Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information for

Recent Developments in First-principles Force Fields for Molecules in Nanoporous Materials

Hanjun Fang[1], Hakan Demir[1], Preeti Kamakoti[2*], and David S. Sholl[1*]

[1]School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, USA

[2]ExxonMobil Research and Engineering, Corporate Strategic Research

1545 Route 22 East, Annandale, NJ 08801, USA

[*] Corresponding authors. Email: preeti.kamakoti@exxonmobil.com, david.sholl@chbe.gatech.edu

Table S1: A summary of first-principles derived force fields for molecules in porous materials

Guest molecule	Porous material	Adsorbent model	QM method	configuration	FF potential form	FF validation		Ref.
						theory	experiment	
H_2	pure, Li-doped IRMOF-1	benzene, metal-based clusters, Li-C_{32} cluster	RI-MP2/TZVPP; X3LYP/6-311G(d,p)	along certain orientations	Morse	compare with MP2 PES for $H_2$with benzene, and MP2 interaction energies at different binding sites	compare with isotherms in undoped IRMOF-1 (Zn, C_6)	1, 2
H_2	pure, Li-doped IRMOF-2	benzene, metal-based clusters, Li-C_{32} cluster	RI-MP2/TZVPP; X3LYP/6-311G(d,p)	along certain orientations	Morse	compare with MP2 PES for H_2 with benzene, and MP2 interaction energies at different binding sites	compare with isotherms in undoped IRMOF-2 (Zn, C_{24})	3
H_2	IRMOFs	Zn-based clusters, BDC-Li_2	RI-MP2/TZVPP	along certain orientations	LJ + Coulomb	compare with MP2 interaction energies at different binding sites	compare with isotherms and Q_{st} in IRMOF-1	4
H_2	MOF UMCM-1	benzene, Zn-based cluster	MP2/cc-PVTZ	along certain orientations	Morse	compare with MP2 PES for H_2 with benzene	compare with isotherms in UMCM-1	5
H_2	metal alkoxide functionalized MOFs	metal alkoxide benzene	MP2/6-311+G(d,p); M06/6-311++G(d,p)	along certain orientations	modified-Morse/LJ + Coulomb	compare with MP2 PES and interaction energies for H_2 with metal alkoxide benzene	compare with isotherms in DO-MOF	6
H_2	CuBTC, other Cu-based MOFs	$Cu_2(bmc)_4$ cluster	PBE/DNP	along certain orientations	Morse	compare with PBE PES for H_2 with the $Cu_2(bmc)_4$ cluster	compare with isotherms in CuBTC, CuBTT, PCN-12	7
H_2	COFs	$B_3O_3H_3$, SiH_4	RI-MP2/QZVPP	along certain orientations	Morse	compare with MP2 PES for H_2 with boroxine and silane	compare with isotherms in COF-5	8
H_2, Ar	pure, Li-doped COFs	benzene, $H_3B_3O_3$, $C(CH_3)_4$, $Si(CH_3)_4$, Li-HHTP cluster	MP2/cc-PVTZ; PW91/6-311g(d,p)	along certain orientations	Morse	compare with MP2 PES for H_2 and Ar with benzene and $H_3B_3O_3$, and MP2 binding energies with clusters	compare with isotherms of Ar in COF-102,103	9
H_2	ZIFs	$C_3N_3H_3$, $C_3N_3Cl_3$, $C_3N_3(NO_2)_3$, ZnN_4H_8	RI-MP2/aug-cc-pVQZ, QZVPP	along certain orientations	Morse	compare with MP2 PES for H_2 with clusters	compare with isotherms in ZIF-8	10
H_2	PAFs	benzene, C_5H_{12}	MP2/cc-PVTZ	along certain orientations	Morse	compare with MP2 PES for H_2 with benzene	compare with isotherms in PAF-302	11
H_2	Silicon nanotube (SiNT)	(5,5)SiNT, (7,7)SiNT, (9,9)SiNT, (14,14)SiNT	PW91/6-311++G(d,p)	along certain orientations	Morse	not presented	not presented	12
H_2	Li-conjugated microporous polymers	Li-$C_6H_3(C_2H)_3$ cluster	UM06-L/6-311G(d,p)	along certain orientations	Morse	compare with UM06-L PES for H_2 with Li-$C_6H_3(C_2H)_3$	compare with isotherms in pure and Li-doped CMP	13

Table S1 (contd.)

Guest molecule	Porous material	Adsorbent model	QM method	configuration	FF potential form	FF validation		Ref.
						theory	experiment	
H_2	Li pillared grapheme sheet, Li-doped pillared carbon nanotubes	C_2 molecule; Li-C_{32} cluster	CCSD(T)/aug-cc-pVQZ; MP4/aug-cc-pVTZ; X3LYP/6-311G(d,p)	along certain orientations	Morse	not presented	compare with H_2 storage capacity in SWNT and Li-P-SWNT	14
CO_2	NaX and NaY	Na-zeolite cluster	B3LYP/TZVP	along certain orientations	Buckingham + Coulomb	not presented	compare with isotherms and Q_{st} in NaX and NaY	15
CO_2	LiY	Li-zeolite cluster	B3LYP/TZVP	along certain orientations	Buckingham + Coulomb	not presented	compare with isotherms in LiY	16
CO_2	siliceous zeolites	primitive unit cell of Si-CHA	periodic PBE-D2	randomly sampled	LJ + Coulomb	compare with PBE-D2 interaction energies for CO_2 with Si-CHA	compare with isotherms, K_H, and Q_{st} in Si-CHA, Si-MFI and Si-DDR	17
CO_2	Na-exchanged zeolites	primitive unit cell of LTA-4A	periodic DFT/CC	randomly sampled and from GCMC	LJ + Coulomb	compare with DFT/CC interaction energies for CO_2 with LTA-4A	compare with isotherms and Q_{st} in LTA-4A, NaX, and NaY	18
CO_2	pure and Li-doped COFs	benzene, $H_3B_3O_3$, $C_6H_3(SiH_3)_3$, $C_6H_3(CH_3)_3$, Li-based cluster	MP2/cc-PVTZ	along certain orientations	LJ + Coulomb	compare with MP2 PES for CO_2 with the Li-cluster	compare with isotherms in COF-102	19
CO_2	functionalized MOFs	benzene, $C_8H_6O_4$, $C_6H_3(CH_3)_3$, $C_6H_3(NH_2)_3$, $C_6H_3(NO_2)_3$, $C_6H_3Cl_3$	RI-MP2/cc-pVQZ	along certain orientations	Morse + Coulomb	compare with MP2 PES for CO_2 with these clusters	compare with isotherms in MOF-5 and MOF-177	20
CO_2, N_2	Mg-MOF-74, Zn-MOF-74, MOF-5	metal-based clusters	RI-MP2, NEMO method for energy decomposition	along certain orientations	Buckingham + 5,6-power term + Coulomb	compare with MP2 energy components for CO_2 with clusters	compare with Q_{st}, isotherms, and K_H in Mg-MOF-74, and isotherms in MOF-5	21
CO_2	ZIF-8, ZIF-71	methyl-Li_2-imidazolate, dichloro-Li_2-imidazolate	DFT-SAPT, energy decomposition	from NVT MD at 3000 K	Buckingham + damped 6-power term + damped Coulomb	compare with SAPT energy components for CO_2 with Li-fragments	compare with isotherms in ZIF-8 and ZIF-71	22
CO_2, N_2	functionalized ZIFs	Li_2-imidazolate, methyl-Li_2-imidazolate, dichloro-Li_2-imidazolate, benzene, nitromethane, methyl bromide	DFT-SAPT, energy decomposition	from NVT MD at 3000 K	Buckingham + damped 6,8,10-power term + damped Coulomb	compare with SAPT energy components for CO_2 and N_2 with Li-imidazolate rings, and configurations from GCMC	compare with isotherms in the ZIFs	23

Table S1 (contd.)

Guest molecule	Porous material	Adsorbent model	QM method	configuration	FF potential form	FF validation		Ref.
						theory	experiment	
CO_2, CH_4	Mg-MOF-74, CuBTC, PCN-14	CO_2: a Mg-based MOF cluster; CH_4: a unit cell of CuBTC	CO_2: B2PLYP-D2/Def2-TZVPP; CH_4: periodic DFT/CC	CO_2: along certain orientations; CH_4: 2000 grid points within the unit cell	MMSV + Buck-CK	compare with B2PLYP interaction energies in the training set and from NVT MD, and periodic PBE-D2 interaction energies	compare with isotherms for CO_2 in Mg-MOF-74, and CH_4 in CuBTC and PCN-14	24
CO_2, CH_4, N_2, Xe	MOMC	TPP cluster	B2PLYP-D3/def2-TZVPP	along certain orientations	vdW3	compare with B2PLYP PES for gas-TPP	compare with isotherms and Q_{st} in the MOMC	25
CO_2, C_2H_2	CuBTC	$Cu_2(formate)_4$	PBE/DNP	along certain orientations	LJ + Coul	compare with PBE PES for CO_2, and C_2H_2 with the $Cu_2(formate)_4$ cluster	compare with isotherms and Q_{st} in CuBTC	26
CH_4	COFs	benzene, $B_3O_3H_3$, $Si(CH_4)_4$	RI-MP2/QZVPP	along certain orientations	Morse	compare with MP2 PES for CH_4 with clusters	compare with isotherms in COF-5 and COF-8	27
CH_4	Pure, Li-doped COFs	benzene, $B_3O_3H_3$, $C_6H_3(CH_3)_3$, $C_6H_3(SiH_3)_3$, Li-HHTP	RI-MP2/cc-PVTZ, PW91/6-311g(d,p)	along certain orientations	Morse	compare with MP2 and PW91PES for CH_4 with clusters	compare with isotherms and Q_{st} in COF-102	28
CH_4	PAFs	benzene, toluene	MP2/6-311+G(d,p)	along certain orientations	LJ	compare with MP2 PES for CH_4 with benzene and toluene	not presented	29
N_2	PAFs	benzene, C_5H_{12}	MP2/cc-PVTZ	along certain orientations	Morse	compare with MP2 PES for CH_4 with benzene	compare with isotherms in PAF-1	30
NH_3	MIL-47, IRMOFs	$C_{10}H_7$-COOH, $C_{10}H_7$-Cl, $C_{10}H_7$-C=O	MP2/6-31+G(d,p)	along certain orientations	Morse/LJ + Coul	compare with MP2 EPS for NH_3 with functional groups	not presented	31
NH_3	H-ZSM5,	5T cluster based	RI-MP2/TZVPP	randomly sampled	LJ + Coulomb	compare with PBE-D2 interaction	compare with adsorption	32
H_2O	CuBTC, other Cu-based MOFs	CuBTC unit cell	periodic PBE-D2	randomly sampled	LJ + Coulomb + energy correction	compare with PBE-D2 interaction energies for H_2O with CuBTC	compare with isotherms in CuBTC, CuMBTC, and CuEBTC	33
propene	CuBTC	$Cu_2(btc)_4$ cluster	PBE/DNP	along certain orientations	Morse + power term	compare with PBE PES for C_2H_4 with the $Cu_2(btc)_4$ cluster	compare with isotherms in CuBTC	34

Force field potential function forms:

The MMSV stands for a piecewise combination of Morse-Morse-spline-van der Waals,[35]

$$E(r_{ij})=\begin{cases} D\left\{\exp\left[\alpha_1\left(1-\frac{r_{ij}}{r_0}\right)\right]-2\exp\left[\frac{\alpha_1}{2}\left(1-\frac{r_{ij}}{r_0}\right)\right]\right\} & for \quad 0\le r_{ij}\le r_0 \\ D\left\{\exp\left[\alpha_2\left(1-\frac{r_{ij}}{r_0}\right)\right]-2\exp\left[\frac{\alpha_2}{2}\left(1-\frac{r_{ij}}{r_0}\right)\right]\right\} & for \quad r_0\le r_{ij}\le r_1 \\ b_1+\left(r_{ij}-r_1\right)\left\{b_2+\left(r_{ij}-r_2\right)\left[b_3+\left(r_{ij}-r_1\right)b_4\right]\right\} & for \quad r_1\le r_{ij}\le r_2 \\ -Cr_{ij}^{-6} & for \quad r_2\le r_{ij}<\infty \end{cases} \qquad \text{(S1)}$$

where D is the well depth parameter, r_0 is the equilibrium energy distance, while α_1 and α_2 determines the shape of the potential; the joining points r_1 and r_2, and the spline-function parameters b_1–b_4 are obtained algebraically by the continuity requirements; C is the dispersion coefficient.

Each term in the DFT-SAPT energy decomposition is described by a corresponding force field potential function,[22, 23]

$$\begin{cases} E_{exch}^{(1)}\left(r_{ij}\right)=\sum_{ij}A_{ij}^{exch}\exp\left(-B_{ij}r_{ij}\right) \\ E_{pol}^{(1)}\left(r_{ij}\right)\cong\sum_{ij}f_1\left(B_{ij},r_{ij}\right)\frac{q_iq_j}{r_{ij}}+\sum_{ij}A_{ij}^{elec}\exp\left(-B_{ij}r_{ij}\right) \\ E_{ind}^{(2)}+E_{ind-exch}^{(2)}\cong U_{shell}+\sum_{ij}A_{ij}^{ind}\exp\left(-B_{ij}r_{ij}\right) \\ E_{disp}^{(2)}+E_{disp-exch}^{(2)}\cong\sum_{i,j}A_{ij}^{disp}\exp\left(-B_{ij}r_{ij}\right)-\sum_{n=6,8,10}\sum_{i,j}f_n\left(\beta_{ij},r_{ij}\right)\frac{C_n^{ij}}{r_{ij}^n} \\ E_{\delta hf}\left(r_{ij}\right)=\sum_{ij}A_{ij}^{\delta hf}\exp\left(-B_{ij}r_{ij}\right) \end{cases} \qquad \text{(S2)}$$

where A_{ij}^{exch}, A_{ij}^{elec}, A_{ij}^{ind}, A_{ij}^{disp}, and $A_{ij}^{\delta hf}$ are the prefactors for each term, and B_{ij} are the exponents and utilized in all the Buckingham-type terms. These Buckingham-type terms were used to account for short-range charge penetration effect, which is proportional to the overlap of electron densities. $f_n\left(\beta_{ij},r_{ij}\right)$ is the Tang-Toennies damping function and used to damp both Coulomb and dispersion interactions; U_{shell} is the total Drude oscillator polarization energy and considered only for adsorbate-adsorbate interactions; C_6^{ij}, C_8^{ij}, C_{10}^{ij} are dispersion coefficients.

References

1 S. S. Han and W. A. Goddard, *J. Am. Chem. Soc.,* 2007, **129**, 8422.
2 S. S. Han, W. Q. Deng and W. A. Goddard, *Angew. Chem. Int. Ed.,* 2007, **46**, 6289.
3 S. S. Han and W. A. Goddard, *J. Phys. Chem. C,* 2008, **112**, 13431.
4 J. Fu and H. Sun, *J. Phys. Chem. C,* 2009, **113**, 21815.
5 Z. H. Xiang, J. H. Lan, D. P. Cao, X. H. Shao, W. C. Wang and D. P. Broom, *J. Phys. Chem. C,* 2009, **113**, 15106.
6 R. B. Getman, J. H. Miller, K. Wang and R. Q. Snurr, *J. Phys. Chem. C,* 2011, **115**, 2066.
7 M. Fischer, B. Kuchta, L. Firlej, F. Hoffman and M. Froba, *J. Phys. Chem. C,* 2010, **114**, 19116.
8 S. S. Han, H. Furukawa, O. M. Yaghi and W. A. Goddard, *J. Am. Chem. Soc.,* 2008, **130**, 11580.
9 D. P. Cao, J. H. Lan, W. C. Wang and B. Smit, *Angew. Chem. Int. Ed.,* 2009, **48**, 4730.
10 S. S. Han, S. H. Choi and W. A. Goddard, *J. Phys. Chem. C,* 2010, **114**, 12039.
11 J. H. Lan, D. P. Cao, W. C. Wang, T. Ben and G. S. Zhu, *J. Phys. Chem. Lett.,* 2010, **1**, 978.
12 J. H. Lan, D. J. Cheng, D. P. Cao and W. C. Wang, *J. Phys. Chem. C,* 2008, **112**, 5598.
13 A. Li, R. F. Lu, Y. Wang, X. Wang, K. L. Han and W. Q. Deng, *Angew. Chem. Int. Ed.,* 2010, **49**, 3330.
14 W. Q. Deng, X. Xu and W. A. Goddard, *Phys. Rev. Lett.,* 2004, **92**.
15 D. F. Plant, G. Maurin, I. Deroche and P. L. Llewellyn, *Micropor. Mesopor. Mat,* 2007, **99**, 70.
16 G. Maurin, Y. Belmabkhout, G. Pirngruber, L. Gaberova and P. Llewellyn, *Adsorption,* 2007, **13**, 453.
17 H. J. Fang, P. Kamakoti, J. Zang, S. Cundy, C. Paur, P. I. Ravikovitch and D. S. Sholl, *J. Phys. Chem. C,* 2012, **116**, 10692.
18 H. J. Fang, P. Kamakoti, P. I. Ravikovitch, M. Aronson, C. Paur and D. S. Sholl, *Phys. Chem. Chem. Phys.,* 2013, **15**, 12882.
19 J. H. Lan, D. P. Cao, W. C. Wang and B. Smit, *Acs Nano,* 2010, **4**, 4225.
20 S. S. Han, D. Kim, D. H. Jung, S. Cho, S. H. Choi and Y. Jung, *J. Phys. Chem. C,* 2012, **116**, 20254.
21 A. L. Dzubak, L. C. Lin, J. Kim, J. A. Swisher, R. Poloni, S. N. Maximoff, B. Smit and L. Gagliardi, *Nat. Chem.,* 2012, **4**, 810.
22 J. G. McDaniel, K. Yu and J. R. Schmidt, *J. Phys. Chem. C,* 2012, **116**, 1892.
23 J. G. McDaniel and J. R. Schmidt, *J. Phys. Chem. C,* 2012, **116**, 14031.
24 L. J. Chen, C. A. Morrison and T. Duren, *J. Phys. Chem. C,* 2012, **116**, 18899.
25 W. L. Li, S. Grimme, H. Krieg, J. Mollmann and J. P. Zhang, *J. Phys. Chem. C,* 2012, **116**, 8865.
26 M. Fischer, F. Hoffmann and M. Froba, *Chemphyschem,* 2010, **11**, 2220.
27 J. L. Mendoza-Cortes, S. S. Han, H. Furukawa, O. M. Yaghi and W. A. Goddard, *J. Phys. Chem. A,* 2010, **114**, 10824.
28 J. H. Lan, D. P. Cao and W. C. Wang, *Langmuir,* 2010, **26**, 220.
29 M. Cossi, G. Gatti, L. Canti, L. Tei, M. Errahali and L. Marchese, *Langmuir,* 2012, **28**, 14405.
30 T. Ben, H. Ren, S. Q. Ma, D. P. Cao, J. H. Lan, X. F. Jing, W. C. Wang, J. Xu, F. Deng, J. M. Simmons, S. L. Qiu and G. S. Zhu, *Angew. Chem. Int. Ed.,* 2009, **48**, 9457.
31 D. C. Yu, P. Ghosh and R. Q. Snurr, *Dalton Transactions,* 2012, **41**, 3962.
32 L. C. Liu, L. F. Zhao and H. Sun, *J. Phys. Chem. C,* 2009, **113**, 16051.
33 J. Zang, S. Nair and D. S. Sholl, *J. Phys. Chem. C,* 2013, **117**, 7519.
34 M. Fischer, J. R. B. Gomes, M. Froba and M. Jorge, *Langmuir,* 2012, **28**, 8537.
35 R. A. Aziz, M. J. Slaman, W. L. Taylor and J. J. Hurly, *J. Chem. Phys.,* 1991, **94**, 1034.