

Supporting information for:

Cooperative Interplay of van der Waals Forces and Quantum Nuclear Effects on Adsorption: H at Graphene and at Coronene

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Abstract

In this document we report some of the results on the various tests of computational set-up performed in order to establish the accuracy of the set-up used. This includes a comparison between different exchange-correlation functionals and tests with different supercell sizes. Then

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the DFT-D3 free energy profile is compared to results from vdW-DF to show that our conclusions are independent of the van der Waals inclusive DFT method used. We also show how the ring-polymer length converges with the number of harmonic quantum transition state theory beads, and similarly with the number of path-integral molecular dynamics beads.

Comparison of exchange-correlation functionals and studies of unit cell size effects

Here we report tests on the sensitivity of the results to the exchange-correlation functional used and on the lateral size of the graphene unit cell. As well as DFT-D3 a number of van der Waals density functionals (vdW-DF) were considered, specifically optB88-vdW, optPBE-vdW, and the original vdW-DF (referred to here as revPBE-vdW).^{1,2} In table S1 the physisorption energies obtained with the various functionals are reported and in figure S1 the complete binding energy curves are shown. It can be seen that there are quite substantial differences between the various functionals. However, in comparison to PBE they all predict the presence of a physisorption well and a substantially lower chemisorption barrier. Specifically, whereas DFT-D3 yields a physisorption energy of about 50 meV, the vdW-DFs tend to predict larger values of about 80-100 meV (table S1). In terms of the chemisorption barriers the PBE value is around 0.2 eV and the vdW-inclusive functionals all predict barriers of about 0.1 eV (relative to the physisorption minimum). Thus qualitatively the same physical effect is predicted by all functionals, with the vdW-DFs predicting an even more significant role for dispersion forces in the physisorption well. As noted in the main text, DFT-D3 is in closer agreement with the experimentally estimated physisorption energy of H on graphite and this is the main reason DFT-D3 results are reported in the main manuscript. Upon considering unit cells from 3×3 to 6×6 we find essentially no dependence of the physisorbed energy on the size of the cell (table S1).

Comparison of the optPBE-vdW and DFT-D3 quantum free energy profiles

The free energy profiles in the main manuscript were obtained from ab initio MD and ab initio PIMD simulations with the DFT-D3 functional. To test that the conclusions of our paper are not affected by this particular choice of functional we also computed the free energy profiles for H atom adsorption on graphene with the optPBE-vdW exchange-correlation functional.¹ This is a modified version of vdW-DF that has been demonstrated to perform very well for both solids and surface adsorption systems.³ The energy profiles shown in figure S2 have been computed with the same approach as used in figure S1 in the main text; the only difference is the exchange-correlation functional. By comparing the free energy profiles shown in figure S2 (middle panel) and figure S1 in the main text it can be seen that there are quantitative differences between the free energies obtained from DFT-D3 and optPBE-vdW. However, the same basic conclusion holds: when quantum effects are accounted for on top of vdW dispersion forces there is a significant reduction of the effective barrier to chemisorption. Indeed, as with the physisorption energy, the influence of vdW dispersion forces is even more pronounced when the optPBE-vdW functional is used.

Table S1: The energies (in meV) of the physisorbed state above a graphene surface computed for different supercell sizes and for different methods of including vdW. The physisorption energy of the hollow, top, bridge and interstitial sites are equal (within 1 meV), so only the binding energy at the top site is shown here.

Supercell size	optB88-vdW	optPBE-vdW	revPBE-vdW	DFT-D3
3×3	95	98	81	47
4×4	95	98	81	47
5×5	96	99	81	47
6×6	96	99	79	47

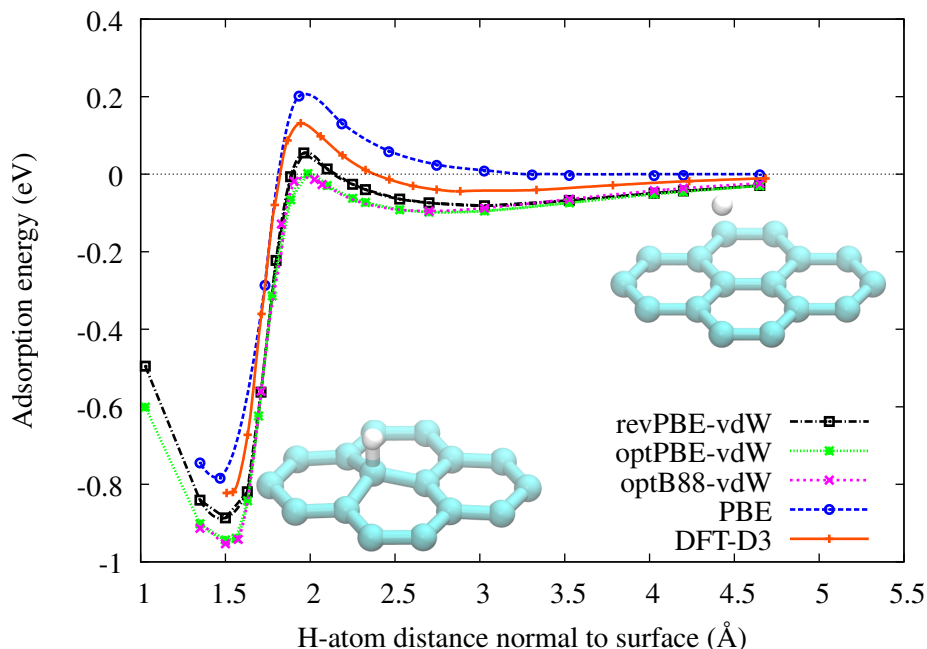


Figure S1: Binding energy profile for a single H atom calculated with DFT-D3, several vdW-DF based exchange-correlation functionals and with PBE on a 3×3 cell. The CI-NEB method was used and the energies presented are relative to the completely desorbed hydrogen atom and clean graphene sheet. There is no physisorbed state present with PBE. The PBE calculations give a barrier of 0.2 eV, whereas methods which include dispersion give lower barriers (around 0.1 eV). The drawings show the geometries of the chemisorbed and physisorbed states. The lines connecting the data are drawn using a cubic spline interpolation.

Convergence of the number of HQTST beads

The convergence of the instanton (HQTST) calculations with the increasing number of the path-integral beads is shown in table S2. We used 200 beads in our calculations, which is extremely well converged relative to our reference calculations with 400 beads.

Table S2: The centroid energies (in eV) and ring-polymer chain lengths (in Å) for HQTST calculations on the DFT-D3 H at coronene chemisorption barrier for 100, 200 and 400 beads.

Beads	Centroid energy (eV)	Ring-polymer length (Å)
100	0.049	1.88
200	0.050	1.80
400	0.049	1.99

Converging the number of path-integral beads for molecular dynamics

To find out how many beads are necessary to obtain an accurate potential of mean force from path-integral molecular dynamics (PIMD), while not wasting computational resources we performed benchmark calculations with 8, 16 and 32 beads. First we tested the length of the ring-polymer (table S3). Then we checked that force on the constrained centroid is comparable (figure S3). We find the length of the ring-polymer is within 0.06 Å, and the force on the centroid of the H atom is similar for 8, 16 and 32 beads.

Table S3: The ring-polymer chain lengths (in Å) for PIMD calculations with the centroid constrained at 2.25 Å above the graphene surface for 8, 16 and 32 beads.

Beads	Ring-polymer length (Å)
8	0.95
16	0.89
32	0.98

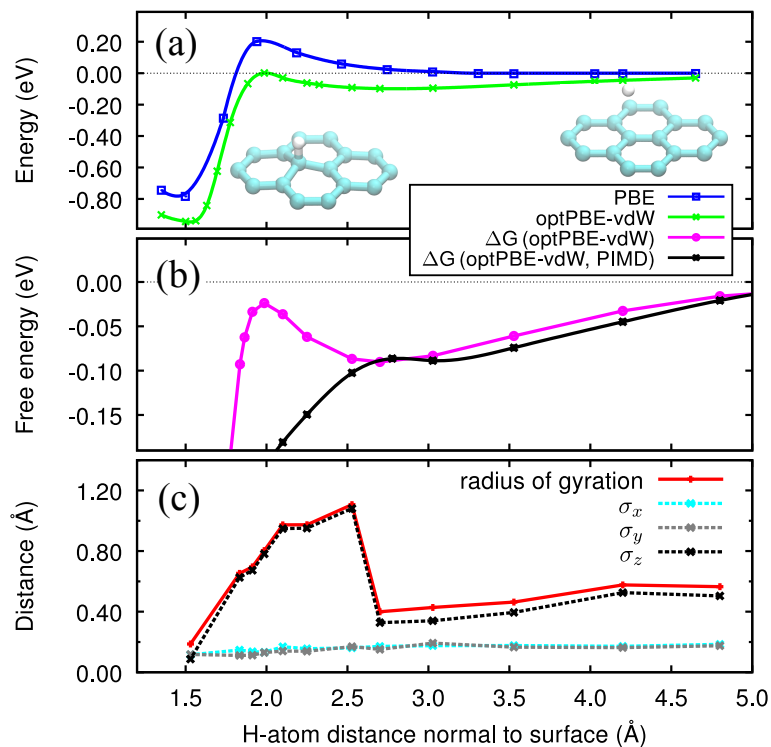


Figure S2: Total energy profiles calculated with the PBE and optPBE-vdW exchange-correlation functionals (a), and free energy profiles calculated with optPBE-vdW (b) for a single H atom at graphene. The profiles in these panels have been computed with the same approach as used in figure S1 in the main text; the only difference is the exchange-correlation functional. The H atom height above the surface is measured from the surface plane of the graphene sheet prior to chemisorption. The energies presented are relative to the completely desorbed H atom and a clean graphene sheet. The free energy profiles (ΔG , in (b)) are computed using both *ab initio* MD and *ab initio* PIMD approaches at 50 K. The statistical uncertainties on each point along the free energy profiles are typically less than about 7 meV. While the free energy profile with classical nuclei (pink line, circles) is a close match to the underlying optPBE-vdW potential energy curve (a), the inclusion of quantum nuclear effects (black line, crosses) very significantly lowers the free energy barrier to chemisorption to about 20 meV. The radius of gyration for the path-integral ring-polymer is shown in (c). This is decomposed into lateral (x,y) and normal (z) components relative to the surface plane.

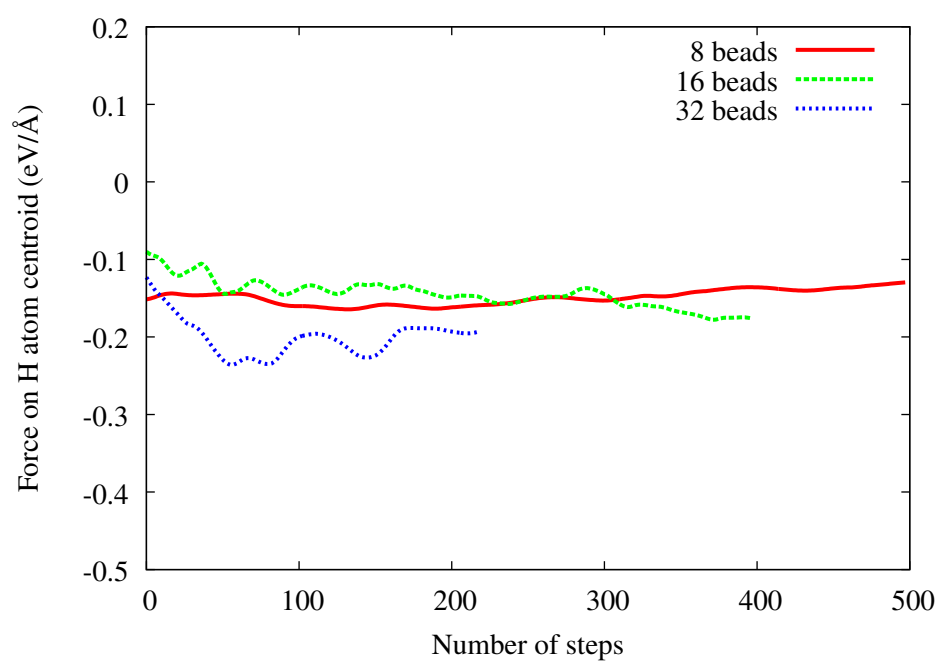


Figure S3: The force on the centroid of the ring-polymer for both 8, 16 and 32 beads for the centroid position constrained at a height of 2.25 Å above the graphene surface.

References

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