implicit water (E_{ads}^{sol}). All energies are in eV. On BN the OH^- and H^+ fragments are respectively on top of a Boron and a Nitrogen atom.

SUPPLEMENTARY METHODS

Restraints

Restraints were defined and applied using the open-source and community developed PLUMED 2.4 library[1, 2]. $d_{\mathrm{O}^*-surf.}$, the distance of the interest Oxygen atom O^* to the surface was defined as the distance to the closest surface atom using the following continuous function as definition:

$$d_{\mathrm{O}^*-surf.} = \frac{\beta}{log\left(\sum_i \frac{\beta}{d_{\mathrm{O}^*-i}}\right)} \tag{1}$$

where β is a parameter taken equal to 500, i designates an atom of the surface and d_{O^*-i} the distance between atom i and O^*. The derivability of this function is required in order to define a bias. When compared to a discontinuous definition of the distance to the surface (i.e. the distance to the closest surface atom), values can slightly vary from the definition of (1). We chose β in order to minimise the differences obtained with the continuous and the non-continuous definitions. Due to numerical limitations, β can not be set too high (e.g. more than 1200).

During the biased trajectories, if below 2 Å, the distances between all Boron atoms and all Oxygen atoms different from O^* are restrained by a harmonic potential, using the "LOWER_WALLS" functionality of PLUMED. A representative example of a PLUMED input file can be found in Supplementary Note 3, with only one "lower wall" defined instead of all of them.

Simulations pressure

The pressure inside the ab-initio molecular dynamics (AIMD) simulation cells was evaluated on 200 snapshots distant by 0.05 ps in the 10 ps trajectory leading to the dissociative adsorption of a water molecule. The atomic forces for each of those snapshots were recomputed after adding an additional 10 Å vacuum separation between liquid water and one of the two sides of the single layer. The average over those snapshots of the mean force per surface atom divided by the section area was considered as the pressure. This resulted in an average pressure of 2 ± 3 MPa.

Movies

Supplementary Movie 1 displays a 10 ps long non-biased trajectory of the ZZ(N)/water interface. Supplementary Movie 2 corresponds to the first 600 fs of the dynamics of the ZZ(B)/water interface, pre-equilibrated with a chemisorbed H_2O molecule. Hydrogen, Boron, Carbon, Nitrogen and Oxygen atoms are respectively represented in white, orange, grey, blue and red while the water molecule of interest and subsequent hydroxide are in cyan and the hydronium is displayed in green. Movies were generated using the Visual Molecular Dynamics (VMD) software version 1.9.2 [3–5] and the Blender freeware version 2.79.

SUPPLEMENTARY REFERENCES

[1] The PLUMED consortium: A community effort to promote openness, transparency and reproducibility in molecular simulations (Submitted).

[2] Tribello, G. A., Bonomi, M., Branduardi, D., Camilloni, C. & Bussi, G. PLUMED 2: New feathers for an old bird. *Comput. Phys. Commun.* **185**, 604–613 (2014).

[3] Visual Molecular Dynamics, http://www.ks.uiuc.edu/research/vmd/.

[4] Humphrey, W., Dalke, A. & Schulten, K. VMD – Visual Molecular Dynamics. *J. Mol. Graph.* **14**, 33–38 (1996).

[5] Stone, J. An efficient library for parallel ray tracing and animation. *Master Thesis, Comput. Sci. Dep., Univ. of Missouri-Rolla* (1998).

SUPPLEMENTARY NOTES

Supplementary Note 1

Typical VASP input file used for static DFT calculations.

```
# Typical VASP input file example for Supplementary Information to:
# "Spontaneous Dissociative Chemisorption of Water at Room Conditions
# on BN/Graphene Heterojunctions."

ISTART = 0
ICHARG = 2
LREAL = Auto
PREC  = Accurate
LSOL = .TRUE.
ENCUT = 800
EDIFF = 1e-6
NELM  = 250
ALGO  = NORMAL
NSW = 101
IBRION = 2
EDIFFG = -0.05
GGA = OR
LUSE_VDW = .TRUE.
AGGAC = 0.0000
ISMEAR = 0
SIGMA  = 0.025
```

Supplementary Note 2

Typical CP2K input file used for biased ab initio molecular dynamics trajectories.

```
# Typical CP2K input file example for Supplementary Information to:
# "Spontaneous Dissociative Chemisorption of Water at Room Conditions
# on BN/Graphene Heterojunctions."

@SET SYSTEM system
@SET DATA_PATH /home/cp2k-data

&FORCE_EVAL
  METHOD Quickstep
  &DFT
    BASIS_SET_FILE_NAME ${DATA_PATH}/BASIS_SETS
    POTENTIAL_FILE_NAME ${DATA_PATH}/GTH_POTENTIALS
    &MGRID
      CUTOFF 600
    &END MGRID
    &QS
      EPS_DEFAULT 1.0E-14
      MAP_CONSISTENT TRUE
      EXTRAPOLATION ASPC
      EXTRAPOLATION_ORDER 4
    &END QS
    &PRINT
     &MULLIKEN
      FILENAME =${SYSTEM}-1.mulliken
      &EACH
       MD 1
      &END EACH
     &END MULLIKEN
    &END PRINT
```

```
&SCF
  MAX_SCF 10
  SCF_GUESS RESTART
  EPS_SCF 1.0E-7
  &OUTER_SCF
    EPS_SCF 1.0E-7
    MAX_SCF 1000
  &END OUTER_SCF
  &OT ON
    MINIMIZER DIIS
    N_DIIS 5
  &END OT
&END SCF
&XC
  &XC_FUNCTIONAL PBE
  &END XC_FUNCTIONAL
  &vdW_POTENTIAL
     DISPERSION_FUNCTIONAL PAIR_POTENTIAL
     &PAIR_POTENTIAL
        TYPE DFTD3
        CALCULATE_C9_TERM .TRUE.
        REFERENCE_C9_TERM .TRUE.
        LONG_RANGE_CORRECTION .TRUE.
        PARAMETER_FILE_NAME ${DATA_PATH}/dftd3.dat
        VERBOSE_OUTPUT .TRUE.
        REFERENCE_FUNCTIONAL PBE
        R_CUTOFF [angstrom] 11.0
        EPS_CN 1.0E-6
     &END PAIR_POTENTIAL
  &END vdW_POTENTIAL
  &XC_GRID
    XC_SMOOTH_RHO NN50
```

```
      XC_DERIV NN50_SMOOTH
    &END
  &END XC
&END DFT
&SUBSYS
  &CELL
    ABC [angstrom] 14.766 25.5755 21.0
  &END CELL
  &TOPOLOGY
    COORD_FILE_FORMAT xyz
    COORD_FILE_NAME coordinate.xyz
  &END TOPOLOGY
  &COLVAR
   &DISTANCE
    ATOMS 16 17
   &END DISTANCE
  &END COLVAR
  &COLVAR
   &DISTANCE
    ATOMS 16 18
   &END DISTANCE
  &END COLVAR
  &KIND H
    BASIS_SET DZVP-MOLOPT-SR-GTH
    POTENTIAL GTH-PBE-q1
    MASS 2
  &END KIND
  &KIND O
    BASIS_SET DZVP-MOLOPT-SR-GTH
    POTENTIAL GTH-PBE-q6
  &END KIND
  &KIND B
```

```
      BASIS_SET DZVP-MOLOPT-SR-GTH
      POTENTIAL GTH-PBE-q3
    &END KIND
    &KIND N
      BASIS_SET DZVP-MOLOPT-SR-GTH
      POTENTIAL GTH-PBE-q5
    &END KIND
    &KIND K
     BASIS_SET DZVP-MOLOPT-SR-GTH
     POTENTIAL GTH-PBE-q9
    &END KIND
    &KIND C
     BASIS_SET DZVP-MOLOPT-SR-GTH
     POTENTIAL GTH-PBE-q4
    &END KIND
  &END SUBSYS
&END FORCE_EVAL
&GLOBAL
  PROJECT ${SYSTEM}
  RUN_TYPE MD
  PRINT_LEVEL LOW
  WALLTIME  1500
&END GLOBAL
&MOTION
  &FREE_ENERGY
    &METADYN
        USE_PLUMED .TRUE.
        PLUMED_INPUT_FILE ./plumed.in
    &END METADYN
  &END FREE_ENERGY
   &MD
     ENSEMBLE NVT
```

```
    STEPS 1000
    TIMESTEP 0.5
    TEMPERATURE 323.15
    &THERMOSTAT
      TYPE NOSE
      REGION GLOBAL
      &NOSE
        TIMECON 500
LENGTH 4
YOSHIDA 9
MULTIPLE_TIME_STEPS 2
      &END NOSE
    &END THERMOSTAT
  &END MD
  &CONSTRAINT
   &COLLECTIVE
    COLVAR 1
    TARGET [angstrom] 1.00
    INTERMOLECULAR .TRUE.
    &RESTRAINT
     K 0.025
    &END RESTRAINT
   &END COLLECTIVE
   &COLLECTIVE
    COLVAR 2
    TARGET [angstrom] 1.00
    INTERMOLECULAR .TRUE.
    &RESTRAINT
     K 0.025
    &END RESTRAINT
   &END COLLECTIVE
  &END CONSTRAINT
```

```
  &PRINT
    &TRAJECTORY  SILENT
      FILENAME =${SYSTEM}-1.xyz
      &EACH
        MD 1
      &END EACH
    &END TRAJECTORY
    &VELOCITIES  SILENT
      FILENAME =${SYSTEM}-1.vel
      &EACH
        MD 1
      &END EACH
    &END VELOCITIES
    &FORCES  SILENT
      FILENAME =${SYSTEM}-1.force
      &EACH
        MD 1
      &END EACH
    &END FORCES
    &RESTART
      FILENAME =${SYSTEM}-1.restart
      &EACH
        MD 1
      &END EACH
    &END RESTART
  &END PRINT
&END MOTION
```

Supplementary Note 3

Typical PLUMED input file used for biased ab initio molecular dynamics trajectories.

```
# Typical PLUMED input file example for Supplementary Information to:
# "Spontaneous Dissociative Chemisorption of Water at Room Conditions
# on BN/Graphene Heterojunctions."

surface_atoms: GROUP ATOMS=586-729
O: GROUP ATOMS=1
DISTANCES GROUPA=surface_atoms GROUPB=O MIN={BETA=500.0} LABEL=d_O_surface
RESTRAINT ...
LABEL=d_O_surface_restraint
ARG=d_O_surface.min AT=1.6 KAPPA=500.0
... RESTRAINT
PRINT ARG=d_O_surface.min,d_O_surface_restraint.bias FILE=plumed.out

DISTANCE ATOMS=4,586  LABEL=d4_586
LOWER_WALLS ARG=d4_586 AT=2.0 KAPPA=500.0 EXP=2 EPS=1 OFFSET=0 LABEL=lwall_1
```