

H₂ Adsorption in Metal-Organic Frameworks: Dispersion or Electrostatic Interactions?

Agnieszka Kuc,^[a, b] Thomas Heine,^{*[b]} Gotthard Seifert,^[a] and H elio A. Duarte^[c]

Materials to store molecular hydrogen for mobile applications have been intensively studied over the past years. In summary, two storage mechanisms have been proposed: chemisorption (e.g. metal hydrides,^[1,2] aminoboranes^[3]), and physisorption in nanoporous materials.^[4–6] In contrast to most hydride storage media, materials physisorbing H₂ offer reversible (un)loading processes without intensive external heating or cooling. As H₂ is a nonpolar molecule, the two principal contributions to the adsorption energy are weak London (dispersion) interactions (LDI) and interactions due to the electrostatic potential of the host material. LDI depend on the polarisability of the host material and on the distance between H₂ and the host surface. Therefore, systems designed for H₂ storage should be highly polarisable and have a large specific surface area with favourable pore sizes of ~0.6 nm.^[6–8] Graphitic (sp²) carbon structures (graphene slit pores,^[8] carbon nanotubes,^[9] fullerenes^[10] and more advanced materials (C₆₀ intercalated graphite,^[11] honeycomb graphite^[12,13] etc.)) belong to this group.

However, with none of them the 2010 goal of the US Department of Energy (6 wt. % of stored H₂ and 45 gL⁻¹ volumetric density)^[14] could be reached for moderate pressure and ambient temperature.^[15,16] Higher H₂ adsorption capacities might be possible if attractive electrostatic interactions are introduced by a non-negligible charge separation in the host. One of the most promising materials with these prop-

erties are metal-organic frameworks (MOFs, see Figure 1a),^[17,18] a family of nanoporous materials that are built of well-defined building blocks, polar metal oxide centers (connectors) and nonpolar organic linkers containing aromatic carbons. As it is possible to tailor their chemical composition and pore size distribution, many potential applications have been proposed for MOFs, among them H₂ storage.^[19–21]

It has been shown experimentally that some MOFs show indeed excellent storage capacities for H₂.^[21,22] It is, however, unclear, which underlying mechanism is responsible for this property. To tune the capability of MOFs to store H₂ the fundamental interactions leading to the adsorption have to be well understood. So far, it is not clear which interaction (LDI or electrostatics, for certain connectors possibly even chemisorption) is responsible for the H₂ adsorption in MOFs. Experimental evidence^[21–24] emphasizes that the strongest H₂ adsorption sites are close to the metal oxide connectors, which is interpreted such that M–O (M = Zn, Cu, Mg, etc.) dipoles are most effective in polarizing the gas molecules and lead to strong interactions.^[21–24] There is no consensus in the interpretation of the adsorption mechanism; the quantification of the adsorption energy depends on various variables and is matter of discussion, but low-energy adsorption sites have been identified in agreement between experiment and theory.^[24] It is important to obtain the host–guest potential theoretically, as it cannot be accessed experimentally due to the complex nature of the interaction. Also, the theoretical determination is not straightforward: So far, severe approximations had to be made in all theoretical approaches, and no final conclusion on the interaction mechanism could be drawn from their results: Either, an extended model for the MOF/H₂ system was made, but the interaction energy has been calculated using density-functional theory (DFT)^[24–30] which is well-known to fail to describe LDI.^[31–33]

The second approach is to reduce the MOF structure to model clusters (MOF connectors and linkers); however, the host–guest interaction is treated at higher computational level, most commonly using MP2 theory, as it is the compu-

[a] A. Kuc, Prof. G. Seifert
Physikalische Chemie, Technische Universit at Dresden
01062 Dresden (Germany)

[b] A. Kuc, Prof. T. Heine
School of Engineering and Science, Jacobs University Bremen
28759 Bremen (Germany)
Fax: (+49) 421 200 49 3223
E-mail: t.heine@jacobs-university.de

[c] Prof. H. A. Duarte
Departamento de Qu mica–ICEx
Universidade Federal de Minas Gerais
31.270-901 Belo Horizonte, MG (Brazil)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200800878>.

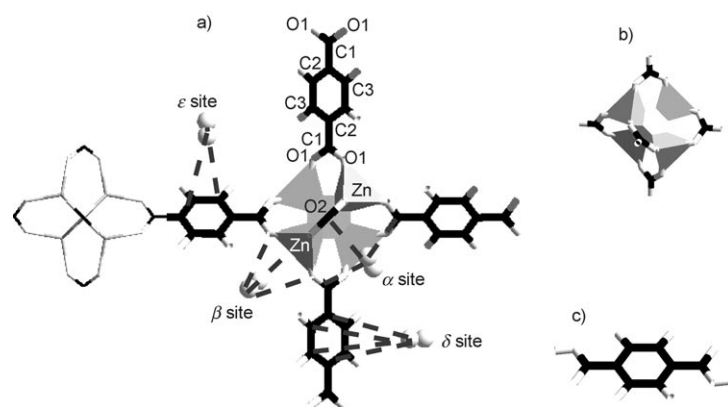


Figure 1. Adsorption sites considered within the IRMOF-1 unit cell (a) and the used model systems: (b) the connector, $\text{Zn}_4\text{O}(\text{HCO}_2)_6$, and (c) the linker, $\text{C}_6\text{H}_4(\text{COOH})_2$.

tationally most inexpensive ab initio method which includes LDI.^[34–39] Even for the model calculations with ab initio methods, reported adsorption energies are not in agreement. In consensus, the interaction energy of H_2 with the organic linkers has been determined to be $3.5\text{--}5\text{ kJ mol}^{-1}$,^[26,35,37,40] but values reported for the interaction energy of H_2 with the zinc oxide based IRMOF-1 connector vary between 2 and 7 kJ mol^{-1} .^[34,37]

The aim of this work is to qualitatively understand the role of the fundamental non-bonding interactions between H_2 and MOFs, LDI and electrostatic interactions between the polar host and the quadrupole moment and induced dipole moment of H_2 . Furthermore, we want to resolve the discrepancy of the results found in the literature. The results will allow a more detailed understanding in the host–guest interactions of MOF– H_2 systems and possibly suggest better strategies to optimize the H_2 storage capacity in MOFs. We have chosen the most widely investigated MOF, IRMOF-1,^[18] as a benchmark system.

Figure 1 shows the model structures used to represent the building blocks of the IRMOF-1 crystal, the $\text{Zn}_4\text{O}(\text{HCO}_2)_6$ (Figure 1b) molecule as a connector and benzene-1,4-dicarboxylate, $\text{C}_6\text{H}_4(\text{COOH})_2$ (Figure 1c) as a linker. The important high-symmetry adsorption sites, known from neutron scattering experiments,^[23,24] are indicated in Figure 1a. All model structures have been optimized at the B3LYP/6-31G(d) level as implemented in Gaussian03;^[41–44] the Cartesian coordinates are given in Table S1a–c in the Supporting Information.

The interaction of H_2 with polyaromatic hydrocarbons has been studied intensively,^[7,45,46] and there is general agreement that correct interaction energies can only be obtained if calculations include explicit treatment of correlation, for example, on the basis of second order Møller–Plesset (MP2) perturbation theory, employ at least moderately large basis sets and are corrected for basis set superposition errors (BSSE).^[47] As discussed in SI, these findings apply also for MOF linkers, which can be treated with good accuracy at the MP2/cc-pvTZ level, while the application of HF or DFT

(LDA, PBE or B3LYP functionals) is not sufficient for this type of interaction (see Figure S2, Supporting Information).

The interaction of H_2 with the metal oxide part is, however, less precisely investigated. The computational protocol to treat the interaction between MOF connectors and H_2 has been developed as discussed in the Supporting Information, see text and Figures S1–S3, and will be part of a more detailed publication.^[48]

A major question to be answered in this work is to attrib-

ute the interaction energy of MOFs to LDI and to electrostatic interactions. The LDI between two separated particles is essentially the intermolecular correlation energy. As Hartree–Fock (HF) does not include electron correlation, but correctly accounts for electrostatics (including dipole interactions induced by charge distributions) and Pauli repulsion, the LDI can be estimated by comparing HF and MP2 intermolecular interaction energies.

The interaction energies of H_2 with various adsorption site models of IRMOF-1 (**I** to **VII** from Figure 2) as function of the H_2 –host distance are shown in Figure 3. The H_2 –linker interaction (Figure 3a) is very similar to that of H_2 with benzene.^[7,46] The intermolecular distance is 3.2 \AA , the strongest interaction is 3.5 kJ mol^{-1} and found if H_2 points to the ring center of the linker in perpendicular orientation (**I**). For orientations of H_2 parallel to the ring (**II**, **III**), the interaction is 1 kJ mol^{-1} weaker, but the intermolecular distance (see Figure 3 and S4) is about the same. As there is no attraction found at the HF level (Figure 3c) this interaction is purely LDI. There are more adsorption sites of H_2 at the linker (see, e.g., the ϵ site in Figure 1), but they show a significantly lower interaction energies (1.4 kJ mol^{-1} , see Table S2). However, as many of these sites present in IRMOF-1 and LDIs are essentially additive they probably also contribute to the high H_2 adsorption capacities reported in experiments.^[20,21,49] For adsorption sites **VI** and **VII**, where Zn is closest to H_2 , the interaction energy depends on the orientation of the guest molecule (Figure 3b). The strongest interaction is found for H_2 perpendicular to the central Zn–O bond, that is, parallel to the “cluster surface”. The distance between the molecular center of H_2 and the closest Zn atom is 3.1 \AA and the interaction energy is 3.1 kJ mol^{-1} , which is 0.3 kJ mol^{-1} less than for the linker. The interaction is independent on the azimuthal orientation of H_2 to the Zn–O axis (see Table S3). Remarkably, the interaction is much weaker, that is only 1.3 kJ mol^{-1} , for the parallel orientation of H_2 to the central Zn–O bond. The minimum is found for a distance of 4.0 \AA from Zn, more than 1 \AA longer than for the perpendicular orientation. Note that if H_2 is rotated by

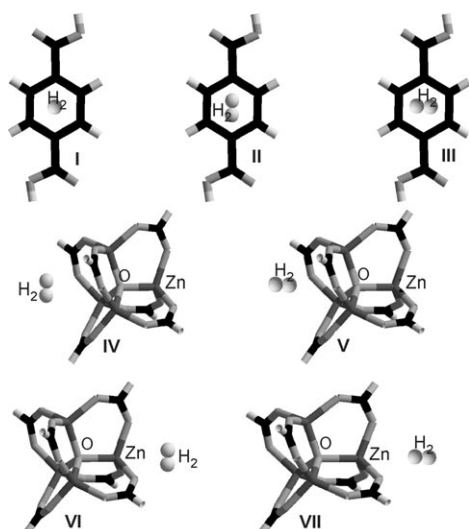


Figure 2. Model structures and H₂ orientations considered: **I–III** for the linker, **IV–VII** for the connector.

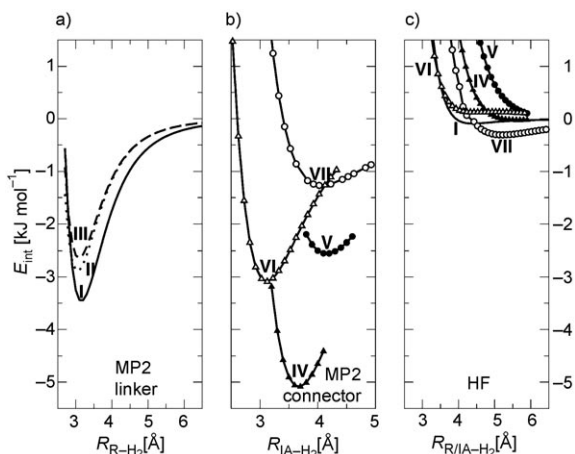


Figure 3. Interaction of H₂ with IRMOF-1 linker (a) and connector (b) as function of the H₂–host distance. In c) the electrostatic contribution to the interaction is shown. Model structures and adsorption sites are given in Figure 2.

90° at the equilibrium distance in complex **VI** one obtains complex **VII**, which has a repulsive H₂–host interaction at this intermolecular distance. This does not allow a stable configuration of the complex for rotating H₂ and we conclude that this site does not contribute significantly to the H₂ storage capacity even at moderately low temperatures.

To explain the role of surface polarization for the electrostatic attraction of H₂ we evaluated the induced dipole moment on H₂ when it is physisorbed at the cluster model (**VII**). For comparison, we calculated the same quantity for a strongly polarized H₂ molecule in a fictitious linear Na⁺–H₂–Cl[−] complex, where Na⁺ and Cl[−] are placed on opposite sites of hydrogen at distances of 3.2 Å from the H₂ center. Dipole moment components have been estimated using the point charge approximation employing Mulliken and Natu-

ral Bond Orbital (NBO) charges. For the Na⁺–H₂–Cl[−] model the dipole moment component at H₂ is 0.73 (0.97) Debye using the NBO (Mulliken) charges. This value nearly vanishes (0.02 (0.04) Debye) for the MOF connector, confirming that MOF fragments are not polar enough to introduce a tangible electrostatic interaction with H₂.

Finally, we calculated the interaction of H₂ placed in a pocket of three surrounding Zn atoms and carboxyl groups (see Figure 3, **IV** and **V**). In model **IV**, H₂ fits very well into the pocket, with various interatomic distances of 3.0–3.7 Å between hydrogens and their surrounding heavier atoms, and consequently we find the strongest interaction energy for this site, 5.1 kJ mol^{−1}. As for the other binding sites of H₂ with the connector, the interaction energy is lowered significantly if the orientation of H₂ is changed, as now only one H-atom has many close contacts to the host structure. For this site (model **V**) we estimate only 2.5 kJ mol^{−1}.

In conclusion, our calculations show that the physisorption of H₂ in MOFs is mainly due to London dispersion between linkers and connectors with hydrogen. Host–guest induced electrostatic interactions are unimportant, as the charge separation in the MOF is not large enough to induce significant dipole moments in H₂. We pointed out that correct application of theory is essential for the assessment of H₂–MOF interaction potentials: If they are treated at a quantummechanical level electron correlation has to be accounted for, the basis set size needs to be sufficient and basis set superposition errors need to be corrected. DFT-based methods with presently available functionals do not qualify due to their deficiency to treat LDI. Model clusters need to have a reasonable size. For our model connector and linker we find similar interaction energies for some adsorption sites. The strength of interaction is in qualitative agreement between experiment^[23,24] and our calculations: both find the strongest interaction for α site, with the sequence $\alpha > \beta > \delta \gg \epsilon$ (Figure 1).

In solid MOF-5, the long-ranged interaction potential of the nanopores will superpose and stronger interaction with H₂ is expected. We interpret the property of metal organic frameworks to physisorb H₂ strongly to their nanoporosity, which can be tuned to maximize the interaction. We expect the highest storage capacity for those MOFs where the pore size is optimized to similar values known for other nanoporous materials (~0.6 nm).^[6] These expectations are in line with recent calculations of Frost et al. who reported that H₂ storage capacities in MOFs are proportional to adsorption energies for low loadings, while they correlate with surface area for high loadings.^[50] We are working on a parameterization of the interaction potential of H₂ with MOFs which will allow to estimate the free energy and the amount of hydrogen uptake using quantum liquid density-functional theory.

Acknowledgements

We acknowledge financial support by Stiftung Energieforschung Baden-Württemberg, DAAD, DFG (Germany) and CAPES (Brazil) and com-

putational support of ZIH Dresden. We thank Dr. A. Jaroń-Becker, L. Zhechkov, Dr. A. F. Oliveira, Dr. H. de Abreu and Dr. A. Enyashin and K. Vietze for helpful and interesting discussions.

Keywords: ab initio calculations • adsorption • electrostatic interactions • hydrogen • metal-organic frameworks

- [1] T. P. Perng, J. K. Wu, *Mater. Lett.* **2003**, *57*, 3437.
- [2] L. Schlapbach, A. Züttel, *Nature* **2001**, *414*, 353.
- [3] C. W. Yoon, L. G. Sneddon, *J. Am. Chem. Soc.* **2006**, *128*, 13992.
- [4] P. Chen, X. Wu, J. Lin, K. L. Tan, *Science* **1999**, *285*, 91.
- [5] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, M. J. Heben, *Nature* **1997**, *386*, 377.
- [6] Y. Gogotsi, R. K. Dash, G. Yushin, T. Yildirim, G. Laudisio, J. E. Fischer, *J. Am. Chem. Soc.* **2005**, *127*, 16006.
- [7] S. Patchkovskii, J. S. Tse, S. N. Yurchenko, L. Zhechkov, T. Heine, G. Seifert, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 10439.
- [8] Q. Y. Wang, J. K. Johnson, *J. Chem. Phys.* **1999**, *110*, 577.
- [9] P. Sudan, A. Züttel, P. Mauron, C. Emmenegger, P. Wenger, L. Schlapbach, *Carbon* **2003**, *41*, 2377.
- [10] J. D. Turnbull, M. Boninsegni, *Phys. Rev. B* **2005**, *71*.
- [11] A. Kuc, L. Zhechkov, S. Patchkovskii, G. Seifert, T. Heine, *Nano Lett.* **2007**, *7*, 1.
- [12] R. A. Kendall, T. H. Dunning, R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.
- [13] A. Kuc, G. Seifert, *Phys. Rev. B* **2006**, *74*.
- [14] <http://www1.eere.energy.gov/hydrogenandfuelcells/storage>.
- [15] P. Kowalczyk, R. Holyst, M. Terrones, H. Terrones, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1786.
- [16] S. Patchkovskii, T. Heine, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2697.
- [17] K. Schlichte, T. Kratzke, S. Kaskel, *Microporous Mesoporous Mater.* **2004**, *73*, 81.
- [18] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705.
- [19] B. Panella, M. Hirscher, *Adv. Mater.* **2005**, *17*, 538.
- [20] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127.
- [21] J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670.
- [22] J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, O. M. Yaghi, *Science* **2005**, *309*, 1350.
- [23] J. L. C. Rowsell, J. Eckert, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 14904.
- [24] T. Yildirim, M. R. Hartman, *Phys. Rev. Lett.* **2005**, *95*, 215504-1.
- [25] T. B. Lee, D. Kim, D. H. Jung, S. B. Choi, J. H. Yoon, J. Kim, K. Choi, S. H. Choi, *Catal. Today* **2007**, *120*, 330.
- [26] T. Mueller, G. Ceder, *J. Phys. Chem. B* **2005**, *109*, 17974.
- [27] F. M. Mulder, T. J. Dingemans, M. Wagemaker, G. J. Kearley, *Chem. Phys.* **2005**, *317*, 113.
- [28] A. Samanta, T. Furuta, J. Li, *J. Chem. Phys.* **2006**, *125*, 084714-1.
- [29] Y. Y. Sun, Y. H. Kim, S. B. Zhang, *J. Am. Chem. Soc.* **2007**, *129*, 12606.
- [30] Q. Y. Yang, C. L. Zhong, *J. Phys. Chem. B* **2006**, *110*, 655.
- [31] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787.
- [32] S. Grimme, *Angew. Chem.* **2006**, *118*, 4571; *Angew. Chem. Int. Ed.* **2006**, *45*, 4460.
- [33] L. Zhechkov, T. Heine, S. Patchkovskii, G. Seifert, H. A. Duarte, *J. Chem. Theory Comput.* **2005**, *1*, 841.
- [34] S. Bordiga, J. G. Vitillo, G. Ricchiardi, L. Regli, D. Cocina, A. Zecchina, B. Arstad, M. Bjorgen, J. Hafizovic, K. P. Lillerud, *J. Phys. Chem. B* **2005**, *109*, 18237.
- [35] C. Buda, B. D. Dunietz, *J. Phys. Chem. B* **2006**, *110*, 10479.
- [36] E. Klontzas, A. Mavrandonakis, G. E. Froudakis, Y. Carissan, W. Kopper, *J. Phys. Chem. C* **2007**, *111*, 13635.
- [37] T. Sagara, J. Klassen, E. Ganz, *J. Chem. Phys.* **2004**, *121*, 12543.
- [38] T. Sagara, J. Klassen, J. Ortony, E. Ganz, *J. Chem. Phys.* **2005**, *123*, 014701-1.
- [39] T. Sagara, J. Ortony, E. Ganz, *J. Chem. Phys.* **2005**, *123*, 214707.
- [40] O. Hubner, A. Gloss, M. Fichtner, W. Kloppner, *J. Phys. Chem. A* **2004**, *108*, 3019.
- [41] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- [42] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724.
- [43] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- [44] C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
- [45] A. Ferre-Vilaplana, *J. Chem. Phys.* **2005**, *122*, 104709.
- [46] T. Heine, L. Zhechkov, G. Seifert, *Phys. Chem. Chem. Phys.* **2004**, *6*, 980.
- [47] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.
- [48] A. Kuc, T. Heine, G. Seifert, H. A. Duarte, *Theor. Chem. Acc.* **2008**, accepted or no journal and unpublished results.
- [49] J. L. C. Rowsell, A. R. Millward, K. S. Park, O. M. Yaghi, *J. Am. Chem. Soc.* **2004**, *126*, 5666.
- [50] H. Frost, T. Duren, R. Q. Snurr, *J. Phys. Chem. B* **2006**, *110*, 9565.

Received: May 8, 2008

Published online: June 24, 2008