On the chemistry and mobility of hydrogen in the interstitial space of layered crystals \( h \)-BN, MoS\(_2\), and graphite

Yun An,\(^1\) Agnieszka Kuc,\(^{1,2}\) Petko Petkov,\(^3\) Marcelo Lozada-Hidalgo,\(^4\) and Thomas Heine\(^{1,2,5*}\)

\(^1\)Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig, Germany

\(^2\)Helmholtz-Zentrum Dresden-Rossendorf, Abteilung Ressourcenökologie, Forschungsstelle Leipzig, Permoserstr. 15, 04318, Leipzig, Germany

\(^3\)Faculty of Chemistry and Pharmacy, University of Sofia, 1 James Bourchier blvd., 1164 Sofia, Bulgaria

\(^4\)School of Physics & Astronomy, University of Manchester, UK

\(^5\)Theoretical Chemistry, TU Dresden, Mommsenstr. 13, 01062 Dresden

*email: thomas.heine@tu-dresden.de

KEYWORDS: proton and atomic hydrogen transport, 2D membranes, quantum confinement, density functional theory, well-tempered metadynamics simulations, free energy landscape.
ABSTRACT: Recent experiments have demonstrated transport and separation of hydrogen isotopes in layered materials, such as hexagonal boron nitride and molybdenum disulphide. Here, based on first-principles calculations combined with well-tempered metadynamics simulations, we report the chemical interactions and mobility of protons (H⁺) and protium (H atoms) in the interstitial space of these layered materials. We show that both H⁺ and H can be transported between the layers of h-BN and MoS₂ with low free energy barriers, while they are immobilized in graphite, in accordance with the experimental observations. In h-BN and MoS₂, the transport mechanism involves a hopping process between the adjacent layers, which is assisted by the low-energy phonon shear modes. Defects present in MoS₂ suppress the transport and act as traps for H species.

Introduction. Recently, Hu et al.¹ reported hydrogen isotope separation by sieving through the interstitial space of layered materials, namely, hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS₂). While the difference in the entry barrier of the hydrogen isotopes into the interstitial space of the layered materials was found to be the driving factor for the isotope separation, there is no conclusive picture yet on the chemical interaction of interstitial hydrogen with the layered materials, and on the transport mechanism through them.

Spatial confinement has a strong impact on the chemical properties of molecules.²⁻⁴ The layers of h-BN, MoS₂, and graphene are chemically very stable, if not inert, and the interlayer interactions impose pressure on the intercalated species.⁵⁻⁷ So, the chemistry in the interstitial space of a layered material is expected to be significantly different from the surface-adsorbed counterpart.

The experimental setup in the work of Hu et al.¹ does not allow to conclude if protons (H⁺) or protiums (H atoms) enter the layered material: For protons, immediate neutralization is expected,
as the proton’s electron affinity of 13.6 eV is significantly higher than the work function of the host materials, even for wide band gap insulators such as h-BN. On the other hand, any two H atoms encountering each other are expected to recombine immediately due to the high formation energy of H₂ (4.52 eV in gas phase).⁸ The observed transport process of hydrogen through h-BN and MoS₂ requires, therefore, further investigation.

Here, we explore, on grounds of density-functional theory (DFT – for details see Methods section and Supporting Information (SI)), the chemical interaction and mobility of both H and H⁺ species in the layered materials of h-BN, MoS₂, and graphite. We show that both H⁺ and H can be accommodated in h-BN and MoS₂, and that diffusion is possible via a low-energy transport mechanism that is assisted by the rigid-layer shear modes,⁹ which have low frequency due to weak interlayer-interactions¹⁰ (these modes have been observed in the Raman spectra at 52.5 cm⁻¹ and 33.7 cm⁻¹ for h-BN⁹ and MoS₂,¹¹ respectively). For both H and H⁺ transport follows a zigzag hopping motion between adjacent layers. Diffusion in MoS₂ has a lower barrier than in h-BN, however, sulfur vacancies – a typical defect in MoS₂¹² – act as hydrogen traps and suppress the transport. In graphite, protons are immediately neutralized to H atoms, which themselves are almost immobile once bound to the carbon atoms.¹³,¹⁴

Results and Discussions

Structure and formation of proton- and protium-intercalated h-BN, MoS₂, and graphite.

We first study the static, fully optimized structures with single proton (H⁺) or protium (H atom) confined in the interstitial space of layered crystals of h-BN, MoS₂, and graphite. Details of the simulations are shown in Methods section and SI (Figures S1-S5). A proton located in the interstitial space of layered h-BN binds to a N atom, forming a N-H bond with a bond length of
1.05 Å, and locally slightly decreases interlayer separation. On the contrary, a H atom forms a B-H bond of 1.32 Å length and slightly increased interlayer separation. Details are shown in Figure 1 and Table S1 in SI. Due to the additional fourth bond, which forms upon binding H+ or H, both N and B atoms transform from sp2 to sp3 hybridization and thus pyramidalize to approach a tetrahedral configuration. In MoS2, proton (or H atom) connects to a S atom, forming a S-H bond of 1.37 (1.43) Å, and also slightly decreases (increases) locally the interlayer distance. For metallic graphite, proton immediately neutralizes once it enters into the interlayer space, and binds to a C atom, forming a C-H bond of 1.12 Å, and the interlayer distance increases due to the pyramidalization of the binding carbon atom, similar to the case of h-BN.

![Figure 1](image.png)

**Figure 1.** Side view of H and H+ bound to layered materials. In h-BN, H binds to B and H+ binds to N; in MoS2 both species bind to S; in graphite, H+ gets neutralized, H binds to C. Binding atoms in h-BN and graphite are pyramidalized. Here, similar to the nomenclature in endohedral fullerenes, @ indicates the H+ or H bound to the crystal.
Considering the experimental setup of Hu et al., we estimate the total transfer energies of H\(^+\) or H from the hydrogenated Pd side electrodes and the layered crystals. The transfer reactions

\[
[Pd_nH_m]^+ + hBN \rightarrow [Pd_nH_{m-1}] + H^+@hBN
\]

\[
[Pd_nH_m] + hBN \rightarrow [Pd_nH_{m-1}] + H@hBN
\]

are described by thermodynamic cycles (see SI for details on partial reactions and details). Both reactions are strongly endothermic with overall 2.18 eV for the transfer of a proton and 2.54 eV for the transfer of an H atom from the PdH\(_x\) electrodes to h-BN. This rough estimate mainly serves to illustrate the expectation that it is much more favorable for a proton to enter the layered material. It is interesting to note that the protium recombination in the lattice, calculated to be 3.46 eV, would lower the energy by 1.73 eV per atom, resulting in 0.81 eV per atom. The full thermodynamic simulation of the process of proton/protium transfer in the device is beyond our present capabilities and requires more detailed atomistic information about the interface from the experiment.

Based on the Hirshfeld atomic charge analysis we check the electronic structures of H\(^+\) or H atom bound to the crystal layers. Due to the high ionization potential of hydrogen, H\(^+\) picks up an electron (\(~0.9\) e\(^-\) both in h-BN and MoS\(_2\)) and is bound to the crystal lattice. This charge is transferred mainly from the atoms that are in closest vicinity. Thus, the proton itself is almost neutralized, while the N or S atoms, to which the proton binds, become positively charged. Also, the second neighbors become slightly more positive, but the effect is much weaker than for the binding atom. This effect is also shown by the electron density isosurfaces (see Figure S6 in SI).

Even though the protons get immediately neutralized by the surrounding atoms of the crystal, in the remainder, we will still use the term proton in order to acknowledge the local charge of the
system. On the other hand, no charge transfer between the h-BN, MoS$_2$ or graphite layers and the bound H atom is observed.

**Diffusion process of proton and protium inside h-BN, MoS$_2$, and graphite.**

Next, we have simulated the diffusion process of the protons and H atoms through the interstitial space between the layers of 2D materials, again focusing first on h-BN. As both H and H$^+$ bind to atoms of the crystal lattice, we investigated the transport process between individual binding sites. As the system has many degrees of freedom, including low-energy vibrational modes, with rather large amplitudes, we employed well-tempered metadynamics$^{15}$ (WTMetaD) to determine the free-energy surface (FES) and to analyze the diffusion barriers of H and H$^+$ travelling through the interstitial space of the layered materials (for details of WTMetaD and DFT calculations see SI). The FES and the diffusion barriers for H$^+$ and H atom are discussed below in detail. Note that WTMetaD diffusion is governed by Brownian motion, thus, the directionality of the diffusion is not defined. However, below, we will refer to this as “path”. The information that is the most important from these simulations is the lowest free energy barrier for the transfer of hydrogen species in between the layers. At the end, we will also comment on the directionality of the diffusion for both species, assuming the conditions present in the experiment.

We first concentrate on h-BN: the low-energy path for H and H$^+$ diffusing through h-BN are shown in **Figure 2a-b** and **Figure 2c-d**, respectively. The estimated free energy is 0.46 eV for H$^+$ and 0.08 eV for H, which is perfectly consistent with the experimental data.$^1$ In our simulations, H$^+$ (H atom) is initially bound to the nitrogen atom N1 (boron atom B1) in one layer (black; **Figure 2a** and e), which are the preferential binding sites. Layered materials, such as h-BN, exhibit low-energy shearing modes.$^9,10$ Once the shearing brings a N atom of the adjacent
layer to the vicinity of the proton, there is a high probability that proton jumps to the closest N atom (N2, red) in the adjacent layer. The next jump (N2 to N3, green) then goes back to the first layer, and so forth, resulting in a zigzag transport path between layers. Thus, after each two successive jumps, the proton can be displaced by 2.5 Å, or the shortest intralayer N-N distance. The diffusion process of H atom follows a similar shear-assisted process, with the difference that the binding sites are now the B atoms, see Figure 2 c and d, and that the FES is shallower due to the lower binding strength of H atom to the lattice, when compared to protons. The trajectory for this process is shown in Figure S3 in SI.

It is important to note that proton carries its charge during the hopping process: even though the proton is nearly neutralized while being bound to N atom, when dislocating to the next N
adsorption site, it leaves the electron behind. The atomic charge analysis shows that the electronic configuration of the layer recovers to the pristine state after the proton has left.

Close inspection of the WTMetD pathway suggests that the shear mode, where the individual layers slide against each other, significantly shortens the distance between the two next low-energy hopping sites (the next N or B atom in the neighboring layer), and thus, has a strong effect on the hopping barrier (and even more so on the tunneling probability, which is neglected in this work), as depicted in Figure S4. Indeed, the barrier for the interlayer shear in \textit{h}-BN has been found to be rather small, as low as 8 meV and 2 meV, for the shearing between the most stable AA’ stacking to the A’B (N over N) and to AB’ (B over B), respectively.\textsuperscript{16,17} We estimate that the transition barrier between the layers in static calculations, as shown in Figure S4, substantially lowers the hopping energy barrier by \textasciitilde0.5 eV, which is expected to lead to a very small free energy barrier of the overall motion. In conclusion, our simulations suggest that the transport of protons, and also of H atoms, through the interstitial space, follows a shear-mode assisted zigzag hopping pathway.

After we have understood the diffusion process of H\textsuperscript+ and H through the layers of \textit{h}-BN, we have to answer the intriguing question: what is the force which drives the diffusion? In other words, what is responsible for the directional diffusion of both species? In the case of H\textsuperscript+, one would assume that Coulomb repulsion between the protons and the electric field gradient between the electrodes can serve as the driving force for the diffusion. For the H atom, the only driving mechanism can be a concentration gradient, which requires the interaction of H atoms with each other. In the gas phase, the formation of H\textsubscript{2} is associated with a large exothermic reaction energy of -4.5 eV (both experimental and our theoretical value).\textsuperscript{8} Confined in the \textit{h}-BN lattice, this energy somewhat reduces to -3.46 eV (calculated in a 7\times7\times2 supercell model). This energy still
suggests that H atoms, even if they manage to enter the $h$-BN lattice as atomic species, strongly prefer recombination inside the lattice, unless there is a substantial kinetic barrier preventing recombination.

The hypothesis of a kinetic barrier was tested by placing two H atoms into the simulation box. Three scenarios, as shown in Figure 3, describe the interaction of two approaching H atoms in the lattice: 1) both H atoms are in the same interstitial space and attached to the same layer, 2) both H atoms are in the same interstitial space and attached to neighboring layers, or 3) both H atoms are in neighboring interstitial spaces and bound to the same layer. Further, we consider all possible spin states of both H atoms. Single H atom carries a single spin, therefore, the following combinations of two H atoms can be considered: either singlet, triplet, or, for large distances, antiferromagnetic singlet. At close distance, only two configurations are possible, which reflect the H$_2$ molecule in the bonding singlet or in the antibonding triplet state. These simulations are summarized in Figure 3.

For large distances, protiums do not interact with each other. If they approach each other, they would not interact in case of parallel spins (Figure 3, red curves, modeled as the triplet state), but spin relaxation will favor the much more stable singlet state. Independent if the protiums are bound to the same (Figure 3a) or neighboring (Figure 3b) layers, for distances above 2 Å, a proton-hydride pair with the hydride bound to a boron and proton bound to the nitrogen is the most stable configuration (black curves), and additional Coulomb attraction will readily form the most stable structure, namely H$_2$ molecule in the interstitial region of the $h$-BN lattice (blue triangles). Also if the H atoms are bound to the same layer, but at opposite interstitial sites, the formation of local proton-hydride pairs is energetically favored (Figure 3c).
Figure 3. Relative energy ($E_{\text{rel}}$) of 2 H atoms in $h$-BN with respect to $H_2$ molecule in the interstitial space of $h$-BN lattice as function of distance between the 2 H atoms. Two H atoms bind to the same layer (a), adjacent layer (b) or the same layer but different interstitials (c). The blue triangles indicate $H_2$ molecule in the interstitial space, black circles proton-hydride ($H^+ - H^-$) pairs, attached to N and B atom. The red squares show two non-interacting protiums (modeled as triplet state). For spin flip energies between the triplet and antiferromagnetic single see Table S2 in SI.

We now turn to the case of MoS$_2$ layered crystals, for which we performed the same type of WTMetaD simulations of $H^+$ and H inside the interstitials. Both protium and proton inside MoS$_2$ bind to S atoms with very similar binding strengths (see SI for details). The transport mechanism is very similar to that in $h$-BN: Initially, $H^+$ or H bind to sulfur atom S1 (see Figure 4a; black). As in $h$-BN, the diffusion is assisted by the shear modes, which allow the transfer from S1 to S2 or S3 in the adjacent layer. The next transfer can then either go back to the starting point, or hop to the next site, and so on. The trajectories are very similar in both cases, therefore, in Figure 4a, we only show the example of $H^+$. Thus, both H and $H^+$ in MoS$_2$ are also transported along a zigzag path, hopping between the neighboring layers and the transfer is supported by low-energy
shear modes. The corresponding FES plots are given in Figure 4b and c. The FES profiles show the free energy barriers of 0.11 eV for H\(^+\) and 0.09 eV for H atom. Unlike in the case of h-BN, the barriers in MoS\(_2\) are very similar, because of the same type of bonding atoms. These energy barriers are smaller than in the case of h-BN for the proton, while slightly higher for H atom inside h-BN.

![Figure 4](image)

**Figure 4.** (a) Schematic of the H\(^+\) transfers path in perfect MoS\(_2\), (b) Free energy surface of H\(^+\) and (c) of H atom transfer along the MoS\(_2\) interstitial.

However, in contrast to graphite or h-BN, defects are much more common in the natural or synthesized MoS\(_2\), typically with a dominant occurrence of sulfur vacancies.\(^{12}\) Therefore, we studied also the diffusion of H species in the presence of this defect type. The WTMetaD results
are shown in Figure S7, revealing that both H and H$^+$ are attracted strongly by the S atoms surrounding the vacancy site. The vacancy traps the travelling species and this effect appears to be stronger for H atoms than for protons. The FES for protons is 0.10 eV, close to the barriers in a perfect material. For H atom, we have obtained two different barriers, 0.06 and 0.25 eV, which might be due to the charge redistribution close to the vacancy and different binding strengths to the S atoms in the vicinity of the vacancy and far from it (see Figure S8). The smaller barrier corresponds to the hopping between binding sites far from the vacancy, which is similar to the case of a perfect system. The higher barrier corresponds to the hopping between binding sites close to the vacancy, showing that these sites interact much stronger with H atoms. The vacancies, therefore, suppress the overall transport properties of MoS$_2$, which could explain why in the experiment h-BN is a better hydrogen conducting material than MoS$_2$.\textsuperscript{1}

Finally, we have investigated H atom inside graphite (proton gets immediately neutralized inside this system). Here, however, we have not observed any H atom transfers with free energy barriers similar to the other materials, meaning that this process would require much higher activation energies and would be improbable in the experimental conditions (see Figure S9). This finding is consistent with the experimental results,\textsuperscript{1,18} which show that graphite does not conduct hydrogen.

In conclusion, both H$^+$ and H atom can diffuse easily through the interstitial space of layered materials h-BN and MoS$_2$, while they are immobile in graphite. The overall lattice of the layered materials remains intact. Locally, protons bind to N (S for MoS$_2$), pick an electron from the lattices and leave a charged site that extends over a few atoms. At low concentration, this charged state will be maintained. Protons could be transported between the layers of such 2D materials due to the Coulomb repulsion between the protons and the electric field gradient
between the electrodes. On the other hand, protiums will bind to B (S for MoS$_2$) atoms. If two protiums are getting close, they will form proton-hydride pairs, and at high concentration, they will recombine to H$_2$. Thus, for low concentration, both pathways are in principle possible. In both carrier materials, the transport process is supported by the shear modes of the material and follows a hopping process between neighboring layers. Our results should be of interest for hydrogen transport in other layered van der Waals materials, which could be important for applications, such as hydrogen isotope separation or proton exchange membranes.

**Methods.** All calculations were performed using density functional theory (DFT) with Perdew-Burke-Ernzerhof (PBE)$^{19}$ functional and D3 correction of van der Waals interactions following the Grimme approach$^{20}$ as implemented in the CP2K 3.0 package.$^{21}$ The Quickstep method was employed, with Goedecker-Teter-Hutter (GTH)$^{22}$ pseudopotentials together with DZVP-MOLOPT-GTH-SR basis set for Mo, S, B, C, and N. Hydrogen was treated with the DZVP-all electron basis set and all-electron potential. The plane-wave energy cutoff was set to 360 Ry. All atomic positions and lattice parameters were fully optimized, the optimized parameters for all the systems are given in Table S1. For more details see Methods in SI.

**ASSOCIATED CONTENT**

**Supporting Information.** Methods description, including models and software setups; binding energies of H species with 2D materials; thermodynamic cycle; Hirschfeld charge analysis; proton and protium transport in defective MoS$_2$ system; protium transport inside graphite; static calculations of energy barriers for H species transfer.

The following files are available free of charge.

SI_H_species_transport (PDF)
AUTHOR INFORMATION

Corresponding Author

*Thomas Heine email: thomas.heine@tu-dresden.de

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We gratefully acknowledge ZIH Dresden for computer time. Y. An acknowledges China Scholarship Council. Y. An and A. Kuc acknowledge Deutsche Forschungsgemeinschaft (DFG) GRK 2247/1 (QM3) for financial support.

REFERENCES

1. Hu, S.; Gopinadhan, K.; Rakowski, A.; Neek-Amal, M.; Heine, T.; Grigorieva, I. V.; Haigh, S. J.; Peeters, F. M.; Geim, A. K.; Lozada-Hidalgo, M., Transport of Hydrogen Isotopes through Interlayer Spacing in Van Der Waals Crystals. Nature Nanotech. 2018, 13, 468-472.
2. Kitagawa, S.; Matsuda, R., Chemistry of Coordination Space of Porous Coordination Polymers. Coord. Chem. Rev. 2007, 251, 2490-2509.
3. Fu, Q.; Bao, X., Surface Chemistry and Catalysis Confined under Two-Dimensional Materials. Chem. Soc. Rev. 2017, 46, 1842-1874.
4. Chen, Z.; Leng, K.; Zhao, X.; Malkhandi, S.; Tang, W.; Tian, B.; Dong, L.; Zheng, L.; Lin, M.; Yeo, B. S.; Loh, K. P., Interface Confined Hydrogen Evolution Reaction in Zero Valent Metal Nanoparticles-Intercalated Molybdenum Disulfide. Nature Commun. 2017, 8, 14548.
5. Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H., 2d Materials and Van Der Waals Heterostructures. Science 2016, 353.
6. Geim, A. K.; Grigorieva, I. V., Van Der Waals Heterostructures. Nature 2013, 499, 419.
7. Britnell, L.; Ribeiro, R. M.; Eckmann, A.; Jalil, R.; Belle, B. D.; Mishchenko, A.; Kim, Y.-J.; Gorbachev, R. V.; Georgiou, T.; Morozov, S. V.; Grigorenko, A. N.; Geim, A. K.;
Casiraghi, C.; Neto, A. H. C.; Novoselov, K. S., Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films. *Science* 2013, *340*, 1311-1314.
8. Blanksby, S. J.; Ellison, G. B., Bond Dissociation Energies of Organic Molecules. *Acc. Chem. Res.* 2003, *36*, 255-263.
9. Kuzuba, T.; Era, K.; Ishii, T.; Sato, T., A Low Frequency Raman-Active Vibration of Hexagonal Boron Nitride. *Solid State Commun.* 1978, *25*, 863-865.
10. Geick, R.; Perry, C. H.; Rupprecht, G., Normal Modes in Hexagonal Boron Nitride. *Phys. Rev.* 1966, *146*, 543-547.
11. Verble, J. L.; Wietling, T. J.; Reed, P. R., Rigid-Layer Lattice Vibrations and Van Der Waals Bonding in Hexagonal MoS2. *Solid State Commun.* 1972, *11*, 941-944.
12. Vancso, P.; Magda, G. Z.; Peto, J.; Noh, J. Y.; Kim, Y. S.; Hwang, C.; Biro, L. P.; Tapasztó, L., The Intrinsic Defect Structure of Exfoliated Mos2 Single Layers Revealed by Scanning Tunneling Microscopy. *Sci. Rep.* 2016, *6*, 29726.
13. Chen, L.; Cooper, A. C.; Pez, G. P.; Cheng, H., Density Functional Study of Sequential H2 Dissociative Chemisorption on a Pt Cluster. *J. Phys. Chem. C* 2007, *111*, 5514-5519.
14. Yazyev, O. V., Magnetism in Disordered Graphene and Irradiated Graphite. *Phys. Rev. Lett.* 2008, *101*, 037203.
15. Barducci, A.; Bussi, G.; Parrinello, M., Well-Tempered Metadynamics: A Smoothly Converging and Tunable Free-Energy Method. *Phys. Rev. Lett.* 2008, *100*, 020603.
16. Constantinescu, G.; Kuc, A.; Heine, T., Stacking in Bulk and Bilayer Hexagonal Boron Nitride. *Phys. Rev. Lett.* 2013, *111*, 036104.
17. Marom, N.; Bernstein, J.; Garel, J.; Tkatchenko, A.; Joselevich, E.; Kronik, L.; Hod, O., Stacking and Registry Effects in Layered Materials: The Case of Hexagonal Boron Nitride. *Phys. Rev. Lett.* 2010, *105*, 046801.
18. González-Herrero, H.; Gómez-Rodríguez, J. M.; Mallet, P.; Moaied, M.; Palacios, J. J.; Salgado, C.; Ugeda, M. M.; Veuillen, J.-Y.; Yndurain, F.; Brihuega, I., Atomic-Scale Control of Graphene Magnetism by Using Hydrogen Atoms. *Science* 2016, *352*, 437-441.
19. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, *77*, 3865-3868.
20. Grimme, S.; Ehrlich, S.; Goerigk, L., Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* 2011, *32*, 1456-1465.
21. Hutter, J.; Iannuzzi, M.; Schöffmann, F.; VandeVondele, J., Cp2k: Atomistic Simulations of Condensed Matter Systems. *Wires: Comput. Mol. Sci.* 2014, *4*, 15-25.
22. Goedecker, S.; Teter, M.; Hutter, J., Separable Dual-Space Gaussian Pseudopotentials. *Phys. Rev. B* 1996, *54*, 1703-1710.

TOC Figure:
Supporting information for

On the chemistry and mobility of hydrogen in the interstitial space of layered crystals $h$-BN, MoS$_2$, and graphite

Yun An,$^1$ Agnieszka Kuc,$^{1,2}$ Petko Petkov,$^3$ Marcelo Lozada-Hidalgo,$^4$ and Thomas Heine$^{1,2,5,*}$

$^1$Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig, Germany

$^2$Helmholtz-Zentrum Dresden-Rossendorf, Abteilung Ressourcenökologie, Forschungsstelle Leipzig, Permoserstr. 15, 04318, Leipzig, Germany

$^3$Faculty of Chemistry and Pharmacy, University of Sofia, 1 James Bourchier blvd., 1164 Sofia, Bulgaria

$^4$School of Physics & Astronomy, University of Manchester, UK

$^5$Theoretical Chemistry, TU Dresden, Mommsenstr. 13, 01062 Dresden

*email: thomas.heine@tu-dresden.de
Methods Description

Models: We have studied three layered materials, namely h-BN, MoS$_2$, and graphite (see Figure S1). For all the systems, the interaction of proton (H$^+$) and hydrogen atom (H) with the layers was investigated. We used the following supercells to describe the interactions: the 4×4×2 supercell was used for both h-BN and graphite, while 4×4×1 supercell for MoS$_2$, resulting in 128 atoms in h-BN and graphite, and 96 atoms in MoS$_2$. The fully optimized lattice parameters of each system are shown in Table S1 and are in a fairly good agreement with the experimental values.$^{1-3}$

![Figure S1](image.jpg)

**Figure S1.** Top and side views of layered materials considered in the present work.

**Table S1.** Calculated lattice parameters ($a$, $b$, and $c$) and the interlayer distances ($d$) in perfect h-BN, MoS$_2$, and graphite, shown with and without H species bound to the layers. Available experimental data are given in parenthesis.$^{1-3}$ Bond distances between H$^+$ or H atom and the binding atoms are also given.

| System      | $a = b$ (Å) | $c$ (Å)        | $d$ (Å)        | X—H (Å)       |
|-------------|-------------|----------------|----------------|---------------|
| h-BN        | 2.512 (2.504) | 6.784 (6.661) | 3.393 (3.330) | -             |
| H$^+$@h-BN  | 2.510       | 6.539          | 3.286          | 1.052 (N-H)   |
| H@h-BN      | 2.513       | 6.845          | 3.427          | 1.322 (B-H)   |
|                | MoS$_2$      | H$^+$@MoS$_2$ | H@MoS$_2$   | Graphite   | H@Graphite |
|----------------|-------------|--------------|-------------|-------------|-----------|
|                | 3.164 (3.150) | 3.150        | 3.160       | 2.466 (2.460) | 2.467     |
|                | 12.320 (12.300) | 12.124       | 12.365      | 6.828 (6.710) | 6.874     |
|                | 6.160 (6.150)   | 6.062        | 6.178       | 3.414 (3.355) | 3.429     |
|                | -            | 1.370 (S-H)  | 1.426 (S-H) | -           | 1.124 (C-H) |

**Methods:** Well-tempered metadynamics$^4$, $^5$ (WTMetaD) simulations were performed using CP2K 3.0 package.$^6$ The canonical NVT ensemble$^7$ (constant number of atoms (N), constant volume (V) and constant temperature (T)) was employed for all WTMetaD simulations; the temperature was set to 300 K using CSVR (canonical sampling velocity rescaling) thermostat,$^8$ with the temperature parameter delta _T of 1500 K and a time step of 0.5 fs. Every 200 steps, a Gaussian hill was spawned, the adopted Gaussian hills height and width were set to 1x10$^{-3}$ hartree and 0.1 (internal cp2k units), respectively. Each simulation was preceded by standard molecular dynamics simulations (MD; NVT, 300K, time step of 0.5 fs). During WTMetaD simulations, we have defined two collective variables (CVs) to trigger the process of H$^+$ or H transfer (see Figure S2). Exemplary explanation for H$^+$ in h-BN supercell of CVs: all the nitrogen atoms in h-BN are divided into three different kinds: N1 (inner layer with H$^+$ bound), N2 (inner layer neighboring N1), and N (outermost layers). One of the collective variables, CV1, is defined as the coordination number of H$^+$ to N1, while the other collective variable, CV2, is defined as the coordination number of H$^+$ to N2. Similar CVs were defined for MoS$_2$ and graphite. The form of the coordination function is defined in CP2K as follows:

$$CN_{H-X} = \sum_i^H \sum_j^X \frac{1 - \left(\frac{r_{ij}}{R_0}\right)^6}{1 - \left(\frac{r_{ij}}{R_0}\right)^{12}}$$

For the CVs defined in each system, the following reference H-X (X = N, C, B, or S) distances ($R_0$) were used: 2.3 bohr for H$^+$@hBN, 2.5 bohr for H@graphite, 2.9 bohr for H@hBN, 3.0 bohr for H@MoS$_2$ and H$^+$@ MoS$_2$. These parameters are slightly larger (up to 10%) than the average value in the fluctuation of the corresponding H-X distances during the BOMD simulations. Thus,
when the H or H\(^+\) is close to the transition state region, the coordination number of H to X is close to 0. Note that in the present models, WTMetaD setup, and the definition of the CVs, the hopping between the layers can be discussed, however, the direction of the transport is not defined and is governed by Brownian motion. To understand the latter, more CVs would need to be defined, e.g., the so-called path CVs, in several different directions, in order to sample the whole free-energy landscape (this is beyond the scope of this work). We have also investigated the case with three CVs specified, where the third one describes the hopping of H species within the same layer. However, such a process was not observed with the employed number of hills, thus in all cases, the free energy barrier for transport within the same layer was much higher than between the layers. Thus, it is a safe choice to reduce the number of CVs to just the two discussed above.

**Figure S2.** The definition of the collective variable in the WTMetaD simulations.

The change of the bond lengths between H species and binding atoms during the WTMetaD trajectories are shown in **Figure S3** (color scheme as in Figures 2a and c in the main text) for h-BN and MoS\(_2\). Note that the time scales are only internal computational parameters and of limited usefulness for direct interpretation. The most important results from the WTMetaD is the free-energy barrier for the H species transferred between the layers.
Figure S3. N-H (a), B-H (b) and S-H (c) bond distance changes during the WTMetaD simulations.

**Static calculations**: Layered materials exhibit low-energy shearing modes, therefore, we have investigated the potential energy barriers for H\(^+\) transfer between the layer in two different layer stackings of h-BN, namely AA’ (N over B) and A’B stackings (N over N).\(^9\) Such exemplary static calculations reveal strong energy barrier reduction when changing the stacking of the layers. For the AA’ stacking, the barrier is as large as 0.65 eV, whereas for the A’B stacking is only 0.17 eV, supporting our conclusion about the shear-assisted transport of H species between layers of the studied systems. For MoS\(_2\), the shear mode also exists, but the transfer barrier is nevertheless very low and in the static simulations, we have obtained 0.16 eV, see Figure S4, close to 0.11 eV in WTMetaD.
Figure S4. Static calculations of the potential energy barriers of H\(^+\) transfer between layers of h-BN in the AA’ and A’B stacking faults (a) and in MoS\(_2\) (b).

**Binding Energies:** The binding energies were calculated as follows (explained on the example of h-BN with H\(^+\)): \(E_b = E_{H^+@h-BN} - E_{h-BN} - E_{H^+}\), with \(E_{h-BN}\) and \(E_{H^+}\) being the energies of the perfect h-BN and proton, respectively, and \(E_{H^+@h-BN}\) being the total energy of the combined structure of H\(^+\)@h-BN. Due to the difficulty to calculate total energies of charged solid-state materials, we have used cluster models. For this purpose, we used Gaussian 09 software\(^{10}\) to calculate the binding energy of proton in h-BN cluster with different flake sizes and number of layers (pyrene and coronene cluster models with 1-4 layers). These calculations were performed using B3LYP functional\(^{11}\) with 6-311+g (d, p) basis set, both with and without zero point energy correction (see Figure S5). We found that the binding energies corrected with zero-point energy converge to -8.55 eV in pyrene and -8.61 eV in coronene cluster models.
Estimation of transfer energy using a thermodynamic cycle: Considering the experimental conditions, the H species are injected from the PdHₓ electrodes, then diffuse through the evaporated Pd thin film before encountering the h-BN layered crystal.¹² The total reaction for H⁺ in h-BN interspace can, therefore, be written as:

\[
[PdₙHₘ⁺] + h-BN \rightarrow [PdₙHₘ⁻₁] + H⁺@hBN
\]

The above equation is the sum of the partial reactions:

\[
[PdₙHₘ⁺] + e^- \rightarrow PdₙHₘ \quad \Delta E = -5.22 \text{ eV, experimental}^{13}
\]

\[
PdₙHₘ \rightarrow PdₙHₘ⁻₁ + 1/2H₂ \quad \Delta E = 0.15 \text{ eV, experimental}^{14}
\]

\[
1/2H₂ \rightarrow H \quad \Delta E = 2.25 \text{ eV, experimental}^{15}
\]

\[
H \rightarrow H^+ + e^- \quad \Delta E = 13.6 \text{ eV, exact}
\]

\[
H^+ + h-BN \rightarrow H^+@hBN \quad \Delta E = -8.6 \text{ eV, calculated, this work.}
\]

Sum of all the above partial energies gives the total transfer energy for H⁺ in h-BN of 2.18 eV.

The total reactions for H atom in h-BN interspace can be written as:

\[
[PdₙHₘ] + h-BN \rightarrow [PdₙHₘ⁻₁] + H@hBN
\]

This equation can be separated to:
PdₙHₘ → PdₙHₘ₋₁ + 1/2 H₂ \quad \Delta E = 0.15 \text{ eV, experimental}^{14}

1/2 H₂ → H \quad \Delta E = 2.25 \text{ eV, experimental}^{15}

H + h-BN → H@hBN \quad \Delta E = 0.14 \text{ eV, calculated, this work}

Therefore, the total reaction energy for H atom transfer in between h-BN layers sums up to 2.54 eV. If H atoms recombine at the interface to H₂, the transfer energy is lowered by 1.73 eV (half of the H₂ recombination energy), resulting in 0.81 eV per H atom.

**The electron density:** The isosurfaces of electron density of h-BN and MoS₂ bulk systems with and without bound H species are shown in Figure S6. In the cases of H atom in h-BN or MoS₂ system, there is no charge transfer between the H atom and the crystal layers.

![Figure S6](image)

Figure S6. Electron density isosurfaces of h-BN (a) and MoS₂ (b) bulk systems with and without H⁺ and H bound to the layers.
**Proton transport in defective MoS$_2$:** The WTMetaD simulations of H$^+$ and H atom in a defective MoS$_2$ system (with one sulfur atom vacancy) is shown in Figure S7. The transfer barriers in the case of proton are still similar to the case of a perfect material, however, the protons are strongly attracted by the S atoms in the vicinity of the vacancy, hindering the movement of the species. An even stronger effect is observed for the H atom, when different free-energy barriers are found. This comes from the fact that the S-H binding strength is different when H species are close or far from the vacancy (see Figure S8). The energy difference between H$^+$ bound close to the vacancy or far from it is only 2.4 kJ/mol, while for H atom, this energy difference is as large as 12.1 kJ/mol, leading to the asymmetric FES. We can conclude here that the defects present in MoS$_2$ will suppress the overall transport between the layers.

**Figure S7.** (a) Schematic of the H$^+$ or H transfers path in defective MoS$_2$. (b) S-H bond distances change during WTMetaD simulations. For (a) and (b), we have similar behavior with H$^+$ and H, therefore, only exemplary plots for H$^+$ are shown. (c) Free energy surface of H$^+$ transfer along the defective MoS$_2$. (d) Free energy surface of H atom transfer along the defective MoS$_2$. 
Figure S8. (a) H⁺ or H atom bound far away from the sulfur vacancy. (b) H⁺ or H atom bound close to the sulfur vacancy. The sulfur vacancy is marked as an empty gray circle.

Hydrogen atom transfer in graphite: In the metallic graphite, a proton will immediately be neutralized by electrons. Therefore, we have only studied the case of H atom in between the layers of graphite. The WTMetaD simulations are shown in Figure S9. The C-H bond is very strong and needs large energy to break it, allowing the H transfer to the other layer. Within the energy barriers that were observed in the other two materials, which are defined by the number of hills used in the WTMetaD simulations, we do not observe any H atom transport in graphite, and the simulation reveals only a single minimum in FES. If more hills were used, higher free energy barrier would be overcome, however, this barrier would be too large to observe such a transfer experimentally.

Figure S9. (a) H atom bound to graphite layers. (b) C-H bond distances change during WTMetaD simulations. (c) Free energy surface of H atom inside graphite.
Spin flip energy: When two H atoms are in the interstitial space of a layered material, different spin states can be considered: singlet, triplet or antiferromagnetic singlet. The spin-flip energy for the latter two spin states of two H atoms were calculated with Crystal 17 at the PBE/TZVP level (see Table S2). These energies are very small, therefore, results obtained for the triplet or antiferromagnetic singlet are nearly the same.

Table S2. Spin flip energies between triplet and antiferromagnetic singlet states of two H atoms.

| System                  | 2H in the same layer | 2H in the adjacent layers | 2H in different interstitials |
|-------------------------|----------------------|---------------------------|------------------------------|
| 2H close                | 53.2 meV             | 26.2 meV                  | 226 meV                     |
| 2H far                  | 0.7 meV              | 0.9 meV                   | 0.6 meV                     |

References

1. Paine, R. T.; Narula, C. K., Synthetic Routes to Boron Nitride. *Chem. Rev.* **1990**, *90*, 73-91.
2. Wakabayashi, N.; Smith, H. G.; Nicklow, R. M., Lattice Dynamics of Hexagonal MoS₂ Studied by Neutron Scattering. *Phys. Rev. B* **1975**, *12*, 659-663.
3. Wyckoff, R. W. G., *Crystal Structures - Volume 1*. Interscience Publishers: New York, 1963.
4. Barducci, A.; Bussi, G.; Parrinello, M., Well-Tempered Metadynamics: A Smoothly Converging and Tunable Free-Energy Method. *Phys. Rev. Lett.* **2008**, *100*, 020603.
5. Vanden-Eijnden, E.; Ciccotti, G., Second-Order Integrators for Langevin Equations with Holonomic Constraints. *Chem. Phys. Lett.* **2006**, *429*, 310-316.
6. Cp2k v3.0: https://www.cp2k.org.
7. Nosé, S., A Molecular Dynamics Method for Simulations in the Canonical Ensemble. *Mol. Phys.* **1984**, *52*, 255-268.
8. Bussi, G.; Donadio, D.; Parrinello, M., Canonical Sampling through Velocity Rescaling. *J. Chem. Phys.* **2007**, *126*, 014101.
9. Constantinescu, G.; Kuc, A.; Heine, T., Stacking in Bulk and Bilayer Hexagonal Boron Nitride. *Phys. Rev. Lett.* **2013**, *111*, 036104.
10. Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G., Gaussian 09, Revision A. 02, Gaussian. *Inc., Wallingford, CT* **2009**, 200.
11. Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785.
12. Hu, S.; Gopinadhan, K.; Rakowski, A.; Neek-Amal, M.; Heine, T.; Grigorieva, I. V.; Haigh, S. J.; Peeters, F. M.; Geim, A. K.; Lozada-Hidalgo, M., Transport of Hydrogen Isotopes through Interlayer Spacing in Van Der Waals Crystals. *Nature Nanotech.* **2018**, *13*, 468-472.
13. Jaeckel, R.; Wagner, B., Photo-Electric Measurement of the Work Function of Metals and Its Alteration after Gas Adsorption. *Vacuum* **1963**, *13*, 509-511.
14. Johansson, M.; Skúlason, E.; Nielsen, G.; Murphy, S.; Nielsen, R. M.; Chorkendorff, I., Hydrogen Adsorption on Palladium and Palladium Hydride at 1 bar. *Surf. Sci.* **2010**, *604*, 718-729.

15. Blanksby, S. J.; Ellison, G. B., Bond Dissociation Energies of Organic Molecules. *Acc. Chem. Res.* **2003**, *36*, 255-263.