Theoretical Adsorption of Lactic Acid Through Benchmark Metal–Organic Frameworks

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Introduction

Metal–organic frameworks (MOFs) are an emerging class of porous crystalline materials that display great potential for efficient gas adsorption.[1] Several benchmark MOFs, HKUST-1, SIFSIX-1-Cu, Mg-MOF-74, MOF-505, MOF-5, In-*soc*-MOF, and ZIF-8 (**Figure 1**), were tested for their theoretical adsorption of lactic acid. The previously mentioned guest molecule has an abundant presence in biological systems, and causes vast biological plight, including both endocrine and metabolic diseases. The purpose here is to test these MOFs' ability to adsorb this perilous substance.
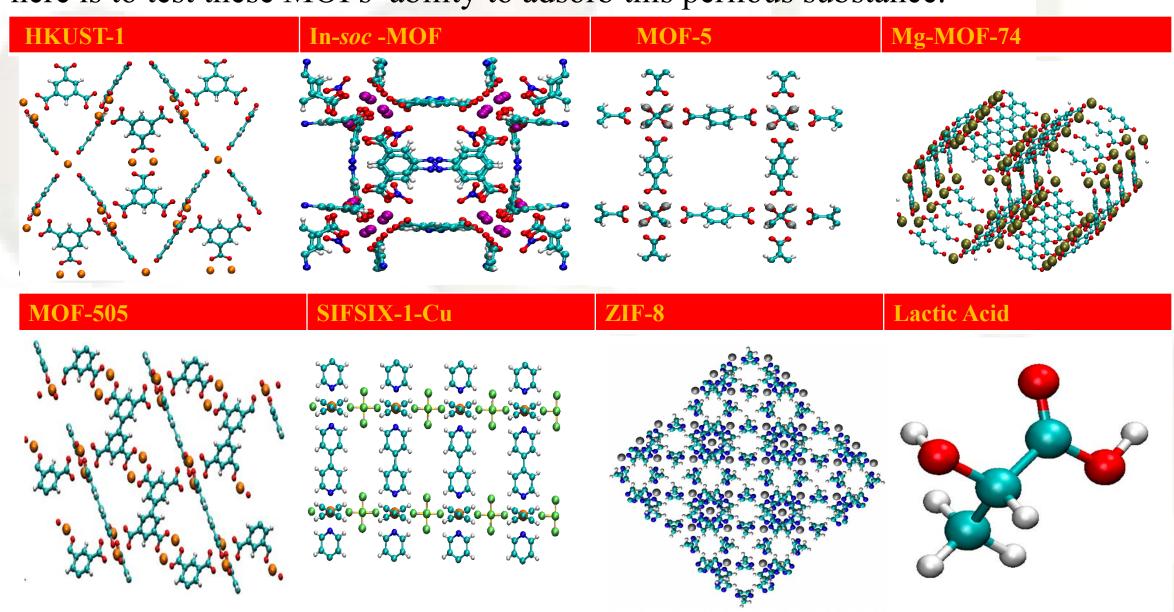

Figure 1: The crystal structures of the benchmark MOFs and a single lactic acid molecule. Atom colors: C = cyan, O = red, H = white, N = blue, F = lime, Si = yellow, Cu = orange, Zn = silver In = purple, Mg = tan

Methods

Identifying the unique atoms and environments within the MOFs was the first step in the research process. All atoms were parametrized with Lennard–Jones ε and σ, partial charges (q), and point polarizabilities ($\alpha°$). The Lennard–Jones parameters for all atoms were taken from the Universal Force Field.[2] The partial charges were determined through electronic structure calculations on a series of gas phase fragments for each MOF. The electrostatic energy was calculated using Ewald summation for periodic systems.[3] The polarizability values were taken from a previously published training set that has been shown to be transferable.[4] The polarization energy was calculated using a Thole–Applequist type model.[5] The program NWChem[6] was used to optimize a single lactic acid molecule at the MP2/aug-cc-pVDZ level of theory. Grand canonical Monte Carlo (GCMC) simulations were performed to obtain the initial lactic acid binding sites and equilibrium energies of the system. These simulations were implemented with the Massively Parallel Monte Carlo (MPMC) code.[7]

$$U_{LJ} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \qquad U_{es} = \frac{kq_iq_j}{r_{ij}} \qquad U_{pol} = -\frac{1}{2}\sum_i^N \vec{\mu}_i \cdot \vec{E}_i^{stat}$$

A PDB file was created and used for each of MOF and lactic acid (shown below). These input files contain the crystallographic coordinates and parameters for each unique atom and serve as the blueprint to run the desired GCMC simulations.

					x (Å)	y (Å)	z (Å)	Mass (amu)	q (e⁻)	$\alpha°$ (Å³)	ε (K)	σ (Å)
ATOM	1	OL1	LAC M	1	−0.149	1.137	1.478	15.99900	−0.71730	0.85200	30.19000	3.11800
ATOM	2	OL2	LAC M	1	0.391	−0.884	−1.452	15.99900	−0.64432	0.85200	30.19000	3.11800
ATOM	3	OL3	LAC M	1	−1.073	0.804	−1.036	15.99900	−0.58528	0.85200	30.19000	3.11800
ATOM	4	CL1	LAC M	1	0.363	0.031	0.750	12.01100	0.57618	1.28860	52.84000	3.43100
ATOM	5	CL2	LAC M	1	0.005	−1.285	1.442	12.01100	−0.18343	1.28860	52.84000	3.43100
ATOM	6	CL3	LAC M	1	−0.192	0.049	−0.661	12.01100	0.61476	1.28860	52.84000	3.43100
ATOM	7	HL1	LAC M	1	−0.821	1.550	0.908	1.00790	0.38255	0.41380	22.14000	2.57100
ATOM	8	HL2	LAC M	1	−0.037	−0.812	−2.324	1.00790	0.45769	0.41380	22.14000	2.57100
ATOM	9	HL3	LAC M	1	1.458	0.128	0.678	1.00790	−0.04319	0.41380	22.14000	2.57100
ATOM	10	HL4	LAC M	1	−1.086	−1.416	1.454	1.00790	0.03867	0.41380	22.14000	2.57100
ATOM	11	HL5	LAC M	1	0.473	−2.136	0.931	1.00790	0.03734	0.41380	22.14000	2.57100
ATOM	12	HL6	LAC M	1	0.364	−1.242	2.478	1.00790	0.06633	0.41380	22.14000	2.57100
END												

Results and Discussion

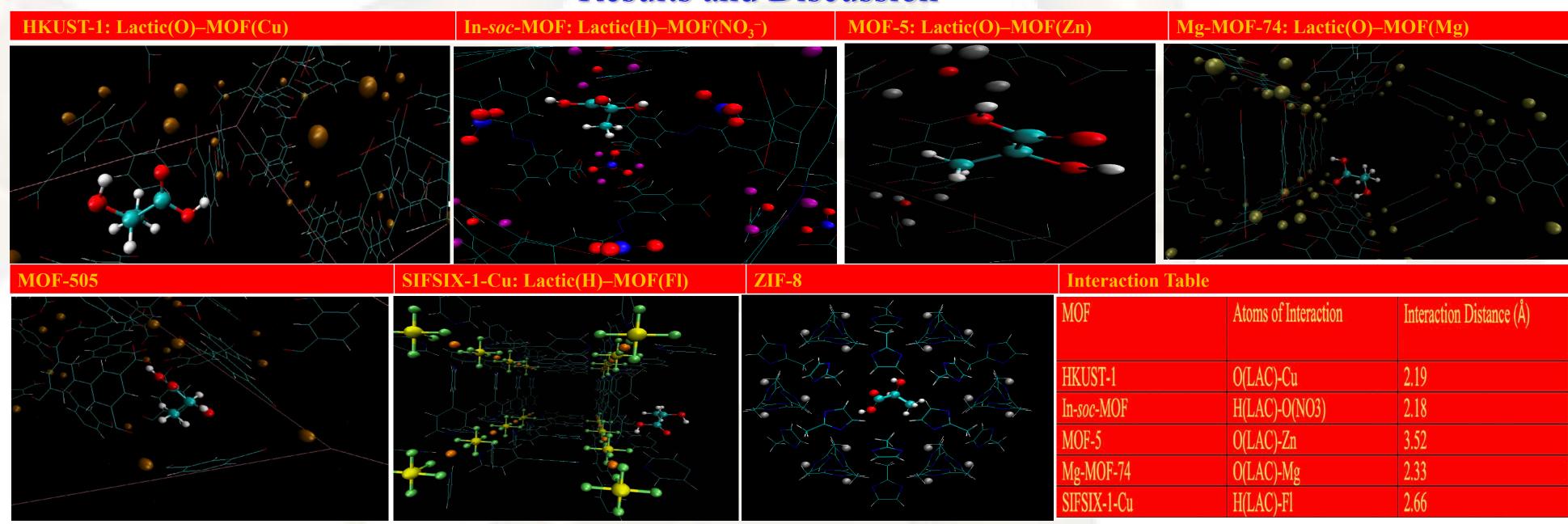| MOF	Atoms of Interaction	Interaction Distance (Å)
HKUST-1	O(LAC)–Cu	2.19
In-*soc*-MOF	H(LAC)–O(NO3)	2.18
MOF-5	O(LAC)–Zn	3.52
Mg-MOF-74	O(LAC)–Mg	2.33
SIFSIX-1-Cu	H(LAC)–Fl	2.66

Figure 2: Initial binding sites of lactic acid within the benchmark MOFs as determined from GCMC simulations. Atom colors: C = cyan, O = red, H = white, N = blue, F =lime, Si = yellow Cu = orange, Zn = silver , In = purple, Mg = tan

The initial binding sites, as displayed in Figure 2, depict the most favorable area of lactic acid adsorption within the respective MOFs. Certain atoms within the lactic acid molecule are attracted toward specific atoms within the majority of the MOFs. For example, the carbonyl O atom in lactic acid is drawn toward the Cu and Mg metal ions in HKUST-1 and Mg-MOF-74, respectively. Within In-*soc*-MOF, the H atoms of lactic acid are attracted to the O atoms of the NO_3^- counterions. In SIFSIX-1-Cu, there is an attraction between the H of the hydroxyl group and the equatorial fluorine atom of the SiF_6^{2-} group. In MOF-5, the lactic acid molecule is attracted to the Zn_4O cluster in the material. It appears that lactic acid prefers to adsorb within a triangular and hexagonal window within MOF-505 and ZIF-8, respectively, with no significant framework–guest interaction. The MOFs that display the most promise for lactic acid adsorption are HKUST-1 and In-*soc*-MOF, as represented by a MOF–adsorbate interaction distance of 2.19 and 2.18 Å, respectively (see Interaction Table). It can be deduced that lactic acid has an affinity toward highly charged open-metal sites and counterions.

Future Work and Outlook

The theoretical information gathered on the initial binding sites will be further supported by carrying out periodic density functional theory (DFT) calculations and creating a more sophisticated model for lactic acid. This study reveals promising preliminary results, which if taken further, can provide conclusive data on the potential of MOFs to trap lactic acid. The applications of this research can be utilized for further studies in computational chemistry and medicine.

References

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