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MOFs modeling and theory

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DISCUSSIONS

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MOFs modeling and theory: general discussion

Matthew Addicoat, Keith Butler, Omar Farha, Laura Gagliardi, Amir Hajiahmadi Farmahini, Christopher Hendon, Miguel Jorge, Susumu Kitagawa, Carlo Lamberti, Jet Lee, Jing Li, Xiaowei Liu, Stephen Moggach, Marco Ranocchiari, Lev Sarkisov, Stephen Shevlin, Ivo Stassen, Katrine Svane, Dirk Volkmer, Aron Walsh, Christopher Wilmer and Omar Yaghi

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DISCUSSIONS

MOFs modeling and theory: general discussion

Matthew Addicoat, Keith Butler, Omar Farha, Laura Gagliardi, Amir Hajiahmadi Farmahini, Christopher Hendon, Miguel Jorge, Susumu Kitagawa, Carlo Lamberti, Jet Lee, Jing Li, Xiaowei Liu, Stephen Moggach, Marco Ranocchiari, Lev Sarkisov, Stephen Shevlin, Ivo Stassen, Katrine Svane, Dirk Volkmer, Aron Walsh,

■ Christopher Wilmer and Omar Yaghi

DOI: 10.1039/c7fd90045g

(300:[300]300) **Marco Ranocchiari** opened a general discussion of the paper by Laura Gagliardi: There seems to be a lack of experimental understanding of what the chemical state of aluminum is within the inorganic nodes. Have you done anything in this direction to support the model, or to understand the nature of the inorganic nodes? What is the best experimental model you have and does it match with your computational model?

Laura Gagliardi responded: Our prior work provides, what we regard to be, convincing evidence that aluminum is present in the form of very small clusters of Al_2O_3 surface passivated with OH groups and water as required to balance charge and coordination number.¹

1 M. Rimoldi, V. Bernales, J. Borycz, A. Vjunov, L. C. Gallington, A. E. Platero-Prats, I. S. Kim, J. L. Fulton, A. B. F. Martinson, J. A. Lercher, K. W. Chapman, C. J. Cramer, L. Gagliardi, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 1058.

(301:[301]301) **Omar Farha** added: We made a MOF with aluminium inside, the Al cluster has been characterized using EXAFS.

(302:[302]302) **Marco Ranocchiari** commented: In your system, there are two post-synthetic modification steps, which makes it very difficult to have an accurate computational model that describes the reason for enhanced catalytic activity.

Laura Gagliardi answered: We do have data from various experimental characterization techniques against which to compare (e.g. EXAFS and DRIFTS spectra). That said, the likely heterogeneity present in the experimental system does introduce significant challenges for accurate modeling.

(303:[303]303) **Aron Walsh** addressed Laura Gagliardi and Omar Farha: Usually atomic layer deposition is associated with surface processes. Is there evidence that bulk penetration of aluminium is achieved in the MOF? Further, can the formation of Al_2O_3 on the MOF surface be excluded?

Laura Gagliardi responded: We studied precisely this question in earlier work focused on the material prior to iridium incorporation. Following aluminum deposition, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) revealed a uniform distribution of aluminum through the NU-1000 crystallites and confirmed retention of the crystal morphology.¹

1 M. Rimoldi, V. Bernales, J. Borycz, A. Vjunov, L. C. Gallington, A. E. Platero-Prats, I. S. Kim, J. L. Fulton, A. B. F. Martinson, J. A. Lercher, K. W. Chapman, C. J. Cramer, L. Gagliardi, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 1058.

(305:[305]305) **Carlo Lamberti** asked: I believe that the main question here is: is your model representative of the actual local environment or not? I also believe that you have enough experimental data to answer this question. From your model, you should simulate the expected XANES spectrum¹ and compare it with the experimental one. Alternatively, the relative ratio of the intensities of the symmetric and antisymmetric stretching of the dicarbonyl complex directly provides the angle θ between the two adsorbed CO molecules in C_{2v} symmetry $\theta = 2 \text{ Arctg} [\text{sqrt}(I_{\text{asym}}/I_{\text{sym}})]$ to be compared with the angle that you have in your DFT optimized structures.²

1 S. A. Guda, A. A. Guda, M. A. Soldatov, K. A. Lomachenko, A. L. Bugaev, C. Lamberti, W. Gawelda, C. Bressler, G. Smolentsev, A. V. Soldatov and Y. Joly, *J. Chem. Theory Comput.*, 2015, **11**, 4512-4521.

2 A. Zecchina, S. Bordiga, G. Turnes Palomino, D. Scarano, C. Lamberti and M. Salvalaggio, *J. Phys. Chem. B*, 1999, **103**, 3833-3844.

Laura Gagliardi answered: Thank you Carlo. These are useful suggestions and we will look into them.

(306:[306]306) **Jing Li** asked: It is interesting to see that aluminum lowers the transition state energy barrier. What is happening from the viewpoint of orbital interactions? Can your calculations provide some insight?

Laura Gagliardi replied: Our calculations can characterize the electronic structure of the species involved, including the partial charges on the various atoms, which are an indication of the Lewis acidity of the catalyst.

(307:[307]307) **Katrine Svane** asked: You show in your paper that you have two Al clusters which are very similar in energy. You could imagine that throughout your material you have a number of different clusters, but only some of them are relevant for catalysis. Is there a descriptor you can use to identify which clusters are relevant for catalysis? Do you calculate the C-O vibrational frequencies for all the metal clusters you test, and how good is your functional in reproducing these frequencies?

Laura Gagliardi responded: The heterogeneity of possible clusters is a significant challenge. We do indeed compute carbonyl stretching frequencies for every

siting that we assess, as this is a descriptor which is considerably easier to access than the free energy of activation for relevant reactions that we know to correlate with carbonyl stretching frequencies. The absolute accuracy of any density functional approach for computing carbonyl stretching frequencies is expected to be subject to the same limitations as for infrared frequencies in general using that functional (*e.g.* accuracy may be expected to improve with a scaling factor specific to the particular functional/basis set combination). However, we are more interested in changes in carbonyl stretching frequencies than absolute values, and we expect that to be insensitive to functional. Disappointingly, we have not yet identified a cluster/siting combination that is consistent with the experimental observation of increased carbonyl stretching frequencies in iridium-decorated Al-NU-1000 compared to NU-1000 itself. This remains an unsolved puzzle.

(308:[308]308) **Katrine Svane** commented: Is there a purely theoretical descriptor you can correlate with the calculated barrier heights for a particular cluster shape? *E.g.* the shape of the orbitals?

Laura Gagliardi answered: We do not have sufficient data to answer that question at this time. Experiment suggests that carbonyl stretching frequency is a useful such descriptor, but as we have yet to reproduce that computationally, we have not yet been able to then look further into whether there is a purely theoretical descriptor that might also serve.

(309:[309]309) **Susumu Kitagawa** remarked: In my experience of theoretical calculations for stretching frequencies of CO, which is bound to a metal ion in a pore of a MOF, the CO stretching frequency is very sensitive to the electrostatic field inside the pore. Have you included this in your calculation? The calculation could include electrostatic potential from the side and upper walls of a pore.

Laura Gagliardi replied: We have not yet tried it, but this is something to explore further.

(701:[310]310) **Jet Lee** commented: After the use of AIM on NU-1000, it is mentioned that ~ 7 Al atoms are incorporated per MOF node, although the distribution of the Al atoms within the MOF are not known.

I am curious about how well this technique allows Al to be incorporated within the material rather than the surface of the powder/particles. Have you considered comparing the Al content by XPS against ICP to compare the surface amount with the overall? Particle size may be important if the difference is large.

Laura Gagliardi responded: We studied precisely this question in earlier work focused on the material prior to iridium incorporation. Following aluminum deposition, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) revealed a uniform distribution of aluminum through the NU-1000 crystallites and confirmed the retention of crystal morphology.¹

1 M. Rimoldi, V. Bernales, J. Borycz, A. Vjunov, L. C. Gallington, A. E. Platero-Prats, I. S. Kim, J. L. Fulton, A. B. F. Martinson, J. A. Lercher, K. W. Chapman, C. J. Cramer, L. Gagliardi, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 1058.

(707:[311]311) **Ivo Stassen** addressed Laura Gagliardi and Omar Farha: Formation of thermodynamically preferred Al_8 clusters through a single ALD cycle seems rather counter-intuitive given the anticipated self-terminating kinetically controlled reaction between the dimethylaluminium isopropoxide dimer and the framework hydroxyls. By definition, no other oxidant species will be present during the first ALD half-cycle, and the cycle is finished through a single water vapor pulse. How do you perceive the mechanism of cluster formation? Are Al-O-Zr(cluster) bonds being hydrolyzed during the second part of the cycle, leading to re-mobilization of the Al species, or does clustering proceed already during the first half-cycle? Related to this, is the isopropoxide ligand crucial or does the observed clustering phenomenon also occur for (the very common ALD precursor) trimethylaluminium?

Laura Gagliardi answered: The formation of clusters, as first described by Rimoldi *et al.*,¹ was not originally expected for exactly the reasons raised. We speculate, however, that the exothermicity of the bond-forming reactions involved in the aluminum deposition cycles, combined with the low heat capacity of the MOF itself, leads to some dehydration of unreacted nodes and thereby generates water that can contribute to local cluster growth. When trimethylaluminum is used, the aggressive character of that reagent leads to substantial loss of crystallinity and internal surface area, although less reactive trimethylindium is useful as an ALD reagent for NU-1000.²

1 M. Rimoldi, V. Bernales, J. Borycz, A. Vjunov, L. C. Gallington, A. E. Platero-Prats, I. S. Kim, J. L. Fulton, A. B. F. Martinson, J. A. Lercher, K. W. Chapman, C. J. Cramer, L. Gagliardi, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 1058.

2 I. S. Kim, J. Borycz, A. E. Platero-Prats, S. Tussupbayev, T. C. Wang, O. K. Farha, J. T. Hupp, L. Gagliardi, K. W. Chapman, C. J. Cramer and A. B. F. Martinson, *Chem. Mater.*, 2015, **27**, 4772–4778.

(313:[313]313) **Carlo Lamberti** opened a general discussion of the paper by Keith T. Butler: In the different ZIF/oxide and ZIF/metal interfaces discussed in your work, there is a non-negligible strain between the substrate and the epistrat lattice parameters (in the 0.5-1.6 % range, see Table 2). Such strain will induce a tetragonal distortion on the epilayers with consequent symmetry reduction of the corresponding unit cell that, in turn, affects the position of both valence and conduction bands. Do you take such strain effects into account in your band calculations?

Keith Butler replied: We have developed an approach to include deformation potentials into the band alignment.¹ As you say, this is important in classical semiconductors, and it is even more important in MOFs, where deformation of the lattice can be large. In ref. 1 we show how the different band edges can deform and link it to the chemical nature of the orbital at the band edge; this will be an important route for designing electroactive MOFs.

1 K. T. Butler, C. H. Hendon and A. Walsh, *ACS Appl. Mater. Interfaces*, 2014, **6**, 22044–22050.

(314:[314]314) **Ivo Stassen** said: Your use of Nobel laureate Herbert Kroemer's phrase 'the interface is the device' seems very applicable indeed, not only because effective interfacing of MOFs with other components is critical to the

development of MOF devices, but also because MOFs contain a lot of intrinsic interfaces, and this might open new options for devices.

My question arises from the fact that all of the energies in your article are calculated relative to a vacuum in the center of the pores. This makes me wonder: do you expect the calculated bands to shift (to a significant degree) when putting guests in the pores? Charge transfer interaction between the MOF and its guest would occur, whereas the metal substrate would remain unaffected. This seems relevant for devices that contain liquid/solid interfaces such as supercapacitors. In other words, do we have to take the guest (or solvent) into account when screening for pairings?

Conversely, would it be a feasible strategy, in your opinion, to systematically utilize guests as ‘dopants’ to align the bands to enable certain applications?

Keith Butler responded: An interesting thought - one could certainly imagine introducing non-benign guests into the framework. If, for example, one introduced molecules with an internal electric field, or which interact with the frontier orbitals of the MOFs, this could be seen as a route to tuning the band structure of the material. This opens up a whole new playground for rational design - imagine scanning databases of MOF and molecular electron energies and choosing the ideal pairings to achieve a given effect. The dopant idea is a feasible route to realising this idea, it is similar in some ways to the work of Alendorf, where they ‘re-wire’ a MOF with TCNQ host molecules.¹ One can imagine tuning band alignment for processes not only of conductivity, but for heterogeneous catalysis.²

1 A. A. Talin, A. Centrone, A. C. Ford, M. E. Foster, V. Stavila, P. Haney, R. A. Kinney, V. Szalai, F. El Gabaly, H. P. Yoon, F. Léonard and M. D. Allendorf, *Science*, 2014, **343**, 66-69.

2 J. Jia, C. Qian, Y. Dong, Y. F. Li, H. Wang, M. Ghossoub, K. T. Butler, A. Walsh and G. A. Ozin, *Chem. Soc. Rev.*, 2017, **46**, 4631-4644.

(315:[315]315) **Jing Li** said: It's wonderful that you can calculate band alignments for these compounds. Since these can also be measured experimentally, how do your calculation results compare with experimental values?

Keith Butler replied: Since the publication of our approach to calculate the ionisation potentials of MOFs in 2014 we have been trying to encourage more measurements. Some CV numbers have been published for HKUST-1, which agree well with our predicted values. We would love to see some XPS/UPS studies of MOFs.^{1,2}

1 S. Sallis, N. Pereira, P. Mukherjee, N. F. Quackenbush, N. Faenza, C. Schlueter, T. L. Lee, W. L. Yang, F. Cosandey, G. G. Amatucci and L. F. J. Piper, *Appl. Phys. Lett.*, 2016, **108**, 263902.

2 N. F. Quackenbush, H. Paik, J. C. Woicik, D. A. Arena, D. G. Schlom and L. F. J. Piper, *Materials*, 2015, **8**, 5452-5466.

(316:[316]316) **Jing Li** said: Since there are very limited experimental data for MOFs, how do the results from your calculations compare with experimental values for other materials such as conventional hybrid semiconductors, for example, hybrid perovskite compounds? Do they match well?

Keith Butler responded: We have actually published a couple of papers of theoretical values for hybrid perovskites.^{1,2} The values for IP/EA and offsets agree very well with experiments, and this gives confidence in the approach.

1 K. T. Butler, J. M. Frost and A. Walsh, *Mater. Horiz.*, 2014, **2**, 228-231.

2 F. Brivio, K. T. Butler, A. Walsh and M. van Schilfgaarde, *Phys. Rev. B.*, 2014, **89**, 155204.

(317:[317]317) **Aron Walsh** added: There are few experimental data points concerning absolute band energies of MOFs. Since the publication of our approach to calculate the ionisation potentials of MOFs in 2014 we have been trying to encourage more measurements. Some values have been reported for the compound HKUST-1, which agree well with our predicted values.

(318:[318]318) **Christopher Hendon** commented: After careful thought about the method presented here, it is unsurprising that extremely dense substrates with small lattice vectors will form relatively strain-free interfaces with a MOF, whose lattice parameters are undoubtedly much larger. Thus, when computing the lattice strain %, surely this only matters in situations where large deformation is possible? For example, finding a commensurate MOF on MOF interface may be more challenging than finding substrates to grow MOFs on.

Keith Butler responded: This is a case in point for choosing your collaborators carefully! A good question from my co-author. I'd actually argue that, in fact, it is entirely possible to point to examples where porous MOFs and dense substrates have no commensurate lattices - indeed, I am sure this is why, in some cases, it is easier to form thin films on some substrates and not others, as we have recently been showing.¹ However, the follow on point stands, I think that this method will be important for considering MOF/MOF interfaces, which we heard some intriguing work about from Rosi *et al.* at this conference.²

1 J. K. Bristow, K. T. Butler, K. L. Svane, J. D. Gale and A. Walsh, *J. Mater. Chem. A*, 2017, **5**, 6226-6232.

2 C. Liu, C. Zeng, T. Y. Luo, A. D. Merg, R. Jin and N. L. Rosi, *J. Am. Chem. Soc.*, 2016, **138**, 12045-12048.

(320:[320]320) **Stephen Moggach** asked: If strain is that important, I wonder about the choice of the direction of growth of the materials, how does this compare with the natural growth directions? If you look at the natural form of a ZIF-8 crystal, and look at the natural growth direction on a surface, have you compared this with your study?

Keith Butler answered: Growth direction is crucial - the IP/EA and offsets are determined by interface/surface dipoles, that are orientation dependent.¹⁻² I would be very grateful for experimental data pertaining to the favoured growth directions of these materials.

1 Y. Kumagai, K. T. Butler, A. Walsh and F. Oba, *Phys. Rev. B*, **95**, 125309.

2 K. T. Butler, Y. Kumagai, F. Oba and A. Walsh, *J. Mater. Chem. C*, 2016, **4**, 1149-1158.

(321:[321]321) **Omar Farha** remarked: How do you know when you can compare experiments to modelling in relation to electronic calculations? I've seen

papers where authors claim that insulating MOFs are conductive, when this can be attributed to an oxide inside the MOF?

Keith Butler replied: This is an eternal and necessary question - how well matched are the model and the reality? We strive to model what is really there, including defects, secondary phases *etc.*, but this can be prohibitively expensive. So what we have to do is construct models that can provide insight. Likewise, it is important that systems be experimentally characterised as well as possible - I am sure that some experimental reports are a result of spurious secondary phases.

(323:[322]322) **Stephen Shevlin** asked: Can you clarify whether the lattice parameters used in your screening of properties of the metal substrate and ZIF interface are those for zero temperature? Furthermore, how much expansion would you expect to see at room temperature? Would this affect the screening procedure?

Keith Butler answered: This is a good point - temperature dependence of lattice parameters is an important factor for many properties.¹ In terms of developing a future more accurate screening procedure, this is something we must account for.

1 A. J. Jackson, J. M. Skelton, C. H. Hendon, K. T. Butler and A. Walsh, *J. Chem. Phys.*, 2015, **143**, 184101.

(703:[323]323) **Carlo Lamberti** commented: In the widely investigated field of III-V semiconductor heterostructures, the valence and conduction band alignment at the interface has, for decades, been a very relevant, complex and debated aspect, on both experimental and computational grounds.^{1,2} How accurate is the band alignment calculation in the case of the ZIF/oxide and ZIF/metal interfaces?

1 C. Lamberti, *Surf. Sci. Rep.*, 2004, **53**, 1-197.

2 *Characterization of Semiconductor Heterostructures and Nanostructures Second Edition*, ed. C. Lamberti and G. Agostini, Elsevier, 2013, pp. 1-813.

Keith Butler responded: This is a great point. In our calculations we are using the Anderson's rule approach^{1,2} - that is, aligning the bands through the IP of the bulk materials.^{3,4} Of course, when one introduces an interface, there can be complex issues such as the formation of an interface dipole from charge transfer,^{5,6} this can affect the band alignment.^{7,8} I think that in the future we will need to (i) build models of explicit interfaces to extract barriers,⁹ and (ii) have quality experimental characterisation of interface barriers.¹⁰ These will allow us to assess how well Anderson's rule works in the porous/solid interface.

1 R. L. Anderson, *IBM J. Res. Dev.*, 1960, **4**, 283-287.

2 A. Walsh and K. T. Butler, *Acc. Chem. Res.*, 2014, **47**, 364-372.

3 Y. Kumagai, K. T. Butler, A. Walsh and F. Oba, *Phys. Rev. B*, 2017, **95**, 125309.

4 K. T. Butler, C. H. Hendon and A. Walsh, *J. Am. Chem. Soc.*, 2014, **136**, 2703-2706.

5 K. T. Butler, J. Buckeridge, C. R. A. Catlow and A. Walsh, *Phys. Rev. B*, 2014, **89**, 115320.

6 K. T. Butler, S. McKechnie, P. Azarhoosh, M. van Schilfgaarde, D. O. Scanlon and A. Walsh, *Appl. Phys. Lett.*, 2016, **108**, 112103.

7 K. T. Butler, Y. Kumagai, F. Oba and A. Walsh, *J. Mater. Chem. C*, 2016, **4**, 1149-1158.

8 K. T. Butler and J. H. Harding, *J. Phys. Condens. Matter*, 2013, **25**, 395003-395012.

9 K. T. Butler and J. H. Harding, *Phys. Rev. B*, 2012, **86**, 245319.

10 F. Boscherini, C. Lamberti, S. Pascarelli, C. Rigo, and S. Mobilio, 1998, *Phys. Rev. B*, **58**, 10745.

(324:[324]324) **Miguel Jorge** opened a general discussion of the paper by C. E. Wilmer: This paper shows an elegant procedure to scan the structural space of porous materials. But where is the chemistry? There is an underlying assumption that adsorption is well described by a simple Lennard-Jones potential (*i.e.* it is dominated by van der Waals interactions). However, many systems will have strongly directional electrostatic interactions (*e.g.* adsorption of polar molecules at functional groups), polarization and/or orbital interactions (*e.g.* MOFs with open metal sites¹), as well as flexibility (*e.g.* breathing MOFs²). How are these phenomena accounted for in the model?

1 M. Fischer, J. R. B. Gomes and M. Jorge, *Mol. Simul.*, 2014, **40**, 537-556.

2 A. Schneemann, V. Bon, I. Schwedler, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062-6096.

Christopher Wilmer replied: It is true that we do not account for flexibility, but we also consider electrostatics and are able to use other potentials besides Lennard-Jones. Note that, even without considering flexibility, we can still set rigorous upper bounds for deliverable gas capacity on flexible MOFs by assuming that a perfectly rigid pseudomaterial contains no residual gas at the 'low' pressure. We are always safe in making assumptions that are generous (*i.e.* push the limits higher).

(325:[325]325) **Amir Hajiahmadi Farmahini** said: In this paper, you produce different generations of pseudomaterials by randomly perturbing values that describe their parent material's structure including coordinates of each pseudoatom, number density, LJ values of pseudoatom types, and unit cell dimensions. In this procedure, pseudomaterials are generated purely based on structural properties of the system, however chemical properties of pseudoatoms and their interactions with each other are not taken into account! Could you explain why there is no energy minimisation step in your algorithm? Geometry optimisation is a key step in predicting feasible structure of new materials, however it is completely neglected here. Please explain how can you predict feasible structure of a new material without even performing any geometry optimisation on its structure?

Christopher Wilmer answered: Since we were not interested in predicting new structures, we did not need to consider energy minimization. The question we were trying to answer had to do with the global limits of adsorption, which is simply a different question than 'what is a good structure we can make in the lab?'

(327:[327]327) **Aron Walsh** asked: Your current model appears to lack a realistic description of atoms and bonds, which loses chemical resolution. Over the past few years a number of interatomic potentials for MOFs have been developed that facilitate accurate low-cost calculations. Could your approach be extended to describe chemically realistic MOF structures?

Christopher Wilmer responded: The interatomic potentials developed by others for MOFs, in the end, are the same as those used here for pseudomaterials. The effort on those works goes towards finding ‘good’ parameters for the potentials, whereas in this work ‘good’ has no relevance — we consider all possible parameters (within reasonable limits).

(328:[328]328) **Matthew Addicoat** commented: In your algorithm, how did you choose your parent selection? The adaptive mutation is allowing more in terms of exploring the lesser known bins, but you could get more out of it using a different parent selection strategy?

Christopher Wilmer answered: Parent selection is currently based on the ‘rareness’ of the material (how infrequently its structure-property combinations are observed). There are probably other parent selection strategies, but this is the most straight-forward way to ensure that the structure-property space is ‘fully’ explored.

(329:[329]329) **Miguel Jorge** asked: Is it correct to say that your model can generate a virtual material that has the same adsorption behaviour of, say, HKUST-1, but that does not actually look like HKUST-1?

Regarding the model, you set some bounds on the sigma and epsilon LJ parameters, which are somewhat arbitrary but based on a physically reasonable parameter space. Have you played around with those bounds, and tested how dependent the results are on those bounds? One can also flip the question around and wonder what are the tightest bounds that still give you the same answer in terms of limiting behaviour? This could perhaps lead to some interesting insight.

Christopher Wilmer answered: If I understand your first question correctly, the model can generate HKUST-1 ‘exactly’ (in so far as it can be described by LJ spheres). It would ‘look’ just like HKUST-1.

The second question is very interesting and we are certainly interested in exploring the tightness of those bounds.

(330:[330]330) **Xiaowei Liu** said: Could you please comment on the selection and modification of the UFF parameters in the paper? Thank you.

Christopher Wilmer responded: We did not use the UFF parameters. Rather, we took the maximum and minimum UFF parameters as guides to set the limits for the range of parameters considered in our study.

(331:[331]331) **Xiaowei Liu** said: In the paper, you generated all the materials. Do you find any similarity between your pseudomaterials and the real materials, or could the top materials be synthesized in real applications? Thank you.

Christopher Wilmer replied: It is an interesting question. There are similarities. The surface areas, pore volumes, and interaction energies, among the ‘top’ materials are the same for the pseudomaterials as they are for MOFs. Trying to synthesize pseudomaterials is somewhat missing the point of the work.

(332:[332]332) **Laura Gagliardi** asked: When you develop your force fields, do you change only the values of the parameters in the force field or do you also try to find new functional expressions that take into account chemisorption rather than physisorption?

Christopher Wilmer answered: We have not tried to take into account chemisorption yet, but it is an interesting idea for the future.

(333:[333]333) **Omar Farha** commented: Do you see including breathable MOFs into this set? I think the upper bound might change, if storage capacity becomes your deliverable.

Christopher Wilmer responded: Making flexible pseudomaterials is an interesting idea which we may pursue in the future!

(334:[334]334) **Lev Sarkisov** remarked: You said that crystalline MOFs are contained within clouds of pseudomaterials. You're setting a huge space of essentially disordered non-crystalline random structures. So you still sample a huge space of possible disordered structures within the unit cell — in the process of sampling these structures do you generate real crystalline structures? It is a probabilistic argument. Out of the vast probabilities you have do you actually/occasionally generate structures which are equivalent to actual crystalline MOFs?

Christopher Wilmer responded: The structures generated, strictly speaking, are ordered and therefore 'crystalline'. Beyond that I'm not sure what the question is.

(335:[335]335) **Omar Yaghi** asked: Please describe to us one MOF that you predict would be perfect for hydrogen storage, that we can go to the lab and make.

Christopher Wilmer responded: This question misses the point of our work. I made no mention of MOFs in my talk or paper.

(337:[337]337) **Laura Gagliardi** added: Theory can be used at various levels. Chris Wilmer's simulations are not meant to look at the material with a molecular eye. He rather explores MOFs at a more macroscopic level with classical simulation techniques and tries to find if there are promising materials for gas separation or storage.

If one, instead, performs quantum chemical calculations, one can follow the bond formation/bond breaking, i.e. the reactivity at the atomic and molecular level. We can then make predictions that could be tested in the lab. However, some of the structures predicted by quantum mechanical calculations may be very challenging to make in the lab. So it is useful to theorists who use quantum mechanics to start from well-defined experimentally known structures, and then propose variants from them that are more promising for a given application and are also realistic. A loop has to be established between theory and experiment and it has to be sustained by both sides. It is not very constructive to say that theory cannot tell experimentalists what they should do. Theory can design some fundamental concepts that can be used to discover novel materials.

1 (338:[338]338) **Omar Yaghi** followed up: Give me something reasonable to go home with - we give you data, and you reproduce what is known. We need something to be predicted that we can make.

5 **Laura Gagliardi** responded: Usually theoretical modeling proceeds in the following way:

We try to reproduce experimental results and this gives us confidence in our methods. Then we try to be predictive. So if, for example, we study a known catalyst, we can then make variants of the catalyst and see if it can be more active and selective. We do that routinely. The problem is that sometimes what we predict is difficult to make. So it is important to have a strong interplay between theory and experiment. There are many predictions that have been subsequently verified, but maybe it takes time because based on a prediction, the experimentalist has to design a new experiment.

15 (340:[340]340) **Omar Yaghi** said: I'd have liked you to give us different, viable conformations which we could go and make?

20 **Laura Gagliardi** responded: I would like to do that too, but that perhaps requires a few iterative steps between theory and experiment. So a theorist and an experimentalist have to work together for some time to achieve that type of synergy.

25 (341:[341]341) **Dirk Volkmer** returned to the discussion of the paper by C. E. Wilmer: The unit cells of the porous pseudomaterials you were showing might contain completely enclosed voids which are physically inaccessible to any kind of atomically defined sorptive. In order to yield structure models which are applicable to sorption and separation processes, would it be possible to include the information of pore-accessibility in the computational screening procedures?

30 **Christopher Wilmer** responded: This is a very interesting question, but it is important to note that including such information would only serve to lower/tighten the theoretical bound (not raise it). It is safer, and more rigorous, to simply ignore pore-accessibility (at least for now).

35 (343:[343]343) **Aron Walsh** commented: Looking to the future, a principal aim should be to bridge the gap between theory and experiment on MOFs and other hybrid solids. One major challenge I see is the description of thermal motion and defects, which are hidden in many experiments that probe the average structure, including X-ray diffraction. In many cases it is these imperfections that give rise to the interesting properties of MOFs and so they deserve greater attention looking forward.

40 **Miguel Jorge** replied: I completely agree with Aron's point. Notwithstanding the challenges involved, there is currently insufficient effort devoted to characterising defective material samples in detail. Apart from crystal imperfections, one should also consider quantifying additional solid phases that are present (crystalline or amorphous), the amount of solvent occluded in the pores and structural changes upon activation/adsorption cycles. Insufficient

1 characterisation of the material makes the job of modellers much harder, as it
often becomes impossible to validate assumptions made.

5 (346:[346]346) **Omar Yaghi** said: The reason MOFs aren't uniquely defined is
because they're molecular, so we need to change the way we think about these
structures because they're not rigid like we think them to be - they're active and
fluctual unlike a rigid dense oxide, so I think this is perhaps why you and your
colleagues in the same centre don't agree.

10 **Laura Gagliardi** answered: You are absolutely right. These materials are much
more complex and thus fascinating than one would have thought and there is
a lot to discover.

15 (348:[348]348) **Miguel Jorge** said: It is important that theoreticians keep in mind
that our work is always based on assumptions to represent reality, and that these
may or may not be valid under specific circumstances. So we should always make an
effort to listen to and interact with experimentalists, instead of assuming that our
models somehow possess an element of inherent truth without seeking it thorough
20 validation. As a concrete example, there is an abundance of studies in the MOF
literature where model parameters are tweaked to match restricted sets of experi-
mental data without adequate consideration of the underlying physics. This leads to
a knock-on effect, propagating incorrect approaches and fallacious conclusions.

25 From the point of view of experimentalists, there is often a temptation to only
report eye-catching discoveries (*e.g.* record-breaking surface areas), then quickly
moving on to the next system without attempting to fully understand the
underlying phenomena. Although this is understandable in the current research
climate, I would argue that more efforts should be made to report also the 'dark
30 side' of materials discovery, *e.g.* characterisation of impurities and undesired
side-products, failed attempts, *etc.*

35 (350:[350]350) **Carlo Lamberti** commented: Based on my experience, the
collaboration with theoreticians has been indispensable to confirm structural
refinements of complex frameworks as well as for the correct and complete
investigation of advanced spectroscopies (IR, Raman, UV-Vis, XAS, XES, *etc.*).

This holds for most of the cases. In some cases, a multistep (iterative) model
modification was needed before reaching convergence between theory and
experiments, while only in few cases the problem was left unresolved. Notwith-
40 standing such failures, the plus value obtained in the other cases fully justify (in
my opinion) the additional effort needed to coordinate and harmonize experi-
mental and theoretical results.

45 1 L. Valenzano, B. Civalieri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K.-P. Lillerud
and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700-1718.

2 L. Valenzano, J. G. Vitillo, S. Chavan, B. Civalieri, F. Bonino, S. Bordiga and C.
Lamberti, *Catal. Today*, 2012, **182**, 67-79.

3 S. Chavan, J. G. Vitillo, D. Gianolio, O. Zavorotynska, B. Civalieri, S. Jakobsen, M. H.
Nilsen, L. Valenzano, C. Lamberti, K. P. Lillerud and S. Bordiga, *Phys. Chem. Chem. Phys.*,
2012, **14**, 1614-1626.

50 4 S. A. Guda, A. A. Guda, M. A. Soldatov, K. A. Lomachenko, A. L. Bugaev, C. Lamberti, W.
Gawelda, C. Bressler, G. Smolentsev, A. V. Soldatov and Y. Joly, *J. Chem. Theory Comput.*,
2015, **11**, 4512-4521.

(351:[351]351) **Omar Farha** remarked: Experimentalists and theorists should complement each other, but giving comments like that is not helpful. Doing synthesis is not simple — imagine going to a lab and making things as precise as possible in terms of purity, characterization, processing, *etc.* This is a tremendous amount of work. Both sides need to collaborate with each other instead of blaming experimentalists when things do not match.