

Exceptional H₂ Sorption Characteristics in a Mg²⁺-Based Metal–Organic Framework with Small Pores: Insights From Experimental and Theoretical Studies

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MOF System Cell

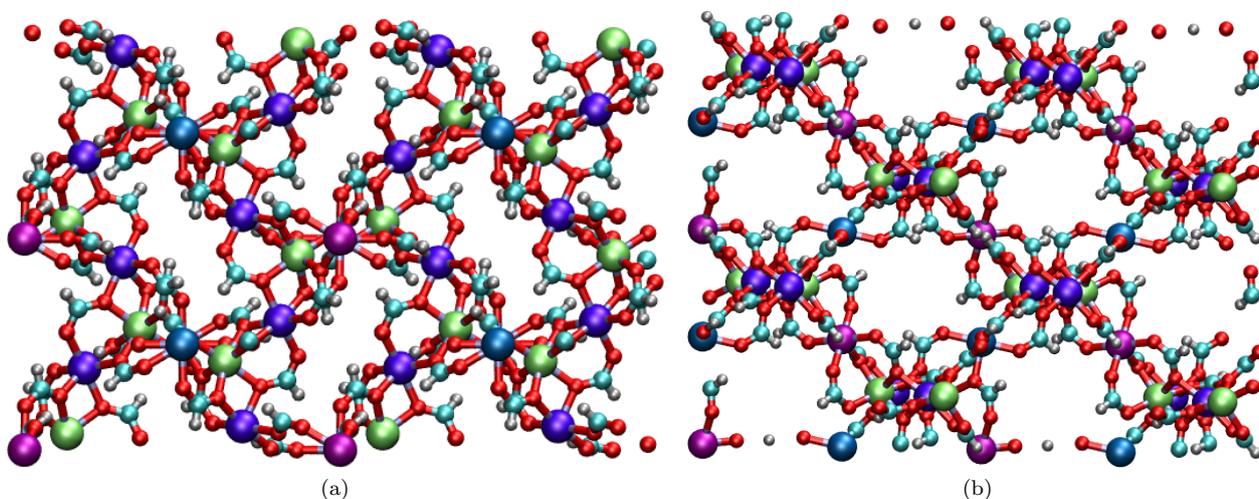


Figure S1. (a) The orthographic *a*-axis and (b) *b*-axis views of the $2 \times 2 \times 2$ system cell of α -[Mg₃(O₂CH)₆]. The Mg²⁺ ions are color-coded to highlight the four chemically distinct Mg²⁺ ions. Atoms colors: C = cyan, H = white, O = red, Mg1 = magenta, Mg2 = lime green, Mg3 = violet, Mg4 = blue.

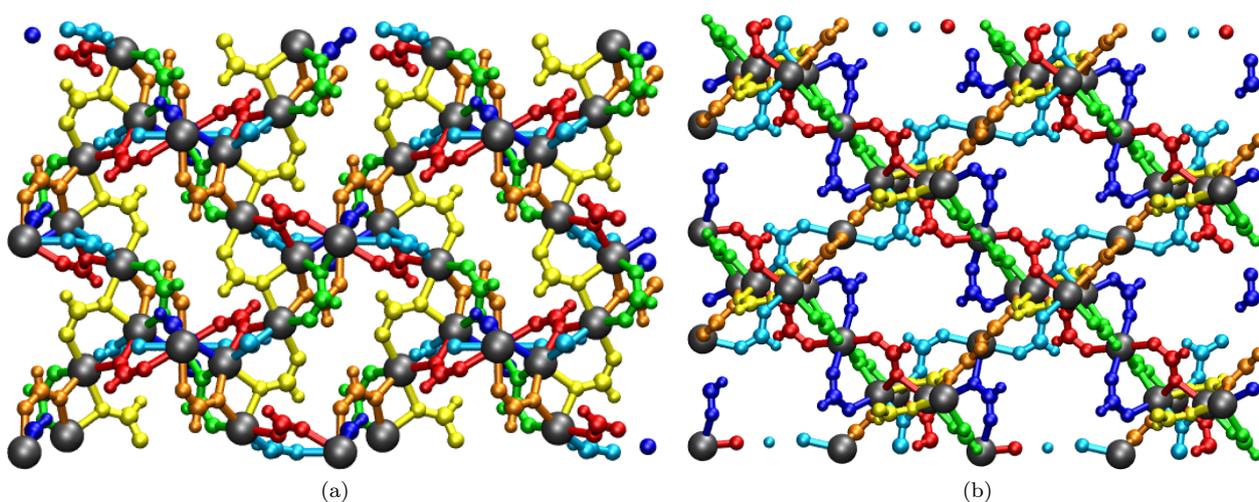


Figure S2. (a) The orthographic *a*-axis and (b) *b*-axis views of the $2 \times 2 \times 2$ system cell of α -[Mg₃(O₂CH)₆]. The formate ligands (L) are color-coded to highlight the six chemically distinct linkers. Atoms colors: Mg = gray, L1 = red, L2 = blue, L3 = green, L4 = yellow, L5 = orange, L6 = cyan.

MOF Partial Charges

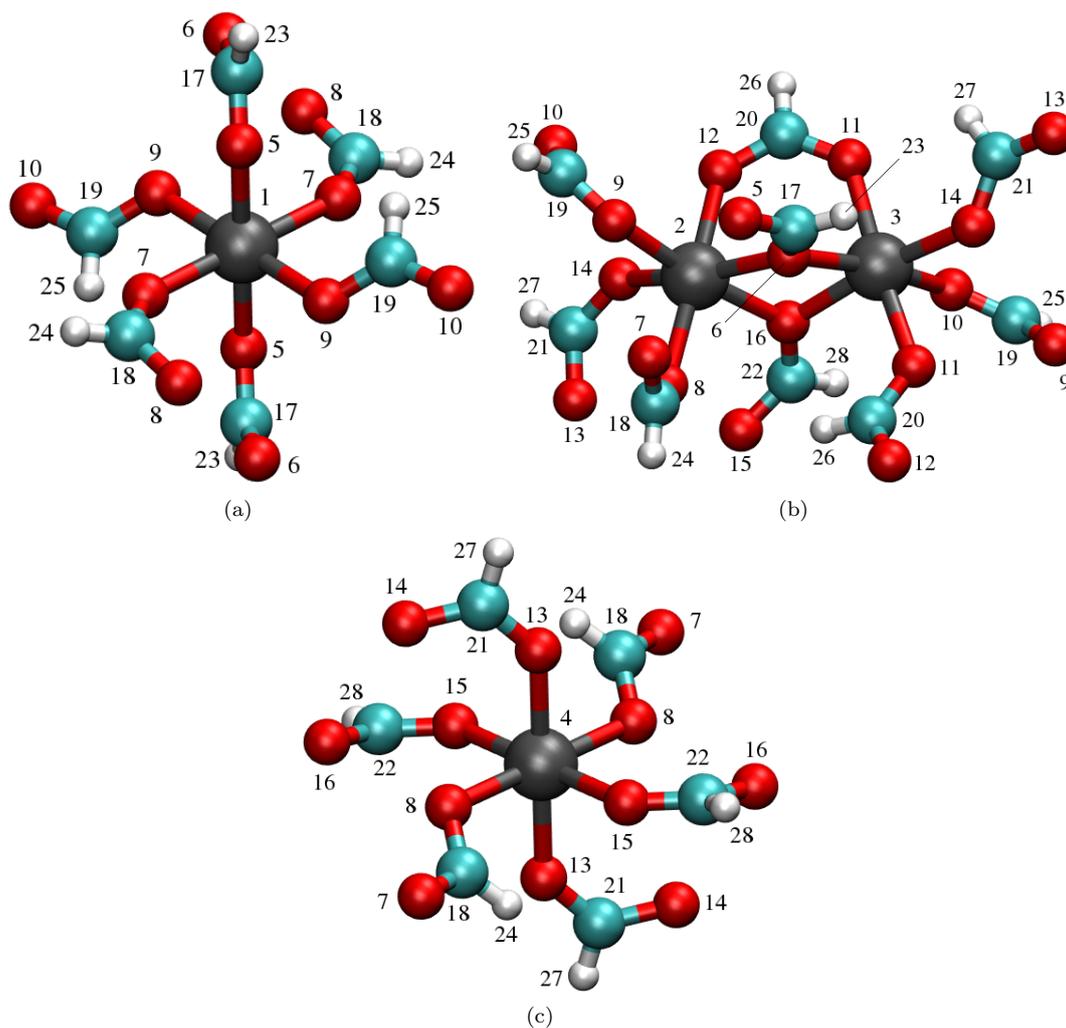


Figure S3. The numbering of the chemically distinct atoms in α -[Mg₃(O₂CH)₆] as referred to in Tables S1 and S2: (a) view showing the Mg1 ion; (b) view showing the Mg2 and Mg3 ions; (c) view showing the Mg4 ion. Atom colors: C = cyan, H = white, O = red, Mg = gray.

Table S1. The calculated partial charges (e^-) for the chemically distinct atoms in α -[Mg₃(O₂CH)₆]. Label of atoms correspond to Figure S3. Component types correspond to Figure S1 for the Mg²⁺ ions and Figure S2 for the formate ligands.

Atom	Label	Component	q (e^-)
Mg	1	Mg1	1.83260
Mg	2	Mg2	1.78830
Mg	3	Mg3	1.72240
Mg	4	Mg4	1.86400
O	5	L1	-0.97390
O	6	L1	-0.92820
O	7	L2	-0.98040
O	8	L2	-0.69340
O	9	L3	-0.82760
O	10	L3	-0.91300
O	11	L4	-0.93010
O	12	L4	-0.84180
O	13	L5	-1.00110
O	14	L5	-0.98990
O	15	L6	-0.79080
O	16	L6	-0.73780
C	17	L1	0.82200
C	18	L2	0.96540
C	19	L3	0.85510
C	20	L4	0.92050
C	21	L5	0.75950
C	22	L6	0.94070
H	23	L1	0.02510
H	24	L2	-0.06720
H	25	L3	0.15290
H	26	L4	-0.02510
H	27	L5	0.08220
H	28	L6	-0.18210

Table S2. The crystallographic distances (in Å) between various atoms in α -[Mg₃(O₂CH)₆]. Label of atoms correspond to Figure S3.

Atom Pair	Distance (Å)
1-5	2.06287
1-7	2.03841
1-9	2.10633
2-6	2.09236
2-8	2.06497
2-9	2.07079
2-12	2.10005
2-14	2.10018
2-16	2.08418
3-6	2.11379
3-10	2.01986
3-11	2.09291
3-12	2.03424
3-14	2.09006
3-16	2.05853
4-8	2.11284
4-13	2.05076
4-15	2.06418

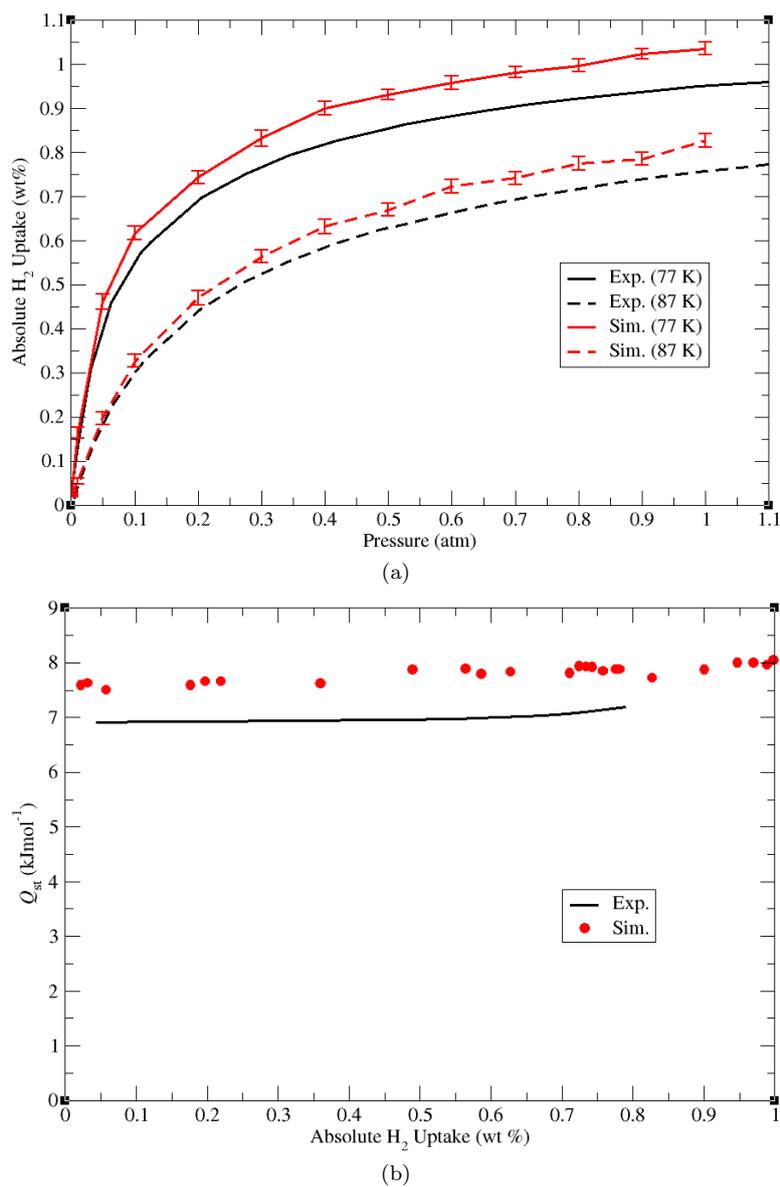
Simulated H₂ Sorption Results

Figure S4. (a) Absolute H₂ sorption isotherms at 77 K (solid) and 87 K (dashed) and (b) isosteric heats of adsorption (Q_{st}) for H₂ in α -[Mg₃(O₂CH)₆] for experiment (black) and simulation (red). The simulations were performed using the nonpolarizable potential by Belof *et al.*¹

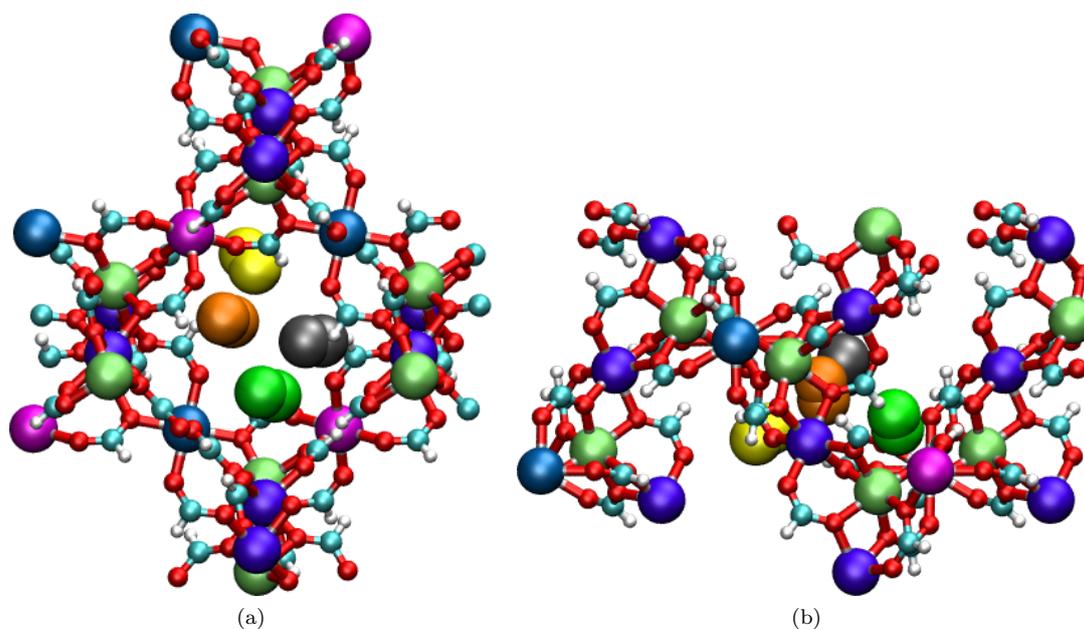


Figure S5. Molecular illustration of the sorbed H₂ molecules within the pore of α -[Mg₃(O₂CH)₆] as determined from simulation: (a) *b*-axis view and (b) *a*-axis view. The H₂ molecules and Mg²⁺ ions are color-coded to highlight the different H₂ sorption sites and chemically distinct Mg²⁺ ions, respectively. H₂ molecule colors: site 1A = green, site 1B = yellow, site 2A = orange, site 2B = gray. Atoms colors: C = cyan, H = white, O = red, Mg1 = magenta, Mg2 = lime green, Mg3 = violet, Mg4 = blue. Note, sites 1B and 2B are reflected on the opposite side of the pore from sites 1A and 2A, respectively, for illustrative purposes.

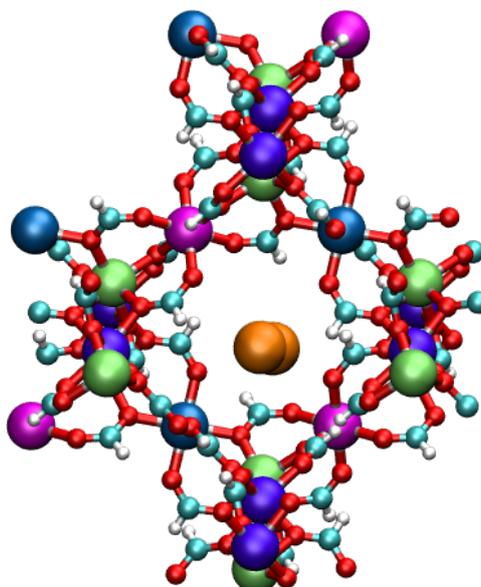


Figure S6. Molecular illustration of the sorbed H₂ molecule within the pore of α -[Mg₃(O₂CH)₆] as determined from simulation. The H₂ molecule (orange) shown is sorbed at site 1C. The Mg²⁺ ions are color-coded to highlight the four chemically distinct Mg²⁺ ions. Atoms colors: C = cyan, H = white, O = red, Mg1 = magenta, Mg2 = lime green, Mg3 = violet, Mg4 = blue.

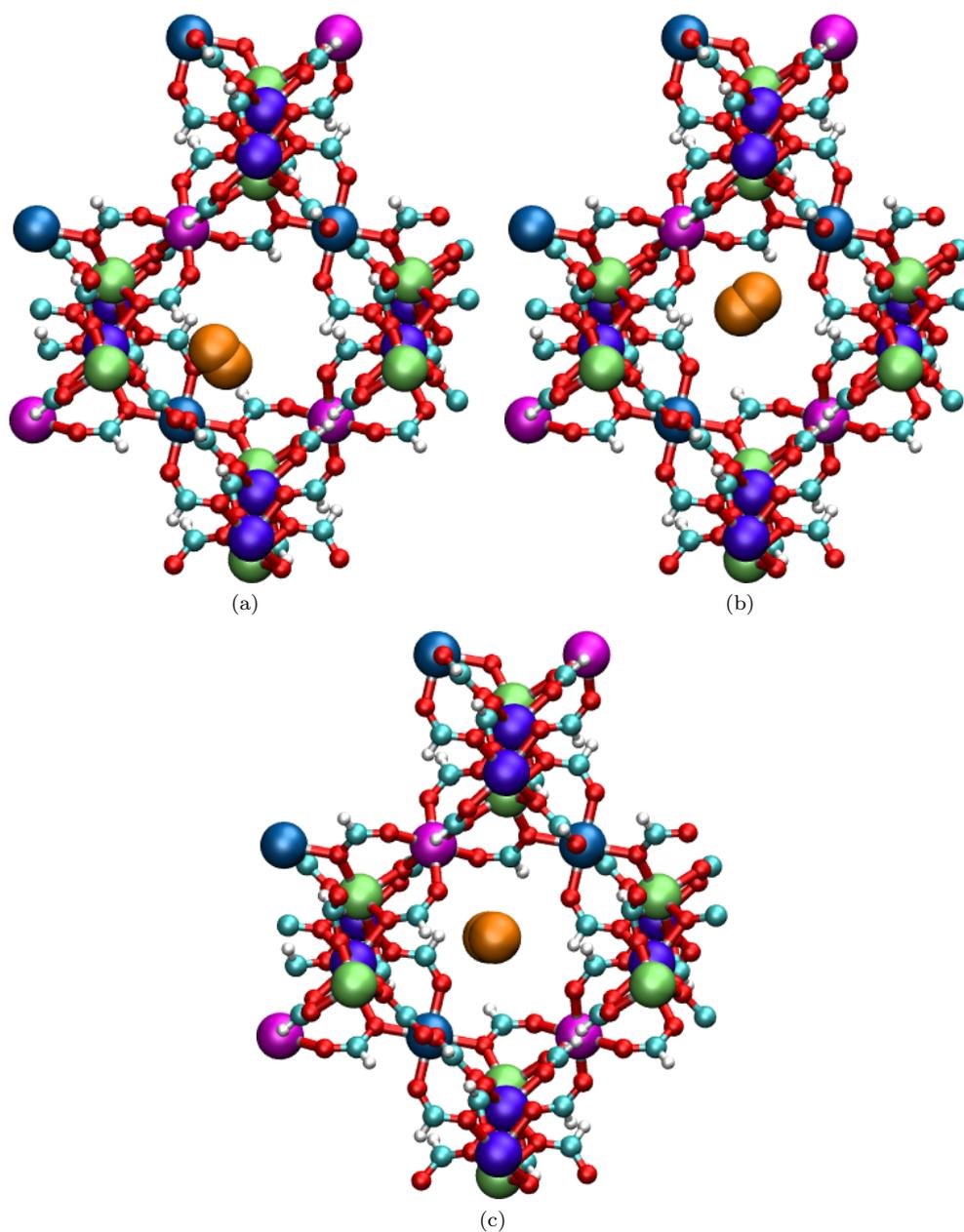


Figure S7. Molecular illustration of the sorbed H_2 molecules within the pore of $\alpha\text{-}[\text{Mg}_3(\text{O}_2\text{CH})_6]$ as determined from simulation. The H_2 molecules (orange) shown are sorbed at: (a) site 3A, (b) site 3B, and (c) site 3C. The Mg^{2+} ions are color-coded to highlight the four chemically distinct Mg^{2+} ions. Atoms colors: C = cyan, H = white, O = red, Mg1 = magenta, Mg2 = lime green, Mg3 = violet, Mg4 = blue.

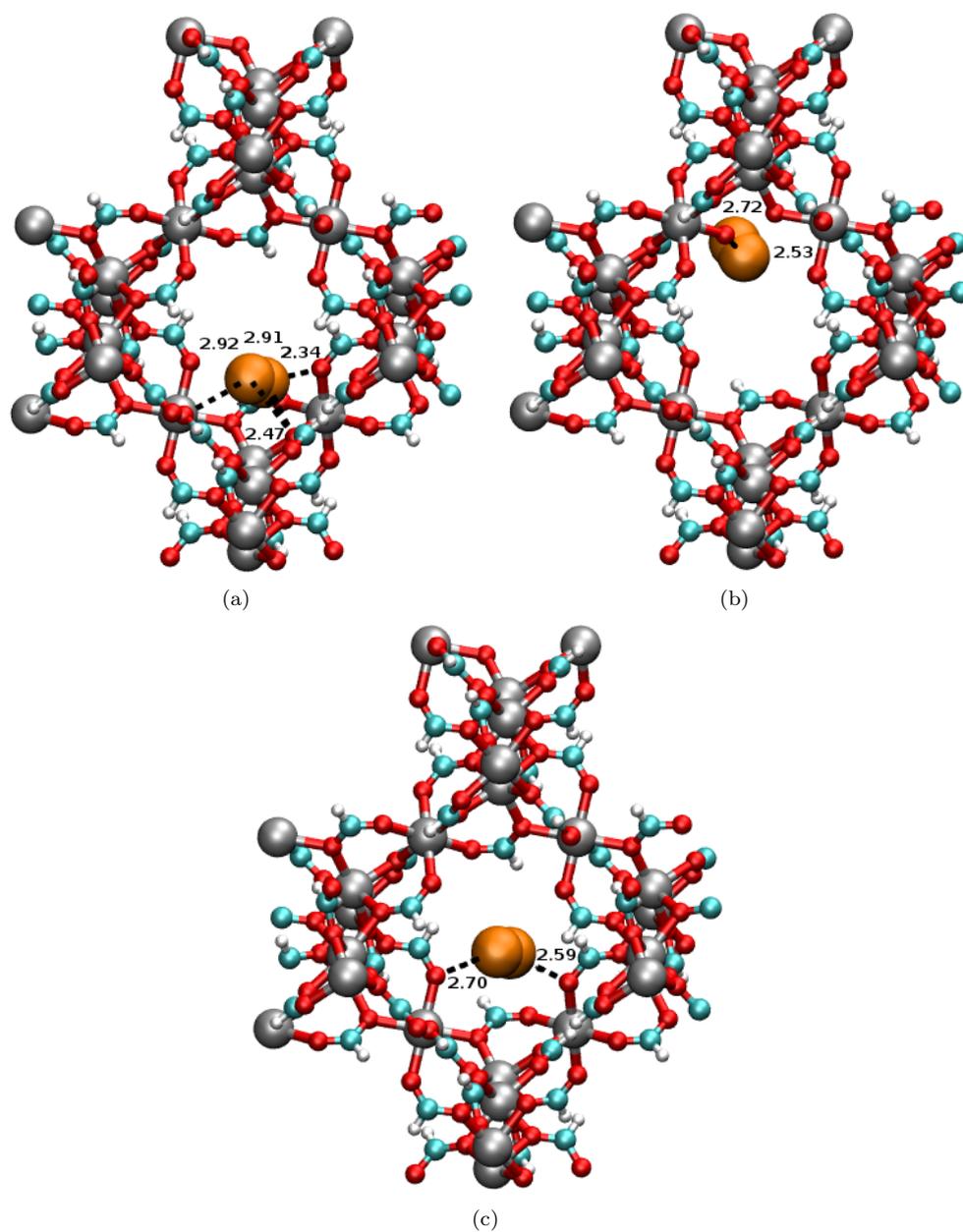


Figure S8. Molecular illustration of a H₂ molecule (orange) sorbed at (a) site 1A, (b) site 1B, and (c) site 1C in α -[Mg₃(O₂CH)₆] as determined from simulation showing the distances between the H atoms of the H₂ molecule and the nearest O atoms of the framework.

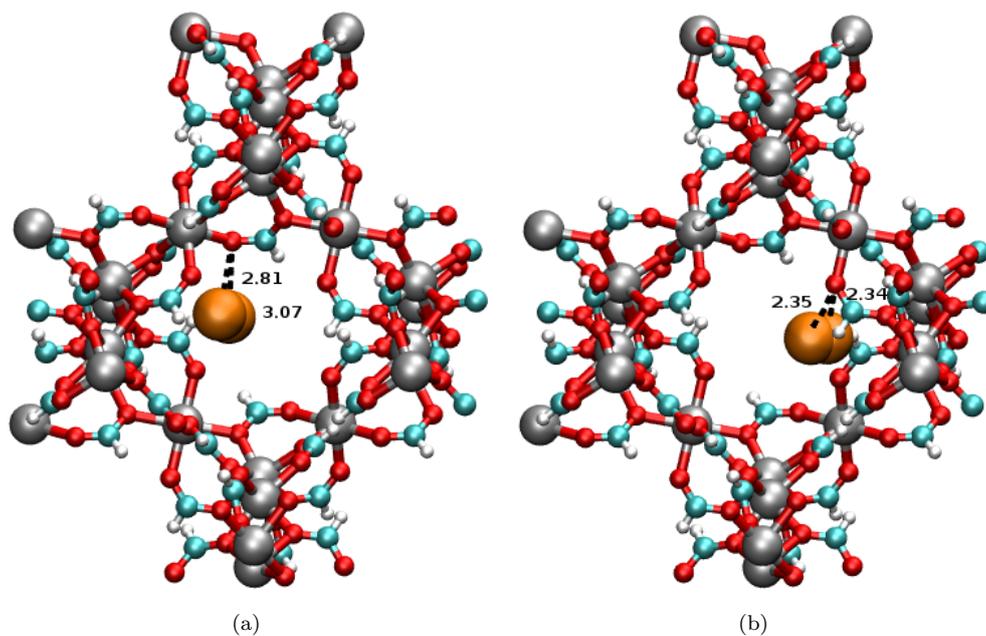


Figure S9. Molecular illustration of a H₂ molecule (orange) sorbed at **(a)** site 2A, **(b)** site 2B in α -[Mg₃(O₂CH)₆] as determined from simulation showing the distances between the H atoms of the H₂ molecule and the nearest O atoms of the framework.

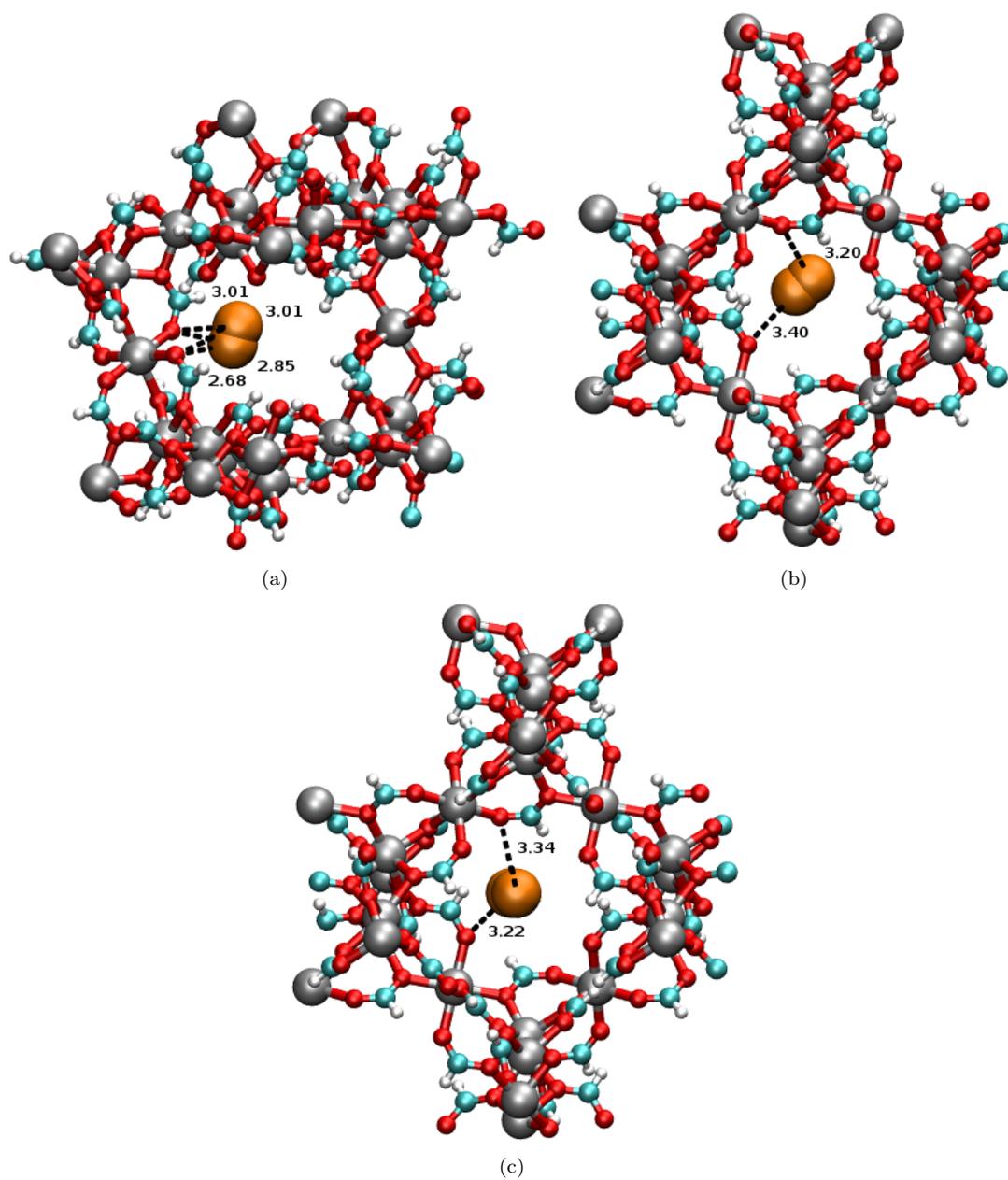


Figure S10. Molecular illustration of a H₂ molecule (orange) sorbed at (a) site 3A, (b) site 3B, and (c) site 3C in α -[Mg₃(O₂CH)₆] as determined from simulation showing the distances between the H atoms of the H₂ molecule and the nearest O atoms of the framework.

Quantum Rotation Calculations

The two-dimensional quantum rotational levels for a H_2 molecule sorbed about the eight considered sites in $\alpha\text{-}[\text{Mg}_3(\text{O}_2\text{CH})_6]$ were calculated by diagonalizing the rotor Hamiltonian in the spherical harmonic basis, Y_{jm} , which is the following:

$$\hat{H} = B\mathbf{j}^2 + V(\theta, \phi) \quad (1)$$

where B is the rotational constant for molecular H_2 (7.35 meV), \mathbf{j}^2 is the angular momentum operator, and $V(\theta, \phi)$ is the potential energy surface for the rotation of the H_2 molecule with its center-of-mass held fixed within the MOF- H_2 system. Each matrix element, $\langle Y_{jm} | V(\theta, \phi) | Y_{jm} \rangle$, was constructed using Gauss-Legendre quadrature³ with a basis set consisting of $\pm m$ functions.⁴ The kinetic energy term, $j(j+1)$, was added to all of the diagonal elements. The matrix was diagonalized using the LAPACK linear algebra package,⁵ yielding the rotational eigenvalues and the eigenvector coefficients. All two-dimensional rotational levels were calculated with $j = 7$, leading to 64 basis functions. The calculated rotational levels for a H_2 molecule sorbed about the eight considered sites in $\alpha\text{-}[\text{Mg}_3(\text{O}_2\text{CH})_6]$ are provided in Table S3.

The rotational barrier for a H_2 molecules sorbed about site 1A was determined by calculating the potential energy of the MOF- H_2 system as the H_2 molecule was rotated at various angles of θ (0 to 180°) and ϕ (0 to 360°). Single point energies were obtained on a sphere (4,096 points based on 64×64 Gaussian quadrature integration) and the rotational barrier was estimated by taking the difference between the high and low values. All calculations were performed using the Massively Parallel Monte Carlo (MPMC) code, which is currently available for download on GitHub.⁶

Table S3. The calculated two-dimensional quantum rotational levels for a H_2 molecule sorbed at the eight considered sites in $\alpha\text{-}[\text{Mg}_3(\text{O}_2\text{CH})_6]$. Sites 1A, 1B, 2A, and 2B are depicted in Figure S5, while site 1C is depicted in Figure S6, and sites 3A, 3B, and 3C are depicted in Figure S7. Relative energies are given in meV.

n	j	Site 1A ΔE (meV)	Site 1B ΔE (meV)	Site 1C ΔE (meV)	Site 2A ΔE (meV)	Site 2B ΔE (meV)	Site 3A ΔE (meV)	Site 3B ΔE (meV)	Site 3C ΔE (meV)
1	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2		2.57	4.19	4.54	6.48	7.07	8.09	8.80	9.18
3	1	31.54	20.77	24.39	19.20	20.45	14.75	19.40	18.22
4		34.47	36.67	29.12	26.33	22.02	27.79	23.19	19.16
5		45.54	39.58	42.59	40.86	42.01	38.86	40.62	41.67
6		47.71	42.73	45.13	41.71	42.34	39.44	43.52	42.49
7	2	51.48	50.68	45.94	45.88	43.59	48.45	46.79	43.20
8		69.44	63.32	60.59	54.93	53.09	53.08	51.80	49.64
9		70.07	70.38	61.60	57.16	52.22	57.88	54.10	49.71

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- ¹ J. L. Belof, A. C. Stern and B. Space, *J. Chem. Theory Comput.*, 2008, **4**, 1332–1337.
 - ² J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, 1947, **15**, 261–267.
 - ³ M. Abramowitz, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, Dover Publications, Inc., Mineola, NY, 1965.
 - ⁴ J. L. Belof, *Ph.D. thesis*, University of South Florida, 2009.
 - ⁵ E. Anderson, Z. Bai, J. Dongarra, A. Greenbaum, A. McKenney, J. Du Croz, S. Hammerling, J. Demmel, C. Bischof and D. Sorensen, Proceedings of the 1990 ACM/IEEE conference on Supercomputing, 1990, pp. 2–11.
 - ⁶ J. L. Belof and B. Space, *Massively Parallel Monte Carlo (MPMC)*, Available on GitHub, 2012, <https://github.com/mpmccode/mpmc>.