Electronic supplementary information

A Computational Approach Towards Understanding Hydrogen Gas Adsorption in Co-MIL-88A

Nguyen Thi Xuan Huynh,[ab] O My Na,[a] Viorel Chihaia[c] and Do Ngoc Son*[a]

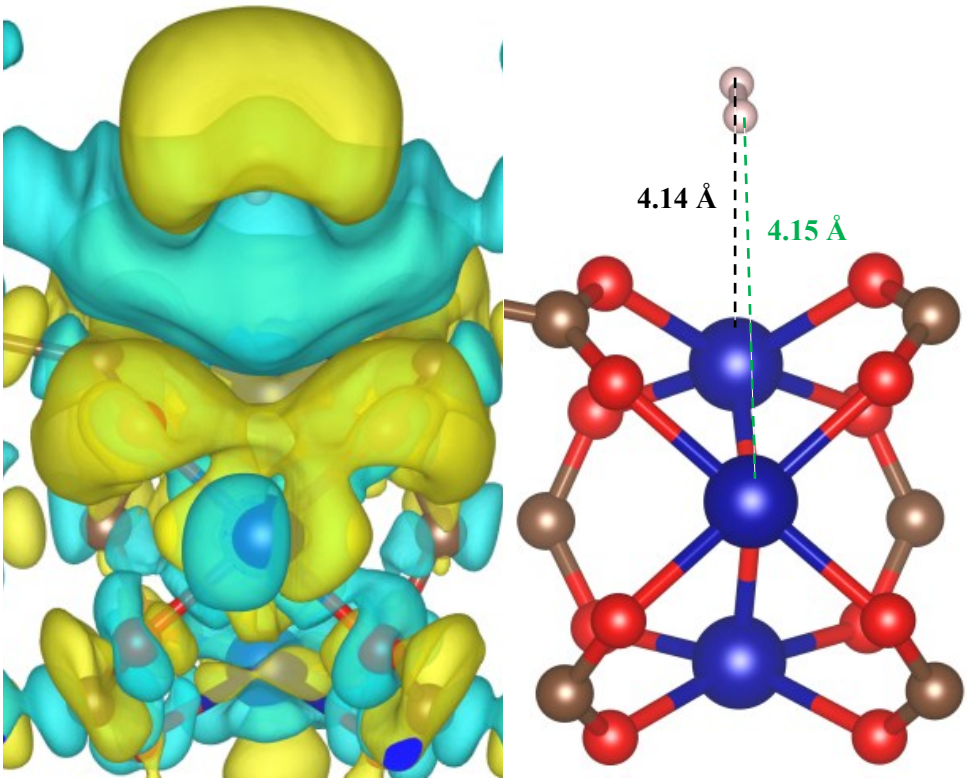
[a]*Ho Chi Minh City University of Technology, VNU-HCM, 268 Ly Thuong Kiet Street, District 10, Ho Chi Minh City, Vietnam*

[b]*Quy Nhon University, 170 An Duong Vuong Street, Quy Nhon City, Binh Dinh Province, Vietnam*

[c]*Institute of Physical Chemistry "Ilie Murgulescu" of the Romanian Academy, Splaiul Independentei 202, Sector 6, 060021 Bucharest, Romania*

** Email : dnson@hcmut.edu.vn*

List of Figures and Tables



a) Charge density difference b) The corresponding geometry

Figure S1. The charge density difference of H_2 at the hollow site with Isosurface = $2x10^{-5}$ *e*/Bohr^3. Yellow and cyan clouds represent the charge gain and loss, respectively.

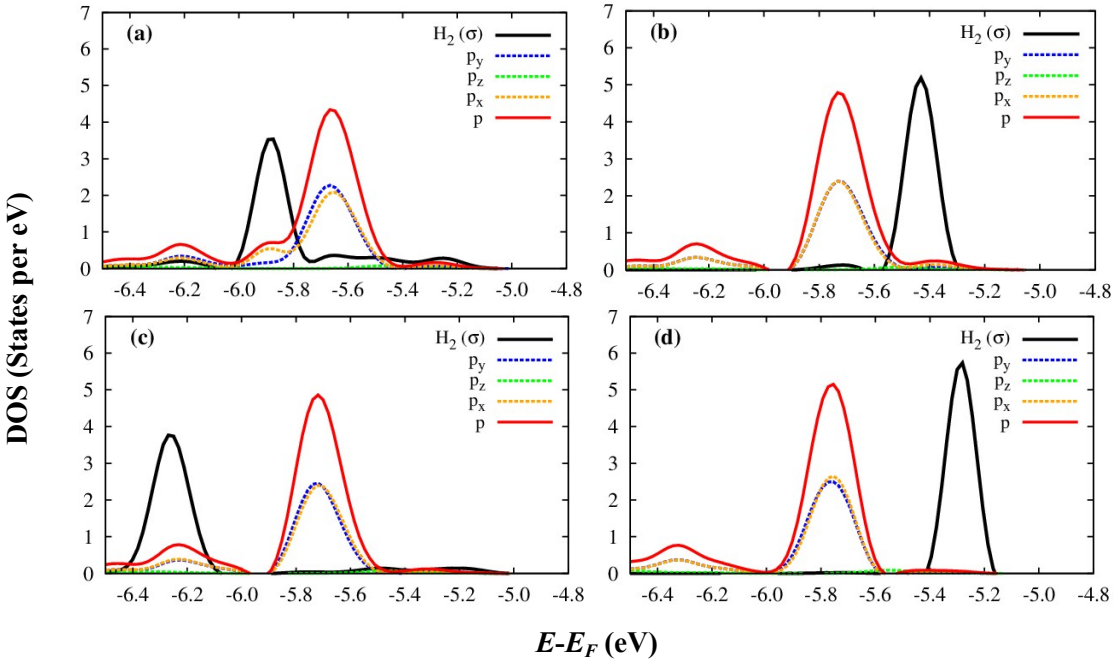


Figure S2. The electronic density of state of the hydrogen molecule and the μ_3-O atoms at the sites: hollow (a), ligand (b), metal side-on (c), and metal end-on (d).

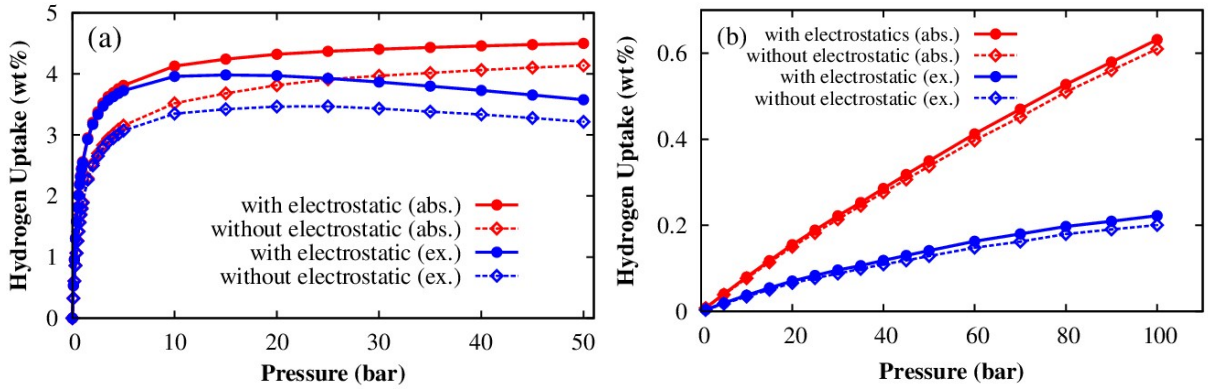
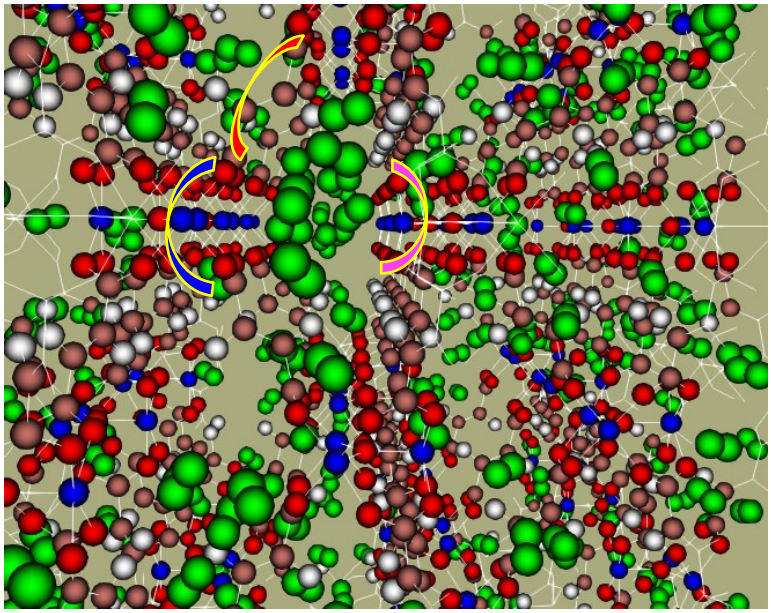
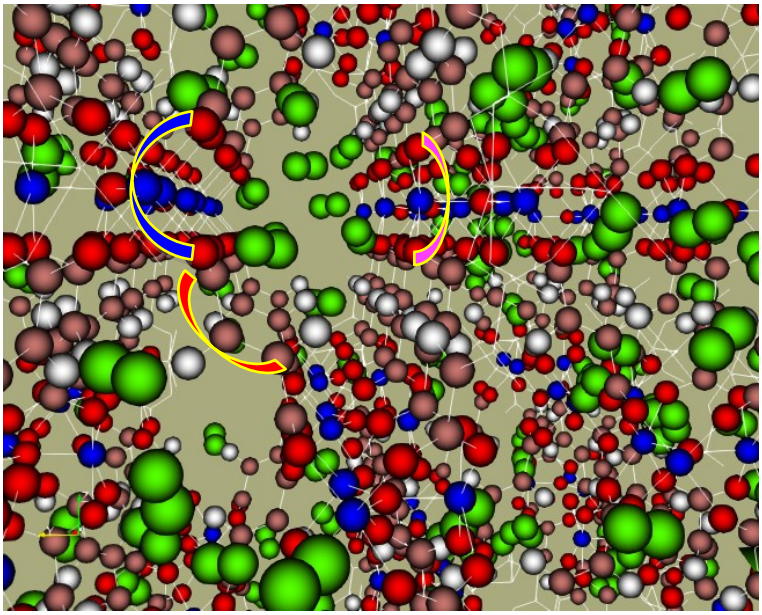


Figure S3. Absolute hydrogen uptake in Co-MIL-88A with and without electrostatic interaction between H_2 and the MOF at 77 K (a) and 288 K (b).



a) At 77 K, 0.1 bar



b) At 298 K, 10 bar

Figure S4. The density of the adsorbed hydrogen molecules in the Co-MIL-88A. The blue, red, brown, white balls represent the cobalt, oxygen, carbon, and hydrogen atoms of MOF, respectively. Each pair of the green balls represents an adsorbed hydrogen molecule. The blue, red and pink bands refer the hollow, ligand and metal sites, respectively.

Table S1. The frequency of the vibrational modes, ν (cm^{-1}) for the favorable H_2 adsorption sites and the free hydrogen molecule.

Sites	f_1	f_2	f_3	f_4	f_5	f_6	Total
Hollow	4402	312	224	193	114	77	5322
Ligand	4402	324	251	187	42	103	5310
Metal side-on	4409	277	139	103	72	37	5036
Metal end-on	4421	119	11	95	182	201	5029
Free H_2	4448	52	10	0	82	103	4695

Table S2. The average atomic point charges used in GCMC simulations

Atom type	Our DDEC charge calculation	Taken from RASPA[1]
Co	1.082	1.139
C1	0.753	0.832
C2	-0.237	-0.292
C3	0.362	0.315
C4	-0.139	-0.110
O1	-0.666	-0.684
O2	-0.606	-0.645
O3	-0.682	-0.731
H	0.133	0.176

[1]D. Dubbeldam, S. Calero, D. E. Ellis and R. Q. Snurr, *Mol. Simul.*, 2016, **42**, 81–101

Table S3. Absolute and excess hydrogen uptakes in Co-MIL-88A with and without electrostatic interaction at 77 K

P (bar)	LJ+Coulomb Interaction (wt%)		LJ Interaction (wt%)		Coulomb Interaction (wt%)		Percentage of Electrostatic Interaction (%)	
	Absolute	Excess	Absolute	Excess	Absolute	Excess	Absolute	Excess
0.1	0.53	0.53	0.33	0.33	0.2	0.2	37.74	37.74
0.2	0.96	0.96	0.61	0.61	0.35	0.35	36.46	36.46
0.3	1.31	1.31	0.86	0.86	0.45	0.45	34.35	34.35
0.4	1.59	1.58	1.07	1.06	0.52	0.52	32.70	32.91
0.5	1.82	1.81	1.27	1.26	0.55	0.55	30.22	30.39
0.6	2.02	2.01	1.43	1.42	0.59	0.59	29.21	29.35
0.7	2.2	2.18	1.58	1.57	0.62	0.61	28.18	27.98
0.8	2.33	2.31	1.7	1.69	0.63	0.62	27.04	26.84
0.9	2.45	2.44	1.8	1.79	0.65	0.65	26.53	26.64
1.0	2.56	2.54	1.9	1.89	0.66	0.65	25.78	25.59
1.5	2.95	2.93	2.29	2.27	0.66	0.66	22.37	22.53
2.0	3.21	3.17	2.53	2.5	0.68	0.67	21.18	21.14
2.5	3.38	3.34	2.7	2.65	0.68	0.69	20.12	20.66
3.0	3.52	3.47	2.83	2.78	0.69	0.69	19.60	19.88
3.5	3.63	3.57	2.94	2.88	0.69	0.69	19.01	19.33
4.0	3.69	3.63	3.01	2.95	0.68	0.68	18.43	18.73
4.5	3.76	3.68	3.09	3.01	0.67	0.67	17.82	18.21
5.0	3.81	3.73	3.15	3.07	0.66	0.66	17.32	17.69
10.0	4.13	3.96	3.52	3.35	0.61	0.61	14.80	15.43
15.0	4.24	3.98	3.68	3.42	0.56	0.56	13.22	14.08
20.0	4.32	3.97	3.81	3.46	0.51	0.51	11.76	12.79
25.0	4.37	3.92	3.91	3.47	0.46	0.46	10.49	11.67
30.0	4.40	3.87	3.97	3.43	0.44	0.44	9.90	11.28
35.0	4.43	3.80	4.01	3.38	0.42	0.42	9.43	11.01
40.0	4.46	3.73	4.06	3.33	0.39	0.39	8.84	10.57
45.0	4.48	3.65	4.10	3.28	0.38	0.38	8.40	10.30
50.0	4.50	3.58	4.14	3.21	0.36	0.36	8.04	10.11

Table S4. Absolute and excess hydrogen uptakes in Co-MIL-88A with and without electrostatic interaction at 298 K

P (bar)	LJ+Coulomb Interaction (wt%)		LJ Interaction (wt%)		Coulomb Interaction (wt%)		Percentage of Electrostatic Interaction (%)	
	Absolute	Excess	Absolute	Excess	Absolute	Excess	Absolute	Excess
1	0.0083	0.0040	0.0079	0.0037	0.0004	0.0004	4.24	8.69
5	0.041	0.020	0.039	0.018	0.002	0.002	3.98	8.28
10	0.080	0.038	0.077	0.035	0.003	0.003	3.70	7.86
15	0.118	0.055	0.114	0.051	0.004	0.004	3.35	7.22
20	0.155	0.071	0.150	0.066	0.005	0.005	3.15	6.91
25	0.189	0.084	0.182	0.077	0.006	0.006	3.38	7.64
30	0.222	0.096	0.214	0.088	0.008	0.008	3.71	8.57
35	0.253	0.106	0.245	0.099	0.007	0.007	2.91	6.93
40	0.286	0.118	0.277	0.109	0.009	0.009	3.16	7.63
45	0.318	0.130	0.306	0.119	0.011	0.011	3.61	8.83
50	0.350	0.141	0.337	0.129	0.013	0.013	3.59	8.87
60	0.412	0.163	0.397	0.148	0.015	0.015	3.64	9.19
70	0.470	0.180	0.452	0.162	0.018	0.018	3.83	9.99
80	0.527	0.197	0.509	0.180	0.018	0.018	3.35	8.96
90	0.579	0.210	0.560	0.190	0.019	0.019	3.32	9.17
100	0.631	0.222	0.609	0.201	0.022	0.022	3.43	9.75

Table S5. The average distance between the H_2 molecule and the nearest atoms of Co-MIL-88A (in Å)

Sites	GCMC	DFT
Hollow	3.19	3.20
Ligand	3.64	3.41
Metal side-on	2.77	3.14
Metal end-on	2.58	3.15

Table S6. The structure of the optimized Co-MIL-88A (the POSCAR format of VASP)

```
Co-MIL-88A
11.2222000000000
   1.0000000000000000   0.0000000000000000   0.0000000000000000
  -0.4999999999999998   0.8660254037844388   0.0000000000000000
   0.0000000000000010   0.0000000000000020   1.3116000000000001
   H    C    O    Co
   12   24   26   6
Direct
  0.5753655182525063   0.1539288745201919   0.9736932754453455
  0.8460751308184772   0.4212869233714625   0.9736636678655390
  0.5785415767105456   0.4245924781705243   0.9736612303969319
  0.5753655182525063   0.1539288745201919   0.5263066933718400
  0.8460751308184772   0.4212869233714625   0.5263363009516464
  0.5785415767105456   0.4245924781705243   0.5263387384202536
  0.1539357948166553   0.5755322808740659   0.0263277690666836
  0.4213021226878529   0.8461034622366895   0.0263130782336863
  0.4248003961115691   0.5787366393329931   0.0262948675373105
  0.1539357948166553   0.5755322808740659   0.4736722205390496
  0.4213021226878529   0.8461034622366895   0.4736869113720469
  0.4248003961115691   0.5787366393329931   0.4737051220684227
  0.5466659005847795   0.0960856617893677   0.1169809288299098
  0.9038971471360248   0.4506893992193957   0.1169587073796239
  0.5495868752647136   0.4534306560693983   0.1169557174156765
  0.5466659005847795   0.0960856617893677   0.3830190607758234
  0.9038971471360248   0.4506893992193957   0.3830412822261093
  0.5495868752647136   0.4534306560693983   0.3830442721900568
  0.0961411840247371   0.5465674082450029   0.8830453362778168
  0.4506381609806948   0.9038773198073615   0.8830050977043666
  0.4530805108753685   0.5491375504336760   0.8830024316105433
  0.0961411840247371   0.5465674082450029   0.6169546325393687
  0.4506381609806948   0.9038773198073615   0.6169948711128188
  0.4530805108753685   0.5491375504336760   0.6169975372066422
  0.5298378976707773   0.0630320631331601   0.0174288882601576
  0.9369440105871333   0.4669311787123340   0.0174111719540563
  0.5331228700754459   0.4700567666212462   0.0174109566428173
  0.5298378976707773   0.0630320631331601   0.4825711013455756
  0.9369440105871333   0.4669311787123340   0.4825888176516769
  0.5331228700754459   0.4700567666212462   0.4825890329629159
  0.0630522645213207   0.5300391731846326   0.9825963072745354
  0.4668674739445529   0.9369786437667679   0.9825548426665409
  0.4699868099148831   0.5330113623903856   0.9825822796437966
  0.0630522645213207   0.5300391731846326   0.5174036615426501
  0.4668674739445529   0.9369786437667679   0.5174451261506516
  0.4699868099148831   0.5330113623903856   0.5174176891733888
  0.4539213114979276   0.1148335366363431   0.1529994574815462
  0.8851572760035797   0.3392856161969601   0.1529721207210744
  0.6609670612222381   0.5463165702499073   0.1529495332707086
  0.4539213114979276   0.1148335366363431   0.3470005321241799
  0.8851572760035797   0.3392856161969601   0.3470278688846518
  0.6609670612222381   0.5463165702499073   0.3470504563350176
  0.1146280828690023   0.4537197023062354   0.8470842057404494
  0.3392464813875953   0.8852609699604856   0.8469708444328599
  0.5457827204728928   0.6606627973903835   0.8469784545305153
  0.1146280828690023   0.4537197023062354   0.6529157630767431
  0.3392464813875953   0.8852609699604856   0.6530291243843327
  0.5457827204728928   0.6606627973903835   0.6530215142866772
  0.6568802599167038   0.1120275356161742   0.1533026751975000
  0.8879898153592521   0.5450695141550302   0.1532957483961259
  0.4553861120868809   0.3430735947291598   0.1532725066995365
  0.6568802599167038   0.1120275356161742   0.3466973144082332
  0.8879898153592521   0.5450695141550302   0.3467042412096074
  0.4553861120868809   0.3430735947291598   0.3467274829061967
  0.1123154662482705   0.6569626133849756   0.8466918854243487
  0.5448806446145089   0.8877997541875062   0.8467236967213784
  0.3428927740112013   0.4547913120362192   0.8466947113482174
  0.1123154662482705   0.6569626133849756   0.6533080833928367
  0.5448806446145089   0.8877997541875062   0.6532762720958071
  0.3428927740112013   0.4547913120362192   0.6533052574689610
  0.6665951903146196   0.3333418282436607   0.2499999948028631
  0.3333928430472100   0.6667234411542977   0.7499999844085963
  0.4787164609619973   0.2405081828716842   0.2499999948028631
  0.2381535604793789   0.7594388298342865   0.7499999844085963
  0.5212633270197765   0.7618115686250516   0.7499999844085963
  0.2404029324859905   0.4784954920472196   0.7499999844085963
  0.7595132335803607   0.2381225681740184   0.2499999948028631
  0.7618942454171965   0.5213384889630274   0.2499999948028631
```