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Mechanisms of adsorbing hydrogen gas on metal decorated graphene

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Hydrogen is a key player in global strategies to reduce greenhouse gas emissions. In order to make hydrogen a widely-used fuel, we require more efficient methods of storing it than the current standard of pressurized cylinders. An alternative method is to adsorb H$_2$ in a material and avoid the use of high pressures. Among many potential materials, layered materials such as graphene present a practical advantage as they are lightweight. However, graphene and other 2D materials typically bind H$_2$ too weakly to store it at the typical operating conditions of a hydrogen fuel cell, meaning that high pressure would still be required. Modifying the material, for example by decorating graphene with adatoms, can strengthen the adsorption energy of H$_2$ molecules, but the underlying mechanisms are still not well understood. In this work, we systematically screen alkali and alkaline earth metal decorated graphene sheets for the static thermodynamic adsorption of hydrogen gas from first principles and focus on the mechanisms of binding. We show that there are three mechanisms of adsorption on metal decorated graphene and each leads to distinctly different hydrogen adsorption structures. The three mechanisms can be described as weak van der Waals physisorption, metal adatom facilitated polarization, and Kubas adsorption. Among these mechanisms, we find that Kubas adsorption is easily perturbed by an external electric field, providing a way to tune H$_2$ adsorption. This work is foundational and builds our understanding of H$_2$ adsorption under idealized conditions.
I. INTRODUCTION

There is an urgent need to reduce the use of fossil fuels and develop alternative, less polluting, methods of energy production. To this end, H$_2$ is long-standing potential candidate fuel.[1] There is an energy cost to producing H$_2$ in the first place, but H$_2$ molecules provide almost three times the energy density by weight as fossil fuels[2] and burning H$_2$ produces water with no additional harmful pollutants. In addition to burning, hydrogen can be combined with oxygen more efficiently in fuel cells, producing electricity and still only water as waste. At present, H$_2$ is stored as pressurised gas and more efficient H$_2$ storage materials are needed to propel this fuel into wide-scale use.

A promising method of storing hydrogen fuel is to physisorb H$_2$ molecules in a lightweight material. Cycling weakly adsorbed hydrogen gas through a material is expected to have minimal degradation effect on the storage material as H$_2$ molecules remain intact. Other adsorption mechanisms of storage, such as the spillover method, rely on H$_2$ dissociating and forming covalent bonds with the storage material which makes the material more susceptible to deformation. In addition, weakly adsorbed hydrogen molecules require less energy to be released from a material relative to chemisorbed hydrogen atoms. The window for ideal H$_2$ adsorption energy can be estimated in a heuristic approach and considering the typical working temperature and pressure of fuel cells. The pressure ($p$), temperature ($T$), and the adsorption energy ($E_{\text{ads}}$), can be approximately related according to:

$$p = \frac{E_{\text{ads}}}{4 \pi m H_2 k_B T} \left( \frac{2 \pi m H_2}{h^3} \right)^{\frac{1}{2}} 2 \sinh \left( \frac{\hbar \omega_z}{2 k_B T} \right)$$

(1)

where ($k_B$) is the Boltzmann constant, ($h$) is Planck’s constant, ($m_{H_2}$) is the mass of H$_2$, ($\omega_z$) is the harmonic frequency of vibration of the H$_2$ molecule with respect to the substrate. For a full account of how Eq. 1 is used and the approximations we make, see the Appendix. Polymer electrolyte membrane (PEM) fuel cells have been developed for a range of operating temperatures, with high temperature PEM fuel cells functioning above 370 K.[3, 4] Taking into account intermediate and high temperature PEM fuel cells, we consider working temperatures of 270-390 K in this work. The typical operating pressure of a PEM fuel cell is 3 bars of H$_2$ pressure[3] which means that the storage material must have a higher H$_2$ vapor pressure to readily release H$_2$ to the fuel cell. In addition, an upper-bound of 100 bar has been proposed for the H$_2$ vapor pressure to avoid similar technological challenges as containing a highly pressurized gas [5]. Under such conditions, the energy of H$_2$ adsorption in a material is $-200$ to $-400$ meV per H$_2$ molecule as can be seen from Fig. 1.

![Temperature-pressure profile of H$_2$ on pristine graphene at different adsorption energies](image)

FIG. 1. The temperature-pressure profile of H$_2$ on pristine graphene at different adsorption energies indicated by the colored lines. The black line corresponds to the reference H$_2$ adsorption energy ($-24 \pm 11$ meV) on pristine graphene from diffusion Monte Carlo.[6] An ideal range of H$_2$ vapor pressures for a typical fuel cell is indicated by the horizontal yellow region and the ideal working temperatures are indicated by the vertical pink region. The overlap in ideal temperature and pressure is roughly bounded by H$_2$ adsorption energies of $-200$ and $-400$ meV. See Eq. 1 for the relation between pressure, temperature and adsorption energy.

The challenge of finding a material that binds H$_2$ suitably is also exacerbated by additional factors such as the weight and volume of the storage material.[1, 2, 7] Evidently, lighter and low-volume materials are required for practical and energy efficient fuel storage for mobile applications. There are various promising materials for H$_2$ storage and among them, we are interested in layered materials, as they are lightweight and are able to adsorb molecular hydrogen. However, the adsorption energy of H$_2$ on pristine graphene is predicted to be less than $-50$ meV[6] which is too weak for viable hydrogen storage (see Fig. 1). Structural defects and decoration by adatoms is known to enhance the adsorption energy of molecules on graphene[8] and there are countless combinations that can be considered. However, it is experimentally challenging to produce well controlled and characterized graphene with defects or adatoms and therefore it is difficult to ascertain the H$_2$ storage capacity of such potentially useful materials.
To date, there have been indications that decorating graphene with alkali and alkaline earth metal adatoms facilitates \( \text{H}_2 \) adsorption,[9–16] potentially yielding adequate \( \text{H}_2 \) capacities by weight. However, experimental information is scarce and computational efforts to understand \( \text{H}_2 \) adsorption on metal decorated graphene are difficult to unify. For example, in different studies \( \text{H}_2 \) adsorption energies have been predicted using different density functional approximations preventing us from drawing reliable trends. In addition, the structure of \( \text{H}_2 \) molecules adsorbed around different metal adatoms on graphene has not received systematic focus and stands to be better understood.

Among alkali and alkaline earth metals, Ca decorated graphene is one of the most studied systems.[9–11, 14, 15, 17, 18] This is partly due to favorable \( \text{H}_2 \) adsorption energies being predicted on this material as well as the relatively low cohesive energy of Ca, which is expected to prevent agglomeration on graphene. Specifically, Ataca et al. suggested over a decade ago that Ca adatoms facilitate the adsorption of \( \text{H}_2 \) molecules via Kubas-type binding.[15] This mechanism involves stabilizing the 3d state of Ca relative to 4s and donating electron density from 3d into the \( \text{H}_2 \) 1σ* state.[19] Since then, a number of wavefunction based methods have been used to understand the Ca\(^{+}\)-4H\(_2\) cluster (without a graphene substrate) and deduce whether a Ca adatom is able to bind \( \text{H}_2 \) using the Kubas mechanism.[13, 17, 20–24] The general conclusion from these works is that Ca is unlikely to bind \( \text{H}_2 \) using a Kubas-type binding and hence, cast doubt on the accuracy of density functional theory (DFT) approximations. However, graphene has been shown to affect adsorption and importantly, some metal adatoms (including Ca) make the adatom-graphene system metallic. Therefore, it is not straightforward to infer the nature of interaction on graphene from predictions on gas phase clusters.

Alongside Ca, other alkali and alkaline earth metal on graphene have been considered for \( \text{H}_2 \) adsorption.[9–12, 16] In brief, previous works have focused on assessing the adsorption strength of \( \text{H}_2 \) on a given material and in some cases methods without dispersion were used to predict adsorption energies.[10, 16] We seek to build a better understanding of the mechanisms underpinning \( \text{H}_2 \) adsorption on different alkali and alkaline earth metal adatoms on graphene. In this work, we systematically compute \( \text{H}_2 \) adsorption on alkali and alkaline earth metal decorated graphene and draw mechanistic insights. We outline our computational setup and methods in Section II. In Section III we report the results of screening 1 to 7 \( \text{H}_2 \) molecules per metal adatom on graphene. We refine and analyze the adsorption of \( \text{H}_2 \) for a subset of systems in Section IV. In doing so, we elucidate the mechanisms of adsorption and find that they can be summarized in three physically distinct categories. We briefly consider the effects of adatom diffusion, \( \text{H}_2 \) dissociation, and alternative substrates in Section V. In Section VI, we report the effect of applying an external electric field on the \( \text{H}_2 \) interaction with the substrate and find that it depends strongly on the binding mechanism. We conclude in Section VII with a brief discussion of the results.

II. METHODS

The initial screening of adsorption energies was performed with CP2K v.7.1[25, 26] and Goedecker-Teter-Hutter pseudopotentials[27, 28] in combination with DZVP-MOLOPT-SR-GTH basis sets.[29] A maximum plane-wave cut-off of 300 Ry was used across 5 grids, with a relative cut-off of 30 Ry. Our CP2K calculations were spin-polarised and performed at \( \Gamma \)-point only for a \((5 \times 5)\) unit cell of graphene. The geometries were optimized with the BFGS method until the maximum force was less than \( 5 \times 10^{-4} \) Ha \( a_0^{-1} \). All parameters of the CP2K geometry optimizations can be seen in the example input in the Supplementary Material (SM).[30] The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[31] was used in combination with Grimme’s D3 dispersion method[32] with zero-type damping and three-body Axilrod-Teller-Muto terms included, to account for van der Waals interactions. It is known that the choice of exchange-correlation functional has a notable impact on the \( \text{H}_2 \) adsorption energy on graphene-type surfaces.[6, 9] Particularly in the case of physisorption, long-range dispersion interactions are expected to play an important role and therefore it is necessary to use a dispersion method. However, in the absence of experimental reference adsorption energies for the systems we are considering, it is difficult to ascertain which dispersion method yields the most accurate results. In general, dispersion methods have been shown to predict consistent structures and relative energies.[33–38]

Absolute adsorption energies, on the other hand, can vary considerably among different density approximations. Previously, we established diffusion Monte Carlo (DMC) reference adsorption energies for \( \text{H}_2 \) inside and outside a carbon nanotube (CNT) and found that add-on dispersion methods are more accurate than seamless density-dependent dispersion functionals for the adsorption of \( \text{H}_2 \) inside a carbon nanotube.[6] Add-on dispersion methods include the D3,[32] D4,[39] and many-body-dispersion (MBD)[40, 41] methods. These partially account for beyond two-body dispersion interactions which can play an important role in graphene-like materials.[42] In our work, we combine results from two DFT packages and therefore, to be consistent, we use PBE+D3 as it is implemented in CP2K and VASP. Note that PBE+MBD and PBE+D3 both predict an \( \text{H}_2 \) adsorption energy of \(-53\) meV on pristine graphene, while DMC yields \(-24 \pm 11\) meV.[6]

Metal decorated graphene (M@Gr) was modelled using a \((5 \times 5)\) unit cell of graphene with unit cell parameters optimized using PBE+D3. A single metal atom (M) was placed at the hollow site and fully optimized for Li, Be, Na, Mg, K, Ca, Rh, Sr, Cs, and Ba. \( \text{H}_2 \) molecules were placed upright relative to graphene and surrounding the metal atom in every initial structure. An inter-layer spacing of 20 Å is applied along the \( z \)-axis between graphene sheets and dipole corrections[43, 44] along \( z \)-direction also computed. Up to 7 \( \text{H}_2 \) molecules were fully optimized on each M@Gr system, totalling 70 systems, with all atoms in the cell allowed to relax. We report the results of this screening in Section III.
For a better understanding of the binding mechanisms and to assess the quality of the initial screening, we performed fine-grained optimizations of the resulting geometries from the screening. We used VASP v.5.4.[45–48] with standard PAW potentials and a 500 eV plane-wave cut-off. Since the neutral metal atoms are easily ionized, potentials with explicit semi-core s states were used for all metals. Na has the highest energy core states amongst the metal atoms we considered and we found that the interaction energy of 4H$_2$ on Na@Gr is converged with a 500 eV plane-wave cut-off to within 2 meV. In addition, the decoration of graphene with metal atoms makes the system metallic and hence we used a dense k-point mesh of 9 × 9 × 1 centred on Γ. We found the interaction energy of 4H$_2$ on Ca@Gr is converged within 1 meV per H$_2$ using a k-point mesh of 5 × 5 × 1 and therefore we expect an even denser mesh to be sufficient for all the systems we considered. The fine-grained geometry relaxations for 3-5 H$_2$ molecules on each substrate were converged with residual forces less than 0.01 eV Å$^{-1}$. Densities of states were obtained using a 15 × 15 × 1 k-point mesh and the SUMO code[49] was used in post-processing the data.

In Section V we report a diffusion barrier for Ca on graphene, H$_2$ dissociative adsorption, and a few H$_2$ binding energies on metal decorated bilayer graphene and metal decorated Gr/Ni(111). The Ca diffusion barrier was computed using the climbing-image nudged elastic band (NEB) method with five replicas and a spring force constant of 5 eV Å$^{-2}$ with nudging.[50–52] For bilayer graphene, a (5 × 5) unit cell of AB stacked double layer graphene was modelled where the inter-layer spacing between the two sheets of graphene is 3.501 Å along the z-axis. The Gr/Ni(111) slab contains a single layer of graphene on five layers of Ni atoms, with two of the lower layers fixed at the experimental bulk lattice constant for Ni. The slab structure contains 125 Ni atoms and 50 C atoms. A k-point mesh of 5 × 5 × 1 was used in these systems. Further details on the setup and numerical settings of the computations for Section V can be found in the SM.[30]

For the application of external electric force fields in Section VI, we used a sawtooth potential as implemented in VASP and applied the field along the z-direction in the unit cell, i.e. perpendicular to the graphene sheet. We also performed geometry optimizations of 4H$_2$ adsorbed on Ca@Gr at two electric fields (0.2 V Å$^{-1}$ and −0.2 V Å$^{-1}$) using a k-point mesh of 5 × 5 × 1.

### III. SCREENING H$_2$ ADSORPTION ON METAL DECORATED GRAPHENE

Decorating graphene with single metal atoms has previously been found to strengthen the adsorption of H$_2$ molecules for some metals such as Ca and Li.[15, 16] In some cases, such as Mg@Gr, the adsorption of H$_2$ remains weak.[12] We focus specifically on alkali and alkaline earth metals, from Li to Ba, with the aim to understand the mechanisms underpinning the interactions. The indication from previous works is that dispersion interactions contribute significantly to the adsorption energy[53] and H$_2$ is bound too weakly to be useful for hydrogen storage.[8, 54] However, it appears from the range of adsorption energies reported, that it is difficult to establish consistent adsorption energies from DFT approximations.[54] Moreover, a systematic analysis of the adsorption geometries is missing from our current understanding and we aim to address that here. An approximate overview of the relative strength of H$_2$ adsorption as the number of H$_2$ molecules are increased is given by the crude screening in this section. The results of the rapid DFT screening of H$_2$ adsorption energies on M@Gr, using CP2K and atom centered basis sets, is shown in Fig. 2. The adsorption energy ($E_{ads}$) is defined as:

$$E_{ads} = (E_{ads}^{tot + M@Gr} - E_{M@Gr}^{tot} - nE_{H_2}^{tot}) / n$$

(2)

where $E_{H_2}^{tot}$ is the total energy of the H$_2$ molecules adsorbed on M@Gr, $E_{M@Gr}^{tot}$ is the total energy of the fully relaxed M@Gr substrate, $E_{H_2}^{tot}$ is the total energy of the gas phase relaxed H$_2$ molecule, and n is the number of H$_2$ molecules adsorbed.

Screening calculations were performed at the Γ-point only and using atom-centered basis sets without correcting for basis set superposition error. As a result, the PBE+D3 adsorption energies in Fig. 2 are likely to be overestimated. For reliable PBE+D3 adsorption energies, as obtained from VASP using a well-converged setup (discussed in Section IV), see Table 1 where we report adsorption details for systems with 3-5 H$_2$ molecules, as well as the adsorption energy of metal adatoms on graphene.

The geometry optimization of H$_2$ molecules on M@Gr broadly yields three orientations of H$_2$ molecules, as can be seen from Fig. 2. There are several features to note from these preliminary adsorption profiles. First, the weakest adsorption profile is seen for Be@Gr and Mg@Gr, where the H$_2$ molecules prefer to be flat on the graphene sheet and pointing radially to the metal atom. An example of this flat radial configuration is illustrated in Fig. 2. This configuration suggests the main contribution to adsorption is between H$_2$ and graphene, with an additional weak interaction with the metal adatom. Note that Be has a degeneracy in its valence states that is known to make it reactive with hydrogen, forming Be–H bonds. This occurs in one of the geometry optimizations, when 6 H$_2$ molecules are placed near Be, leading to the dissociative adsorption of a H$_2$ molecule. Therefore, Mg and Be are not likely to be suitable adatoms on graphene for H$_2$ storage via weak adsorption. Second, all alkali M@Gr substrates adsorb H$_2$ in the upright bond-facing (BF) configuration and the adsorption energy profile is near-linear with increasing number of molecules. For K, Rb, and Cs, the adsorption profile is particularly flat, varying by less than 30 meV in the adsorption energy per H$_2$ molecule, from 1 to 7 H$_2$ molecules. Adsorption is strongest among alkali metals for Li@Gr with up to 3 H$_2$ molecules. However the H$_2$ adsorption energy on Li@Gr shows a steady weakening with increasing number of H$_2$ molecules. This is due to H$_2$ molecules not fitting around the small Li adatom and therefore spreading further away on the surface. In the case of Na@Gr, there is a small ∼ 40 meV variation in the H$_2$ adsorption energy, with the most favorable binding
FIG. 2. Preliminary screening of \( \text{H}_2 \) adsorption on group 1 (solid lines) and group 2 (dashed lines) M@Gr. PBE+D3 adsorption energies shown here (in meV) are approximate only. For a converged PBE+D3 adsorption energies, see Table 1 where a subset of systems are reported. The symbols indicate the optimized orientation of \( \text{H}_2 \) molecules around the metal atom. Triangles indicate upright bond-facing (BF), squares indicate flat BF, and crosses indicate flat radial configuration. The three mechanisms are also depicted on the right. The circle (6H\(_2\)+Be@Gr) indicates dissociative adsorption of \( \text{H}_2 \) has occurred. Average H-H bond lengths are also given for each mechanism of binding. The yellow shaded region from \(-200\) to \(-400\) meV indicates an estimated range of suitable adsorption energies for storage in operation with fuel cells.

Our screening of \( \text{H}_2 \) adsorption on alkali and alkaline earth metal decorated graphene suggests that the strongest non-dissociative adsorption of \( \text{H}_2 \) for more than 3 molecules per adatom, occurs on Ca, Sr, and Ba decorated graphene. For less than 3 \( \text{H}_2 \) molecules per adatom, Li@Gr is predicted to bind \( \text{H}_2 \) strongly. However, adsorption energies in this screening are only approximate as loose technical parameters have been used and the PBE+D3 method is also a source of uncertainty. In the next section we report adsorption energies from well-converged basis set, Brillouin sampling, and geometry optimizations for a subset of systems with PBE+D3.

IV. MECHANISM OF ADSORPTION AND THE ROLE OF GRAPHENE

To understand the electronic structure mechanisms underlying the three distinct configurations of \( \text{H}_2 \) adsorption we find, we performed well-converged geometry relaxations on all adatom systems with 3-5 \( \text{H}_2 \) molecules from Section III. The computational details are given in Section II and we note that the main improvement is in the \( \mathbf{k} \)-mesh density (using a \( 9 \times 9 \times 1 \) grid on a


TABLE I. Adsorption properties of 3-5 H\textsubscript{2} molecules adsorbed on alkali and alkaline earth M@Gr from PBE+D3. \(E_{\text{M@Gr}}\) is the fully relaxed adsorption energy of the metal adatom (M) on a (5 \times 5) unit cell of graphene (Gr) and \(d_{\text{M--Gr}}\) is the corresponding separation distance along the z-axis considering the average position of all carbon atoms. \(E_{\text{ads}}\) is the average adsorption energy per H\textsubscript{2} molecule when nH\textsubscript{2} molecules are adsorbed (in eV). The H-H bond lengths, \(d_{\text{H--H}}\), and average M-H\textsubscript{2} distances, \(d_{\text{M--H}}\), are reported for the 4H\textsubscript{2}+M@Gr system in Å. In the upper section, Li to Cs, the H\textsubscript{2} molecules are in an upright bond-facing. H\textsubscript{2} molecules are in flat radial configuration on Be@Gr and Mg@Gr. In the lower section of the table, Ca to Ba, H\textsubscript{2} molecules are in a flat bond-facing configuration. The values reported here correspond to spin-polarized geometry optimizations performed with 9 \times 9 \times 1 k-point mesh and force convergence criterion of 0.01 eV Å\textsuperscript{-1}.

| Adatom (M) | \(E_{\text{M@Gr}}\) (eV) | \(d_{\text{M--Gr}}\) (Å) | \(E_{\text{ads}}\) (eV) | \(E_{\text{ads}}^{3\text{H}}\) (eV) | \(E_{\text{ads}}^{4\text{H}}\) (eV) | \(E_{\text{ads}}^{5\text{H}}\) (eV) | \(d_{\text{H--H}}\) (Å) | \(d_{\text{M--H}}\) (Å) |
|------------|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Li         | 1.279           | 1.704          | 0.187          | 0.161          | 0.141          | 0.755          | 2.348          |
| Na         | 0.719           | 2.189          | 0.176          | 0.173          | 0.156          | 0.756          | 2.516          |
| K          | 1.200           | 2.571          | 0.137          | 0.137          | 0.121          | 0.754          | 2.964          |
| Rb         | 1.262           | 2.730          | 0.128          | 0.128          | 0.112          | 0.754          | 3.209          |
| Cs         | 1.466           | 2.903          | 0.117          | 0.118          | 0.102          | 0.753          | 3.435          |
| Be         | 0.181           | 3.218          | –              | 0.088          | –              | 0.754          | 2.875          |
| Mg         | 0.281           | 3.322          | –              | 0.068          | –              | 0.754          | 3.180          |
| Ca         | 0.741           | 2.314          | 0.142          | 0.190          | 0.178          | 0.784          | 2.287          |
| Sr         | 0.753           | 2.497          | 0.096          | 0.135          | 0.132          | 0.779          | 2.478          |
| Ba         | 1.198           | 2.577          | 0.159          | 0.181          | 0.163          | 0.771          | 2.722          |

FIG. 3. The 4H\textsubscript{2}+Ca@Gr system showing the geometry of H\textsubscript{2} molecules around Ca and the charge redistribution upon adsorbing H\textsubscript{2} molecules. The unit cell used is indicated in the middle panel. Charge density difference is shown between 4H\textsubscript{2} and Ca@Gr using an isosurface level of 0.002 e Å\textsuperscript{-3}. Charge density depletion is shown in blue and charge density accumulation is shown in yellow.

(5 \times 5) unit cell of graphene) and the use of a plane-wave basis set as implemented in VASP. We have also performed calculations with alternative starting geometries to see if flat BF configurations can be stabilized over upright BF on alkali metals, and vice versa on alkaline earth metals. We find that the orientation of H\textsubscript{2} molecules predicted in Section III is consistent and that the graphene-adatom distances change by less than 5% or 0.16 Å. Similarly, the H\textsubscript{2}-adatom distance changes by, at most, 10% or 0.28 Å. A detailed report of the separation distances for each system from CP2K and VASP is provided in Table S1 of the SM.[30]

The PBE+D3 H\textsubscript{2} adsorption energies on M@Gr substrates and metal adatom adsorption energies on graphene are reported for well-converged optimized structures in Table 1. The PBE+D3 metal adatom adsorption energies (\(E_{\text{M@Gr}}\)) show that Mg and Be adsorb weaker than \(-300\) meV on graphene, while other metal adatoms adsorb by over \(-700\) meV. The average H\textsubscript{2}-metal adatom and graphene-metal adatom separation distances are also reported in Table 1 for each metal considered. We can see that stronger H\textsubscript{2} adsorption is accompanied by shorter H\textsubscript{2}-metal adatom separation distances and that Ca and Ba adatoms best facilitate the adsorption of H\textsubscript{2} molecules with adsorption energies of up to \(-190\) and \(-181\) meV per H\textsubscript{2} molecule, respectively. It is evident that the screening in Section III led to overestimated adsorption energies, but we note that the most favorable adsorption energy predicted here with PBE+D3 is within 10 meV of the range that is expected to be useful for H\textsubscript{2} storage. It is important to note, however, that the accuracy of PBE+D3 is not established for predicting M@Gr systems as there is no experimental or theoretical reference information – nonetheless we expect that the physical trends obtained from DFT are physically consistent.
First, we focus on the 4H\textsubscript{2}+Ca@Gr system, where the adsorption energy is the strongest and there is a long-standing effort to establish whether the system is viable for H\textsubscript{2} storage. The unit cell, adsorption configuration, and charge density difference for adsorbing 4H\textsubscript{2} molecules can be seen in Fig. 3. We can see that there is charge accumulation in the region between the Ca adatom and the H\textsubscript{2} molecules and charge depletion above the Ca adatom and within the H–H bonding regions, in agreement with the work of Ataca et al. [15] Charge depletion along H\textsubscript{2} covalent bonds is consistent with longer H–H bond lengths, from 0.75 Å in the gas phase equilibrium structure to 0.78 Å in the adsorbed flat BF configurations. This form of binding has been discussed previously[15, 54] and is known as a Kubas interaction. More specifically, it arises from stabilization of the 3d state of Ca over the 4s state and back-donation of electron density from the valence Ca 4d state to the 1σ* state of the H\textsubscript{2} molecule. This mechanism is corroborated in the projected density of states (PDOS) of 4H\textsubscript{2}+Ca@Gr, shown in Fig 4(c). In addition, a Bader charge analysis[50, 55, 56] of the system shows that Ca has a partial positive charge of +1.3e on the Ca atom, which is consistent with the partial de-population of the Ca-4s state. We also find that one H atom in each H\textsubscript{2} molecule has accumulated a small Bader partial charge of −0.15e. H\textsubscript{2} bond-weakening can also be found on Sr@Gr and Ba@Gr, indicating that the Kubas mechanism underpins the adsorption of H\textsubscript{2} in these systems also.

Adsorbed H\textsubscript{2} molecules on Li, Na, K, Rb, and Cs metal decorated graphene, which are in an upright BF configuration, do not exhibit H–H bond weakening and the effect on the charge density from adsorption is also distinctly different (see SM[30] for the charge density difference for H\textsubscript{2} on Na@Gr). Indeed, the PDOS of 4H\textsubscript{2} on K@Gr in Fig. 4(a) shows no K occupied states near the Fermi energy, indicating complete charge transfer of the K valence electron to graphene and no occupation of the 1σ* states of the H\textsubscript{2} molecules. This is confirmed by a Bader analysis of the system, showing that K has a positive partial charge of +0.9e and H atoms have not gained (or lost) electron density. Given that alkali adatoms lose their single valence electron to graphene, the resulting positively charged adatom facilitates the adsorption of H\textsubscript{2} on the surface through a direct static polarization interaction with H\textsubscript{2} molecules. We can see from the adsorption energies in Table 1 that the order of H\textsubscript{2} adsorption strength coincides with the polarization strength of the alkali cation for 3H\textsubscript{2} adsorbed, such that the Li adatom binds H\textsubscript{2} the most strongly and the Cs adatom binds H\textsubscript{2} the least among the alkali metal adatoms we consider. With more than three H\textsubscript{2} molecules adsorbed, the trend holds from Na as Li is small and H\textsubscript{2} molecules become sterically hindered.

When the adsorption of H\textsubscript{2} is very weak, as in the case of Be and Mg decorated graphene, H\textsubscript{2} is radially orientated to the adatom while lying flat on graphene. The resulting H\textsubscript{2} configuration is similar to H\textsubscript{2} physisorption on pristine graphene.[6] Indeed, it was previously reported that the PBE+D3 adsorption energy of H\textsubscript{2} on pristine graphene is −53 meV,[6] while we find that the adsorption energy is −68 meV on Mg@Gr. The different adsorption mechanism of H\textsubscript{2} on Mg and Be adatoms to other alkaline earth metals can be understood in terms of the metal atom electronic structure. First, the valence 2s and 3s electrons of Be and Mg, respectively, cannot be stabilized to a d state and therefore they cannot bind H\textsubscript{2} molecules via Kubas bonding. Second, the ionization energies of Be and Mg are too high for graphene to oxidize the adatoms. Indeed, a Bader charge analysis of 4H\textsubscript{2}+Mg@Gr shows that Mg has only a small positive partial charge of +0.3e. The PDOS of 4H\textsubscript{2}+Mg@Gr in Fig. 4(b) demonstrates the intact Mg valence state and can be seen as an occupied s state just under the Fermi energy of graphene. As a result, Be and Mg remain uncharged atoms that H\textsubscript{2} molecules weakly interact with.

### V. INSIGHTS FOR BRIDGING TOWARDS EXPERIMENT

The binding mechanisms we outlined based on static thermodynamic models are foundational and several physical effects can be considered to bridge towards experiment. Here, we gauge the effect of a few important physical contributions that can play role in H\textsubscript{2} binding, specifically: adatom diffusion, H\textsubscript{2} dissociation, and the experimental form of graphene. Details of the computational setups can be found in Section II and the SM.[30]

First, we gauge the feasibility of Ca adatom diffusion across the graphene surface and the dissociative adsorption of H\textsubscript{2} on Ca@Gr as it is one of the most promising systems for H\textsubscript{2} binding according to our screening. We used the NEB method[51, 52] to predict the energy barrier for a Ca adatom to diffuse from its most stable adsorption site on pristine graphene, to the next most stable adsorption site. We find that the PBE+D3 energy barrier for Ca diffusion on graphene is 0.14 eV which can be considered thermally accessible under ambient conditions. Previous works report similar energy barriers, 0.12-0.16 eV, for Ca diffusion on graphene.[15, 57, 58] Meanwhile, H\textsubscript{2} dissociating on Ca@Gr would indicate storage via the spillover effect instead and we gauge the likelihood of this by fully relaxing 2H+Ca@Gr, with H atoms chemisorbed on graphene in the vicinity of Ca for two configurations. The fully relaxed structures can be found in the SM.[30] We find that 2H+Ca@Gr is 1.7 eV less stable than H\textsubscript{2}+Ca@Gr, suggesting that intact H\textsubscript{2} is thermodynamically stable on Ca@Gr. These calculations provide preliminary indications, but further work is needed to cement our predictions.

Second, in experiment, graphene can be found stacked in a few single layers, known as multi-layer graphene, and is also typically supported by a substrate such as silicon dioxide or a metal surface. A great deal of work has focused on uncovering the effects of different metal substrates on the structural and electronic properties of graphene. Here, we briefly explore the role of AB stacked bilayer graphene (GrGr) and near-fully commensurate metal substrate, Ni(111), on the H\textsubscript{2} binding mechanisms found in Section IV.

We fully relax three different binding motifs with GrGr: 4H\textsubscript{2}+Ca@GrGr, 4H\textsubscript{2}+K@GrGr, and 4H\textsubscript{2}+Mg@GrGr. The resulting
FIG. 4. The projected density of states (PDOS) within ±2 eV of the Fermi energy for 4H₂ adsorbed on (a) K@Gr, (b) Mg@Gr, and (c) Ca@Gr. The PDOS has been shifted to the Fermi energy for each system. The grey shaded region indicates the total DOS. H-s projection shown in orange and C-p projection shown in blue. H-s near the Fermi energy is due to the 1σ^* state of H₂, while the 1σ state around −8 eV relative to the Fermi energy cannot be seen in this energy window. The projection is over spherical functions centred on the atoms and as such, the sum of projected states may not sum to the total DOS. A schematic of the configuration of 4H₂ for each M@Gr system is shown in the insets.
binding configurations and the adsorption energies per H₂ molecule are in close agreement to those established on single layer graphene in Section IV. The adsorption energy per H₂ molecule is only 2 meV weaker on GrGr for Mg and Ca adatoms, and 7 meV stronger with K as the adatom. Therefore, we expect the effect of multi-layer graphene to be small for the binding mechanisms of H₂. Note that we only consider adatoms at the surface and not in the inter-layer regions.

Ni(111) is a widely-used and commercially available metal substrate for graphene, which minimally strains graphene thanks to the commensurate structure of the surface. Interestingly, Gr/Ni(111) exhibits two binding minima according to first principles predictions: a physisorption minimum (≥3 Å) and a more thermodynamically favourable chemisorption minimum (≈ 2 Å) that is in-line with experiment.[60] We briefly consider the impact of chemisorbed graphene on a Ni(111) substrate (GrNi) on the binding mechanisms in 4H₂+Ca@GrNi, 4H₂+K@GrNi, and 4H₂+Mg@GrNi. We find that the adsorption structure and energy in 4H₂+K@GrNi is practically unaffected with respect to 4H₂+K@Gr. In 4H₂+Mg@GrNi, we find that H₂ and Mg remain weakly physisorbed and in the same orientation, while the adsorption energy per H₂ is strengthened by ∼37 meV with respect to 4H₂+Mg@Gr. Most notably, we find that H₂ molecules relax into an upright bond-facing orientation in 4H₂+Ca@GrNi and the adsorption energy per H₂ molecule is also strengthened by ∼38 meV with respect to 4H₂+Ca@Gr. Therefore, there is a promising indication that the metal substrate used to support graphene can have a significant impact on the binding of H₂ and can be an important feature to exploit in future works.

VI. TUNING THE H₂ ADSORPTION ENERGY USING AN ELECTRIC FIELD

An ideal storage material for H₂ would allow the reversible cycling of gas and easy tuning of the H₂ adsorption energy would be an additional welcome feature. To this end, we report the effect of applying an electric field on the interaction with H₂ bound via the three mechanisms we have established. For the results in Fig. 5 we do not allow the atomic positions to relax under the applied electric field and as such, the results indicate the response of only the electron density to an applied field (i.e. the high-frequency limit). Specifically, we look at the interaction defined as:

\[ E_{\text{int}} = \left( E_{\text{ads@0}} - E_{\text{M@Gr}} - E_{\text{4H₂ bound}} \right) / 4 \]  

where \( E_{\text{ads@0}} \) is the total energy of the system with 4H₂ adsorbed on M@Gr fully optimized at zero-field, while \( E_{\text{M@Gr}} \) and \( E_{\text{4H₂ bound}} \) are the total energies of unrelaxed M@Gr and 4H₂ in the adsorption configuration at zero-field. Since Eq. 3 does not take into account any atomic relaxation, the resulting interaction energies do not convey the final adsorption energy at the applied electric field (low frequency limit). For example, it can be seen from Fig. 5 that \( E_{\text{int}} \) at zero-field is lower than \( E_{\text{ads}} \) reported in Table I and this is due to the unrelaxed reference subsystems in the definition of \( E_{\text{int}} \).

It can be seen from Fig. 5 that the effect of an external electric field (applied in the \( z \)-direction) on the H₂ interaction energy with K and Mg decorated graphene is minimal. The results suggest that interaction with H₂ is not easily perturbed for H₂ bound using weak physisorption (flat radial configurations on Be@Gr and Mg@Gr) or static polarization interactions (upright BF on alkali@Gr systems). However, it can be seen from Fig. 5 that the H₂ molecule interaction with Ca and Sr decorated graphene is strongly affected by an external electric field. With electric fields from −0.3 V Å⁻¹ to 0.3 V Å⁻¹ in the \( z \)-direction, the
interaction is decreased by $\sim 100$ meV per H$_2$ molecule. Since a positive electric field perpendicular to the graphene sheet draws electrons from the adatom towards graphene, H$_2$ adsorption weakens as the adatom electron density is depleted.

On relaxation of the 4H$_2$+Ca@Gr system under a positive electric field, we find that the H$_2$ molecules reorient themselves to the upright BF configuration (see Fig. 6) while the H–H bond length remains elongated (0.78 Å). This is also reflected in the PDOS of 4H$_2$+Ca@Gr shown in Fig. 6(c), where the Ca 3$d_{xy}$ and 3$d_{z^2}$ states at the valence band edge overlap with H$_2$ 1$\sigma^*$ state under zero-field and $-0.2$ V Å$^{-1}$ electric field, whereas under a positive electric field the 3$d_{z^2}$ state of Ca is overlapping with H$_2$ 1$\sigma^*$. In addition, it can be seen that the exchange splitting between the occupied spin-up 3$d_{z^2}$ state and the corresponding unoccupied spin-down state is ca. 0.5 eV under a positive electric field which indicates single electron occupancy of this state.

Under zero or negative electric field, the exchange splitting is smaller ($\sim 0.2$ eV) and we see that the corresponding spin-down state is partially occupied. In addition, it can be seen from Fig. 6 that occupation of Ca states near the Fermi energy increases with the electric field decreasing (i.e. from +0.2 to $-0.2$ V Å$^{-1}$). This corroborates that there is a higher density of electrons around the Ca adatom under zero and negative electric fields, facilitating a stronger Kubas interaction with H$_2$ molecules. By relaxing a single gas phase hydrogen molecule and the Ca@Gr substrate at $-0.2$ and $0.2$ V Å$^{-1}$ electric force fields (along the same z-direction), we find that the adsorption energy of 4H$_2$ on Ca@Gr is $-211$ and $-167$ meV, respectively, per H$_2$ molecule.

The difference of $\sim 50$ meV in H$_2$ adsorption energy on Ca@Gr when applying $-0.2$ and $0.2$ V Å$^{-1}$ electric force fields is consistent with the difference in the interaction energy reported in Fig. 5.

### Appendix: Derivation of eq. 1.

The H$_2$ vapor pressure is a key factor in determining the suitability of H$_2$ storage materials. Theoretical estimations of ideal H$_2$ vapor pressures have been proposed previously,[61, 62] resulting in ca. $-150$ to $-600$ meV adsorption energy range which is typically considered. The window of adsorption energies ultimately depends on several factors including the choice of fuel cells, device functionality, and the properties of the storage material. In our estimate we considered pressures from 3 bar to 100 bar and temperatures from 270 K to 390 K which covers intermediate and high temperature fuel cells.[3, 4] In the following heuristic approach, we show how we evaluate the H$_2$ vapor pressure, using coronene as a model substrate for flat
FIG. 6. Projected density of states (PDOS) for \( \text{4H}_2 + \text{Ca@Gr} \) with external electric fields of \(-0.2 \text{ V } \text{Å}^{-1}\) (a,b), no-field (c,d), and \(+0.2 \text{ V } \text{Å}^{-1}\) (e,f). The left panel shows close-ups around the Fermi level (shifted to zero) of the corresponding PDOS on the right. The legend corresponds to all plots. The total DOS (black line, area shaded in grey) is normalized while the projected states are shown only if their contribution is more than 1%. The blue shaded regions correspond to C-\( p \) states. The projections over spheres centred on the atoms in the unit cell may not add up to the total DOS due to missing interstitial regions. The fully-optimized adsorption structure at each electric field is also shown.

carbon based materials such as graphene, to arrive at our ideal adsorption energy estimate. We begin with the Gibbs free energy:

\[
G(p,T) = U + pV - TS,
\]

where \( p \) is pressure, \( T \) is temperature, \( U \) is the internal energy, \( V \) is volume and \( S \) is entropy. The chemical potential, \( \mu \), is the Gibbs free energy normalized for the number of particles \( N \):

\[
\mu(p,T) = \frac{G(p,T)}{N}.
\]

For the system at equilibrium: \( \mu_{\text{H}_2@Gr} = \mu_{\text{H}_2} + \mu_{\text{Gr}} \), and we can separate the electronic contribution to the energy, \( E_{\text{el}} \), which we compute from DFT, leaving the chemical potential of the phase-state (ps), \( \mu_{\text{ps}} \): \( \mu = E_{\text{el}} + \mu_{\text{ps}} \), where \( E_{\text{el}} \) accounts for the electronic energy at 0 K without zero-point energy contributions. According to Eq. 2, \( E_{\text{ads}} \) follows from the electronic contributions and thus we can write:

\[
0 = E_{\text{ads}} + \mu_{\text{H}_2@Gr}^{\text{solid}} - \mu_{\text{H}_2}^{\text{gas}} - \mu_{\text{Gr}}^{\text{solid}} \]  

(A.1)
where the phase-state is gas for H$_2$ and we assume H$_2$@Gr and Gr are solids. As H$_2$ is a homonuclear diatomic gas we assume it here to be ideal such that $\mu_{H_2}^{gas}$ can be expressed as:

$$\mu_{H_2}^{gas} = -k_B T \ln \frac{k_B T}{\rho \lambda^3} - k_B T (\ln Z_r + \ln Z_v)$$

(A.2)

where $\Lambda = \sqrt{\frac{h^2}{2\pi \hbar^2}}$ is the de Broglie thermal wavelength, $Z_r$ is the rotational partition function and $Z_v$ is the vibrational partition function. As a first approximation $Z_r \sim \frac{h k_B T}{\hbar^2}$, where $I = \frac{m_H \bar{r}^2}{4}$ is the moment of inertia. Within the harmonic approximation, the vibrational partition function is $Z_v = \frac{\exp(-\frac{\hbar \omega_j}{k_B T})}{1-\exp(-\frac{\hbar \omega_j}{k_B T})}$, where $\omega_j$ is the harmonic vibrational frequency of H$_2$.

In the case of solids only phonons need to be considered (in the leading approximation, as the volumes are negligible with respect to the gas phase, so the $pV$ term can be neglected) such that,

$$\mu_{solid} = -k_B T \ln Z_v^{solid}$$

(A.3)

for H$_2$@Gr and Gr, where the vibrational partition function can be evaluated within the harmonic approximation as $Z_v^{solid} = \prod_j \frac{\exp(-\frac{\hbar \omega_j}{k_B T})}{1-\exp(-\frac{\hbar \omega_j}{k_B T})}$; here $\omega_j$ is the vibrational frequency of the $j$-th normal mode. H$_2$@Gr has 6 more vibrational modes than Gr due to 5 vibrations from H$_2$ interacting with Gr and 1 mode corresponding to the H$_2$ internal vibration. As a leading order approximation, we assume that the vibrations of H$_2$ and Gr are the same in H$_2$@Gr, which allows us to simplify $\mu_{H_2@Gr} - \mu_{Gr}$ in Eq. A.1 as follows:

$$\mu_{H_2@Gr}^{solid} - \mu_{Gr}^{solid} + k_B T \ln Z_v^{H_2} = -k_B T \ln Z_v^{\mu}.$$  

(A.4)

Here, $Z_{iv} = \prod_{j=1}^{5} \frac{\exp(-\frac{\hbar \omega_j}{k_B T})}{1-\exp(-\frac{\hbar \omega_j}{k_B T})}$ is the vibrational partition function for the 5 inter-system modes, having the vibrational frequencies $\omega_j$, $j = 1, ..., 5$.

Thus, by using Eq. A.2 and Eq. A.4 in Eq. A.1, we arrive at an expression:

$$-k_B T \ln \frac{k_B T}{\rho \lambda^3} - k_B T \ln Z_r = E_{ads} - k_B T \ln Z_v$$

(A.5)

From this expression we extract the H$_2$ vapor pressure:

$$p = e^{\frac{E_{ads}}{k_B T}} \frac{k_B T}{\rho \lambda^3} \frac{Z_r}{Z_v}$$

(A.6)

In computing the vapor pressure, we can make a further approximation by assuming that physisorbed H$_2$ rotates freely such that $Z_r$ drops out along with two inter-system vibrational frequencies (which are essentially H$_2$ rotating on the substrate). Furthermore, we assume that 2 inter-system vibrations parallel to the surface (xy-plane) that are $\sim$ 80 cm$^{-1}$ are too weak for the harmonic approximation to be useful and thus we can neglect them, leaving us with the working equation:

$$p \sim \frac{k_B T}{\lambda^3} e^{\frac{E_{ads}}{k_B T}} \frac{1}{Z_v}$$

(A.7)

Expanding $\Lambda$ and $Z_v$, in Eq. A.7 yields Eq. 1. We consider the effect of this last approximation in Fig. 7 by comparison with using three inter-system vibrations (i.e. including those along the xy-plane that we deem too weak for the harmonic approximation).

We can see that the inclusion of the weak vibrational modes would suggest that even lower adsorption energies could be sufficient at the operating conditions of a fuel cell.

Finally, it is important to note that we used a molecular system, H$_2$ on coronene, as a model for H$_2$ on pristine graphene, to have an estimate frequency $\omega_z$, which is ca. 200 cm$^{-1}$. The ORCA quantum chemistry package,[63] and the PBE+D3 functional was used to compute vibrational frequencies. For a more accurate pressure-temperature profile, the inter-system vibrational frequencies would need to be known for each substrate material that is considered. Nonetheless, it is interesting that our estimated window of ideal adsorption energy is consistent with previous estimations.[61, 62]
FIG. 7. Temperature-pressure adsorption profile for $\text{H}_2$ according to the approximations shown in the legend. The red line corresponds to Eq. A.7. An adsorption energy of $-200$ meV is used to demonstrate the effect of different approximations and PBE+D3 inter-system vibrational frequencies of the $\text{H}_2$-coronene molecular system.

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