Hydrogen storage in MOF-5: A van der Waals density functional theory study

Yue Huang1 and San-Huang Ke1,2*

1Key Laboratory of Advanced Microstructured Materials, MOE, Department of Physics, Tongji University, 1239 Siping Road, Shanghai 200092, P. R. of China
2Beijing Computational Science Research Center, 3 Heqing Road, Beijing 100084, P. R. of China

Physisorption of hydrogen molecules in metal-organic frameworks (MOFs) provides a promising way for hydrogen storage, in which the van der Waals (vdW) interaction plays an important role but cannot be described by the density functional theory (DFT). By using the vdW density functional (vdW-DF) method, we investigate systematically the binding energies of hydrogen molecules in MOF-5 crystal. We first examine the accuracy of this methodology by comparing its results with those from the correlated quantum chemistry methods for several fragment models cut out from the crystal. Good comparable accuracy is found. By performing calculations for the true crystal structure adsorbing one or multiple H2 in the primitive cell, we show that these fragment models which have been focused previously cannot represent well the property of the crystal which cannot, however, be dealt with by the quantum chemistry methods. It is found that the binding energy with the organic linker is much smaller than with the metal oxide corner, which limits the H2 loading. We show that this can be improved significantly (from 5.50 to 10.39 kJ/mol) by replacing the H atoms of the organic linker with F atoms which cause extra electrostatic interaction.

I. INTRODUCTION

Hydrogen as a substitution for fossil fuel in applications of energy carrier has stimulated extensive research because of its abundance on earth and especially its clean outcome (water). However, a safe and efficient hydrogen storage technique still remains as an obstacle in practice, in spite of various chemical and physical schemes proposed [1–4], in which hydrogen is stored in atomic and molecular forms, respectively. In this regards, metal–organic frameworks (MOFs) was found to be a promising materials family for hydrogen storage based on physical adsorption. So far, a series of MOFs has been synthesized and their structural properties and hydrogen loading under different temperatures and pressures have been investigated by powder x-ray diffraction (XRD) and inelastic neutron scattering (INS) techniques [5, 6]. Compared with other schemes, MOFs have several outstanding advantages, such as very large surface/volume ratio, tailorable chemical composition and structure, and the regular high-symmetry periodic crystal structure. MOF-5 as the first one in the series has become a particular focus of MOFs study [5–13]. It has been found experimentally that MOF-5 with the cubic three-dimensional extended porous structure can achieve a gravimetric H2 capacity up to 4.5%wt at 78K [5, 6]. However, a common problem exists with MOFs for hydrogen storage: Around room temperature the H2 binding energy is still not large enough. How to increase the adsorption enthalpy to above 15 kJ/mol [14–16] under room temperature has become a challenge in practice, which may be possible by tailoring the chemical species and atomic structure. To achieve this goal we need to first gain a full understanding of H2 interaction with MOF-5 on the different adsorption sites in the internal space of MOF-5.

To accurately calculate these interactions is, however, a big challenge to theoretical studies because the van der Waals (vdW) interaction plays an important role in the physisorption, which is a quantum dispersion force and is related to the nonlocal correlation effect. This nonlocal correlation is absent in the density functional theory (DFT) and can only be described by the many-body perturbation theory or the correlated wavefunction methods. The lowest level of theory which can deal with the vdW interaction is the Møller-Plesset second-order perturbation (MP2) theory [17]. More sophisticated methods include the coupled-cluster method, such as the coupled-cluster singles and doubles and noniterative triples (CCSD(T)) [18]. These correlated quantum chemistry methods also face challenges for the study of hydrogen storage in MOFs. First, these methods cannot deal with periodic crystal structures. Consequently, one has to use some fragment models cut out from the crystal structure to mimic the different parts of MOFs [16–19, 20]. Considering the long-range nature of the electrostatic and vdW forces present in the physisorption, whether and to what extent these fragment models can represent the behavior of the crystal is a question to answer. These correlated methods are also computationally very demanding and cannot deal with large fragment models. Furthermore, as usually implemented with the Gaussian basis functions, these methods have a strong basis set dependence and, therefore, the result becomes reliable only when a very large basis set is used or some elaborate correction techniques are applied [21].

To simply add empirically a 1/\(r^6\) term to conventional DFT calculations, as did in the DFT+Dispersion (DFT+D) method [22–23], may be a solution for studying the H2 adsorption in the full crystal structure, but its accuracy and reliability of result still needs to be examined [11, 19]. On the other hand, in the vdW-DF method developed by Dion et al. [24, 25] the vdW interaction can be included perturbatively in a seamless fashion into an first-principles Kohn-Sham DFT calculation. This is achieved by expanding the correlation energy to the second order in terms of a carefully chosen quantity for the long-range part of the correlation functional. This method has been applied to different separational systems [21, 24] and shown reasonable accuracy. For the extended crystal structure

*Corresponding author, E-mail: shke@tongji.edu.cn
of MOFs interacting with H$_2$, whether and to what extent the binding energy can be determined by the vdW-DF method has not been studied in the literature, to our best knowledge.

In this work, we adopt the vdW-DF method to study systematically the binding energy of H$_2$ in MOF-5 crystal for two major adsorption sites. We first test the accuracy of the methodology by considering the fragment models already studied in the literature. The comparison with the MP2, CCSD(T), and DFT+D calculations shows a good accuracy which is better than the empirical DFT+D method. Calculations for the full crystal structure, however, show that these fragment models cannot represent well the hydrogen-storage property of the crystal due to the long-range interaction of H$_2$ with the environment. Besides the single H$_2$ binding behavior, multiple H$_2$ adsorption is also considered to investigate the effect of H$_2$ density. Furthermore, to illustrate the possibility of enhancing the average H$_2$ binding energy in MOF-5 crystal, we consider the substitution of F atoms for the H atoms of the organic linker part. It is found that in this way the H$_2$ binding energy can be almost doubled due to the extra electrostatic interaction, indicating a possible way to improve the performance of MOFs for hydrogen storage.

II. THEORY, MODELS, AND COMPUTATIONAL DETAILS

Electrostatic force and vdW force are the sources of the physisorption for the hydrogen storage in MOFs. Therefore, both of them are important for getting computationally accurate binding energy of H$_2$. Since the vdW interaction is absent in DFT we adopt the recently developed vdW-DF method which includes the nonlocal electronic correlation effect into the Kohn-Sham DFT calculation in a seamless fashion\cite{24}. This is achieved by expanding the correlation energy to the second order in terms of a carefully chosen quantity for the long-range part of the correlation functional. In this way, long-range dispersion effects are included as a perturbation to the correlation term of the local or semilocal density approximation\cite{25}. This method has been successful in describing various groups of materials, ranging from molecules to surfaces and bulk materials\cite{21, 24, 25}. Considering the limitation of the sophisticated quantum chemistry methods for periodic systems, this method may provide a useful tool for the study of hydrogen storage with MOF crystals, which has not been reported in the literature to our best knowledge.

The crystal structure of MOF-5 is composed of inorganic [OZn$_4$]$_{6+}$ octahedral groups linked by 1,4-benzenedicarboxylate (BDC) organic linkers, forming a highly microporous cubic framework, as shown in Fig. 1(a). It has a symmetry of face-centered cubic Fm$\bar{3}$m with an experimental lattice constant of 25.89 Å\cite{5} for the conventional cell. The conventional cell contains eight formula units Zn$_4$O(BDC)$_3$ (424 atoms in total) while the primitive cell contains only two (106 atoms in total), as shown in Fig. 1. The large empty hole formed can be an ideal space for hydrogen storage where the physisorption takes place. Specifically, both the OZn$_4$ cluster in the corner and the organic linker in the pillar can interact with H$_2$ molecules with different interaction strengths. Here, we consider two adsorption sites, one is above the C$_3$ plane of the corner (the cup site, see Fig. 2(a)) and the other is above the benzene ring of the organic linker (linker site, see Fig. 2(b)). Previous theoretical and experimental studies showed that the cup site is the most favored one and will be taken up by hydrogen molecules first, then the linker site will be occupied\. 6, 31

In order to examine the reasonability of fragment models in representing the different parts of the full crystal, three fragment models, corner model, BDC model, and edge model, are considered, which are used to represent the metal oxide corner, organic linker, and one edge of MOF-5, respectively (see Fig. 3). These models are also used to examine the accuracy of the vdW-DF method by comparing its results to the existing results from the correlated quantum chemistry methods as
FIG. 2: Optimized structures of the three fragment models: (a) the corner model with a $\text{H}_2$ adsorbed on the cup site, i.e., above the $\text{C}_3$ plane indicated by the dashed-line triangle, (b) the BDC model with a $\text{H}_2$ adsorbed above the benzene ring, and (c) the edge model which is made up of the two corner models linked by one BDC linker.

As well as DFT+D.

Our calculations are carried out by using the pseudopotential plane-wave formulism of the vdW-DF theory, as implemented in the Quantum ESPRESSO package [26]. The O, Zn, C, and H atoms are described by the ultrasoft pseudopotentials [27, 28] and a kinetic energy cutoff of 30 Ry is used for the wavefunction expansion. Considering the fact that the force acting on $\text{H}_2$ is much smaller than those in usual bonded systems, we set a very high total-energy convergence criteria, $1.0 \times 10^{-7}$ Ry, for the selfconsistent vdW-DF calculation to obtain accurate forces on atoms. The structures of the fragment models (with and without $\text{H}_2$) are optimized by minimizing the forces on each atom to be smaller than $1.0 \times 10^{-4}$ Ry/Bohr. The structures of the crystall (with and without $\text{H}_2$) are optimized by performing full variable-cell relaxations until the forces on atoms are smaller than $1.0 \times 10^{-4}$ Ry/Bohr and the change in total energy of the primitive cell between two neighboring variable-cell steps is smaller than $1.0 \times 10^{-5}$ Ry. A $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh is used to sample the Brillouin zone of the crystall.

III. RESULTS AND DISCUSSION

A. Structure optimization with a single $\text{H}_2$ adsorbed

We first consider a single $\text{H}_2$ molecule adsorbed on the fragment models and in the MOF-5 crystal structure. Since the physisorption is quite weak, the most stable adsorption configuration needs to be determined very carefully. For the fragment models we do the structure optimization in two steps. First, we perform a series of single point total-energy calculations for different adsorption distances within a roughly chosen range (see Fig. 3). Second, based on the lowest-energy adsorption distance obtained we then do a full structure relaxation with a very high convergence criteria, as mentioned previously, to ensure an accurate final adsorption configuration. The final optimized adsorption distances are also used as the initial input for the calculation of the crystal structure. For example, for the BDC model the result from the first step (see Fig. 3(a)) gives a lowest-energy distance of 3.40 Å in line with the typical vdW interaction distance [16]. The final fully optimized distance from the second step is 3.48 Å. For the corner model, the total-energy curve in Fig. 3(b) shows a lowest-energy distance of 2.28 Å and the fully relaxed one is 2.01 Å. The corresponding results for the crystal structure are 3.49 Å and 2.06 Å for the two adsorption sites, respectively. The full results are listed in Table I.

B. Binding energy of a single $\text{H}_2$ and the accuracy of the vdW-DF method

We first examine the accuracy of the vdW-DF method by performing calculations for the fragment models and comp-
| distance | vDW-DF | CCSD(T) | MP2 | PBE+D |
|----------|--------|---------|-----|-------|
| corner+H₂ | 2.01   | 3.48    | 3.46| 2.06  |
| BDC+H₂   | 8.68   | 4.55    | 5.31| 9.39  |
| edge+H₂  | 7.50a  | 4.32b   | 5.10a| 5.50  |
| p(c)+H₂  |        |         |     | 5.30a |
| p(l)+H₂  |        |         |     |       |

TABLE I: The calculated adsorption distance (distance, in Å) and binding energy (vDW-DF, in kJ/mol) of a single H₂ molecule adsorbed on the cup site or linker site of the fragment models (corner+H₂, BDC+H₂, and edge+H₂) and crystal structure (p(c)+H₂, p(l)+H₂). Results of binding energy from some previous calculations (including CCSD(T), MP2, and PBE+D) are also listed for a comparison.

a data from Reference [11].
b data from Reference [29].

pare the results of H₂ binding energy to the existing results from the correlated quantum chemistry methods. The calculated results are listed in Table I together with reliable results from CCSD(T), MP2, and DFT+D using PBE functional (PBE+D). Sagara et al has reported H₂ binding energy for the BDC model using the CCSD(T) and MP2 methods adopting the large QZVPP basis set [18] and got results of 4.32 and 5.41 kJ/mol, respectively. Our vDW-DF result is 4.55 kJ/mol which is very close to the CCSD(T) one. For the corner model, a MP2 calculation [11] using a basis set of aug-cc-pVQZ plus diffuse functions gave a result of 7.50 kJ/mol while a PBE+D calculation [11] adopting a plane-wave basis set with 400 eV kinetic-energy cutoff showed 5.30 kJ/mol. Our result of 8.68 kJ/mol is closer to the MP2 result than the PBE+D one does. For the edge model, the present result of 5.31 kJ/mol is also quite close to the MP2 result 5.1 kJ/mol obtained in Ref. [11]. From the above comparison, we can conclude that the vDW-DF method can describe well the physisorption of H₂ molecule in MOF-5 and its accuracy is comparable to that of the MP2 and CCSD(T) methods and seems better than the DFT+D. An outstanding advantage of the DFT-based methods is that, unlike the correlated quantum chemistry methods, they are not so strongly dependent on the basis set used. For the latter, although the theories themselves are more accurate but their results are very scattered in the literature, varying largely with different basis sets used, and only become reliable when the very big basis sets (as mentioned above) are adopted. Consequently, even for the small fragment models they are computationally very demanding.

C. Fragment models vs. crystal structure

As one can see in Table I the fragment modes and the crystal structure give quite different results of binding energy for a single H₂ adsorbed. The binding energy with the corner model (corner+H₂) is 0.71 kJ/mol lower than that with the crystal structure (p(c)+H₂) and the binding energy with the BDC model (BDC+H₂) is 0.95 kJ/mol smaller than the crystal one (p(l)+H₂). This difference is due to the effect from the extended environment in the crystal structure which may provide an accumulated electrostatic and vdW forces because of their long-range nature. Additionally, there will be some charge transfer between a fragment and its environment, which will also change the strength of the physisorption. Our result shows that this effect is particular significant when the H₂ molecule is adsorbed on the organic linker part: Without connecting to the metal oxide corner part the BDC model underestimates the binding energy by about 20%. After this connection is made, as in the case of the edge model (edge+H₂), then the result becomes closer to (but still smaller than) that of p(l)+H₂. However, this connection will increase significantly the size of the model and make the higher-order quantum chemistry CCSD(T) calculation a big challenge.

Our calculation demonstrates that, compared to the true crystal structure calculation, the small fragment modes can still capture the main feature of the physisorption of H₂ on the different adsorption sites: Both show that the binding on the cup site of the OZn₄ corner is much stronger than that on the linker site. This has also been confirmed experimentally by inelastic neutron scattering spectroscopy [30] and neutron powder diffraction measurement [31]. The physics underlying is that the metal ion induced charge polarization around the corner causes stronger electrostatic force on the H₂. However, our calculation shows that the small fragment models ignoring the influence of the adjacent components are not quantitatively sufficient to represent the different parts of MOFs. For example, the PBE+D model (corner+H₂) is 0.95 kJ/mol smaller than the BDC model (BDC+H₂) and the binding energy with the DFT+D (p(l)+H₂) is also much closer to the MP2 one than the DFT+D (p(c)+H₂). The difference may be partly due to the fact that the DFT+D method (corner+H₂) is comparable to that of the MP2 and CCSD(T) methods and seems better than the DFT+D. Additionally, the DFT+D method requires a much larger basis set and is computationally much more demanding.

D. Effect of multiple H₂ adsorbed

In the practice of hydrogen storage many H₂ molecules will be adsorbed in the primitive cell of a MOF crystal. Here, we investigate the effects of hydrogen density on the binding energy by considering multiple H₂ molecules adsorbed in the MOF-5 crystal, on the corner site (p(c)) and the linker site (p(l)), as shown in Fig. 4. The lattice constant and the average binding energy per H₂ for difference H₂ densities are listed in Table II. One can see that when the number of H₂ adsorbed in the primitive cell increases, the lattice constant actually decreases a little bit (by 0.02 Å) and the binding energy also decreases by 0.34 kJ/mol and 0.36 kJ/mol for the p(c) and p(l), respectively. This small decrease of the lattice constant implies that there exists an attractive force among the adsorbed H₂ molecules, which increases with the increasing H₂ density. This behavior is different from the case of chemisorption where an increase in adsorbate density will usually lead to an expansion of the volume. For the highest H₂ density considered in the present work, the smallest H₂...H₂ distance is around 4.1 Å, which is quite close to that in the bulk H₂ solid (3.8 Å) [32]. For even higher H₂ density comparable to that in the solid state, a previous calculation by Yildirim et
al [31] showed that a unique three-dimensional interlinked H₂ nanocage will be formed, which will enhance further the interaction among the H₂ molecules. Since the attraction among the H₂ molecules is in the opposite direction to their binding to the MOF-5 crystal, it reduces the binding energy consequently.

As a comparison to the crystall case, we also check the multiple H₂ effect using the fragment models. As shown in Table II for the corner model, when the four cup sites are occupied by H₂, the average binding energy actually increases by 0.1 kJ/mol compared to the case of only one H₂ adsorbed. For the BDC model, this change is much smaller but is still increased (by 0.01 kJ/mol) with H₂ adsorbed on both sides of the benzene ring compared to only on one side. This qualitative difference between the crystall and the fragment models for multiple H₂ adsorption can be understood by considering the fact that in the fragment models the H₂ molecules are adsorbed only on the surface of the cluster, and therefore, the interlink between H₂ molecules adsorbed in a cage of the crystall structure is absent. In this case, when multiple H₂ molecules are adsorbed the synergistic effect of electrostatic and vdW forces leads to the small increase of the binding energy. Thus, our calculation shows that, compared to the true crystall structure, the fragment models not only underestimate

![FIG. 4: The MOF-5 primitive cell with (a) one H₂ adsorbed on the cup site, (b) 8 H₂ adsorbed on the cup sites, (c) one H₂ adsorbed on the linker site, and (d) 12 H₂ adsorbed on the linker sites.](image-url)
the binding energy when a single H\(_2\) molecule is adsorbed but also give an opposite trend of the binding energy when multiple H\(_2\) molecules are adsorbed.

Another important effect of multiple H\(_2\) adsorption is an perpendicular-to-parallel rotation of the H\(_2\) molecules adsorbed on the cup site: When only one H\(_2\) is adsorbed, it prefers to be perpendicular to the C\(_3\) plane (see Fig. 4(a)). However, when multiple H\(_2\) molecules are adsorbed on the cup site, their adsorption configuration will undergo an perpendicular-to-parallel transition and becomes parallel to the C\(_3\) plane (see Fig. 4(b)). This transition reflects the interaction between the H\(_2\) molecules adsorbed on the same corner unit.

### E. Substitution of F atoms for the H atoms of the organic linker

As is already shown, the H\(_2\) binding energy with the organic linker is significantly smaller than with the metal oxide corner, which largely limits the H\(_2\) loading for hydrogen storage application. The reason is that the electrostatic force coming from the OZn\(_4\) cluster is much stronger than the vdW force coming from the organic linker. This implies a way for improving the average binding energy of H\(_2\) molecules in the MOF-5 crystall: It may be achieved by creating extra polarization in the organic linker part and therefore enhancing the binding energy by the induced electrostatic force.

Here we consider a possibility that the 4 hydrogen atoms of an organic linker are replaced with 4 fluorine atoms (see Fig. 5) which have a much stronger electronegativity leading to a larger charge transfer and, therefore, will give rise to extra polarization. Fluorine atom has also a small mass for a good gravimetric hydrogen loading. The results of binding energy after the fluorine substitution are also given in Table II (F-p(c)+H\(_2\) and F-p(l)+H\(_2\)). One can see that for one H\(_2\) adsorbed on the cup site the binding energy increases slightly from 9.39 kJ/mol to 9.82 kJ/mol. However, for one H\(_2\) adsorbed on the linker site the binding energy is enhanced significantly from 5.50 kJ/mol to 10.39 kJ/mol which is now even larger than the binding energy with the corner, showing that the proposed extra electrostatic interaction is really working. This result casts a light on possible ways for improving the performance of MOFs for hydrogen storage.

### IV. SUMMARY

By using the vdW-DF method implemented with plane-wave basis functions we have investigated systematically the physisorption of hydrogen molecules in MOF-5 crystall as used for hydrogen storage. We first examined the accuracy of this methodology by comparing the results for three fragment models to those from the correlated quantum chemistry methods, CCSD(T) and MP2, as well as from the DFT+D method. Good accuracy was found, which is comparable to that of the CCSD(T) and MP2 with very large basis sets. By comparing the results for the fragment modes with those for the true crystall structure we have shown that the fragment models underestimate largely the binding energy and therefore cannot represent well the hydrogen-storage property of the crystall which, however, cannot be dealt with by the quantum chemistry methods. For many hydrogen molecules adsorbed, the fragment models even give an opposite trend of the binding energy.

Our calculations for the true crystall structure show that the binding energy with the metal oxide corner is significantly larger than with the organic linker due to the metal ion-induced electrostatic force. With many hydrogen molecules adsorbed the crystall volume and the average binding energy decrease a little bit because of the small attraction among the hydrogen molecules, which leads to the regular interlinked H\(_2\) nanocage structure for higher H\(_2\) density found previously. For many hydrogen molecules adsorbed on the corner they undergo a perpendicular-to-parallel transition and prefer to be parallel to the C\(_3\) plane.

The present work shows that the much weaker binding with the organic linker can be improved significantly by introduc-
ing extra polarization and the resulting electrostatic interaction: The substitution of F atoms for the H atoms can increase the binding energy from 5.50 kJ/mol to 10.39 kJ/mol which is now very close to the binding energy with the corner. This casts a light on possible ways for improving the hydrogen loading of MOFs for hydrogen storage.

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[1] W.Luo, Alloys Compd. 381, 284 (2004).
[2] J.Sandrock, J.Alloys Compd. 877, 1999 (1999).
[3] R. Zacharia, K. Y. Kim, S. W. Hwang, and K. S. Nahm, Catal.Today 120, 426 (2007).
[4] C. O. Areán, O. V. Manoilova, B. Bonelli, M. R. Delgado, G. Turnes-Palomino, and E. Garrone, Chem. Phys. Lett. 370, 631 (2003).
[5] N. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O’Keeffe, and O. M. Yaghi, Science 300, 1127 (2003).
[6] J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, and O. M. Yaghi, Science 309, 1787 (2006).
[7] T. Sagara, J. Klassen, and E. Ganz, J. Chem. Phys. 121, 12543 (2004).
[8] B. Civalleri, F. Napoli, Y. Noël, C. Roetti, and R. Dovesi, Cryst. Eng. Comm. 8, 364 (2006).
[9] S. S. Kaye, A. Dailly, O. M. Yaghi, and J. R. Long, J. Am. Chem. Soc. 129, 14176 (2007).
[10] I. Cabria, M. J. López, and J. A. Alonso, Phys. Rev. B 78, 205432 (2008).
[11] K. Sillar, A. Hofmann, and J. Sauer, J. Am. Chem. Soc. 131, 4143 (2009).
[12] T. A. Maark and S. Pal, International Journal of Hydrogen Energy 35, 12846 (2010).
[13] J. T. Hughes and A. Navrotsky, J. Am. Chem. Soc. 133, 9184 (2011).
[14] S. K. Bhatia and A. L. Myers, Langmuir 22, 1688 (2006).
[15] A. W. C. van den Berg and C. O. Areán, Chem.Commun. p. 668 (2008).
[16] Lochan and Head-Gordon, Phys. Chem. Chem. Phys. 8, 1357 (2007).
[17] M. Head-Gordon, J. A. Pople, and M. J. Frisch, Chemical Physics Letters 153, 503 (1988).
[18] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. 157, 479 (1989).
[19] T. Mueller and G. Ceder, J. Phys. Chem. B 109, 17974 (2005).
[20] C. Buda and B. D. Dunietz, J. Phys. Chem. B 110, 10479 (2006).
[21] T. Thonhauser, V. R. Cooper, S. Li, A. Puzder, P. Hylgaard, and D. C. Langreth, Phys. Rev. B 76, 125112 (2007).
[22] S. J. Grimme, Comput. Chem. 25, 1463 (2004).
[23] S. J. Grimme, Comput. Chem. 27, 1787 (2006).
[24] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 92, 246401 (2004).
[25] V. R. Cooper, Phys. Rev. B 81, 161104 (2010).
[26] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., Journal of Physics: Condensed Matter 21, 395502 (2009).
[27] D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
[28] K. Laasonen, A. Pasquarello, C. Lee, R. Car, and D. Vanderbilt, Phys. Rev. B 47, 10142 (1993).
[29] T. Sagara, J. Klassen, J. Ortony, and E. Ganz, J. Chem. Phys. 123, 014701 (2005).
[30] L. J. Murray, M. Dincă, and J. R. Long, Chem. Soc. Rev 38, 1294 (2009).
[31] T. Yildirim and M. R. Hartman, Phys. Rev. Lett. 95, 215504 (2005).
[32] I. F. Silvera, Rev. Mod. Phys 52, 393 (1980).
[33] K. Park, N. R. Kittingerham, and P. M. O’Neill, Annu. Rev. Pharmacol. Toxicol. 41, 443 (2001).
[34] D. O’Hagan and H. S. Rezpa, Chem. Commun. 7, 645 (1997).
[35] B. E. Smart, J. Fluorine Chem 109, 3 (2001).
[36] M. Schlosser and D. Michel, Tetrahedron 52, 99 (1996).
[37] A. Bondi, J. Phys. Chem 68, 441 (1964).
[38] E. R. T. Tieckink and J. Zukerman-Schpector, The improtance of Pi-interactions in crystal engineering: frontiers in crystal engineering (John Wiley and Sons,Ltd, 2012).