Supporting information for "Ab initio, physically-motivated force fields for CO_2 adsorption in zeolitic imidazolate frameworks"

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Note: Electronic resources enabling the implementation of the force fields developed in this work are available for download at our website: http://schmidt.chem.wisc.edu.

Section 1

Comparison of the electron density on the imidazolate rings of the $Zn_2Im_7Li_6^{3+}$ fragment to the corresponding rings of the periodic system. Shown in Figure 1 is an isosurface of the difference in electron density between the model fragment system and the periodic crystal.

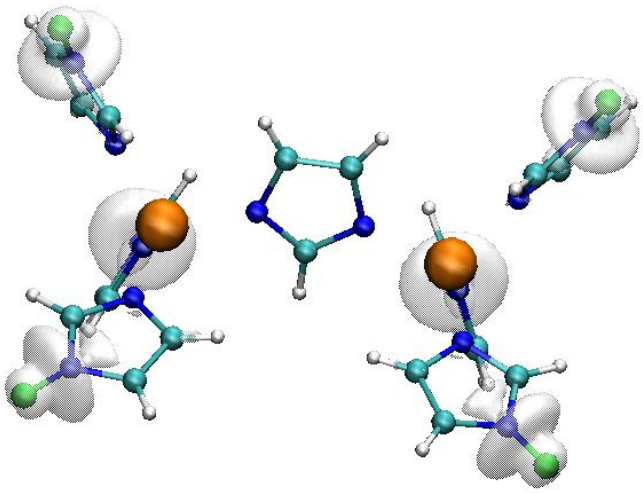

Figure 1. Isosurface of electron density difference between the $Zn_2Im_7Li_6^{3+}$ fragment and the corresponding periodic system. The isosurface value shown corresponds to ~3% difference in the electron density of the two systems.

Section 2

Shown in Figure are the exchange, electrostatic, induction, and δhf SAPT interaction energies for the ~200 configurations of the $Zn_2Im_7Li_6^{3+}$ fragment and a CO_2 molecule, fit using parameters from calculations involving a Li-capped imidazolate (Li_2Im) ring. Dispersion interactions were calculated for

twelve of these configurations, and the corresponding fit is shown in Figure . The charges were generated using a DMA analysis; C6, C8, and C10 parameters were generated using CAMCASP; and the other parameters were generated by fitting SAPT interaction data between the Li_2Im ring and CO_2 molecule.

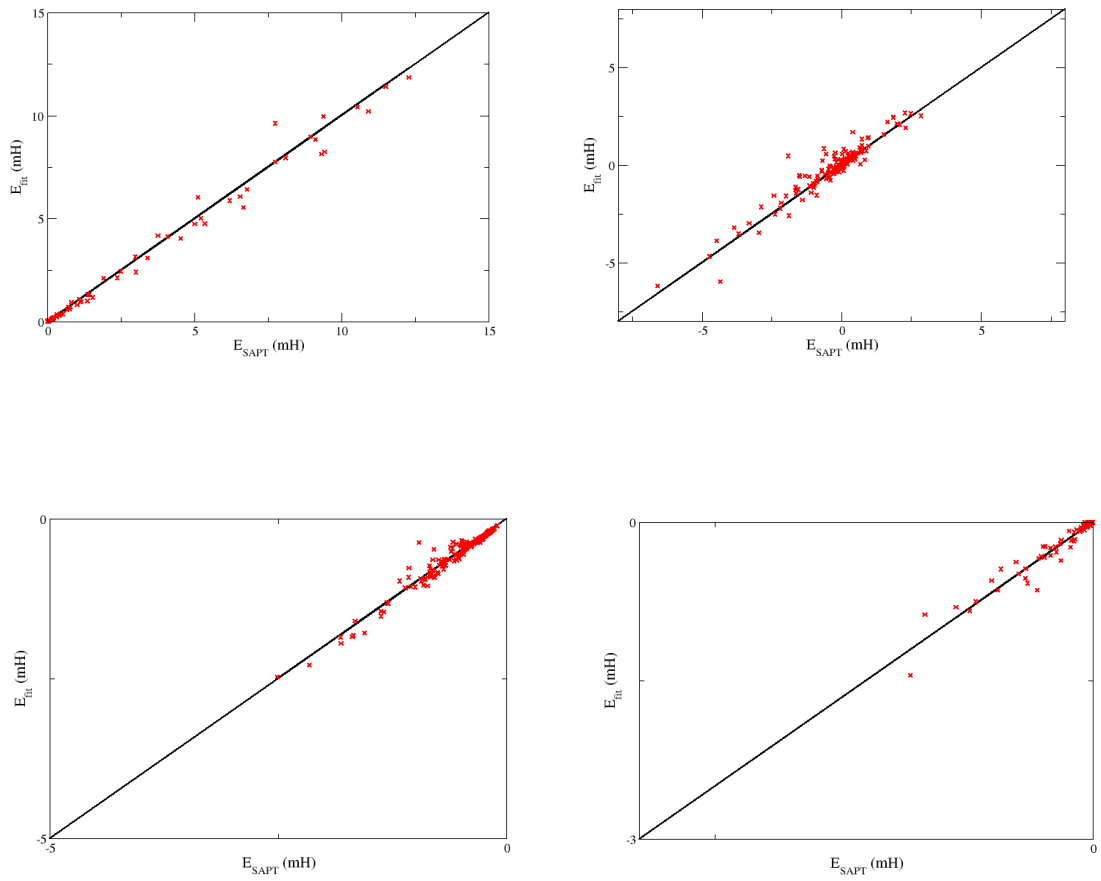

Figure 2. Fits for SAPT interaction energies between $Zn_2Im_7Li_6^{3+}$ fragment and a CO_2 molecule. From top left and clockwise: Exchange, electrostatic, δhf, and induction energies.

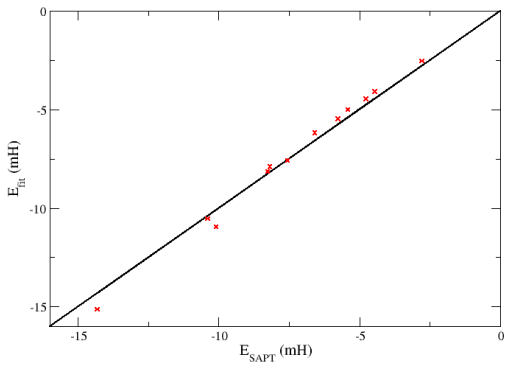

Figure 3. Fit for the dispersion energy between $Zn_2Im_7Li_6^{3+}$ fragment and a CO_2 molecule.

Section 3

Parameters for the CO_2–ZIF-8 force field are given in Tables 1-4. The atom labels corresponding to the atoms of the methyl imidazolate linker rings are shown in Figure 4. Note that most of the CO_2 parameters listed in Table 1 are from our previous paper[1], with the exception of the A^{disp} and C6-C10 parameters. The parameters listed are for solute-framework interactions, whereas all CO_2-CO_2 interactions are given entirely by the parameters of reference 1. Shown in Figure 5 are the fits for the SAPT interaction energies for the ~700 configurations of the Li_2mIm ring and a CO_2 molecule. Note that the total energy was not explicitly fit, and the plot shown is the sum of all the individual components.

	C	O
q(e)	0.6574	-0.3287
q_{shell}(e)	-0.8971	-0.7797
A^{exch}(kJ/mol)/10^4	9.551	52.190
A^{elect}(kJ/mol)/10^4	-2.785	-16.391
A^{ind}(kJ/mol)/10^4	-1.345	-0.448
$A^{\delta hf}$(kJ/mol)/10^4	0.207	-2.604

A^{disp}(kJ/mol)/10^4	0.000	-9.783
C6[kJ/(mol*$Å^{-6}$)]/10^2	11.885	8.221
C8[kJ/(mol*$Å^{-8}$)]/10^3	10.848	3.411
C10[kJ/(mol*$Å^{10}$)]/10^4	4.952	0.664

Table 1. Atomic parameters of CO_2 used in the solute-framework interactions for ZIF-8.

	C1	C2	C3	H2	H3	N	Zn
q(e)	0.6786	0.1198	-0.1498	0.1182	0.0682	-1.0135	1.6352
A^{exch}(kJ/mol)/10^4	4.179	9.168	7.054	0.265	0.316	28.312	0
A^{elect}(kJ/mol)/10^4	-1.801	-3.511	-2.211	-0.055	-0.062	-10.994	0
A^{ind}(kJ/mol)/10^4	0	0	0	-0.037	-0.037	-2.092	0
$A^{\delta hf}$(kJ/mol)/10^4	0.825	0.901	0.785	0.050	0.048	8.672	0
A^{disp}(kJ/mol)/10^4	0	-0.522	-0.868	-0.078	-0.054	0	0
C6[kJ/(mol*$Å^{-6}$)]/10^2	8.470	21.746	28.428	0.462	0.478	9.185	0
C8[kJ/(mol*$Å^{-8}$)]/10^3	13.490	21.365	21.540	0	0	19.671	0
C10[kJ/(mol*$Å^{10}$)]/10^4	10.924	10.073	7.6745	0	0	19.848	0

Table 2. Framework parameters for ZIF-8.

	C1	C2	C3	H2	H3	N	Zn
B($Å^{-1}$)							
C	3.2222	3.2222	3.2222	3.3920	3.3920	3.4476	3.9167
O	3.3960	3.3960	3.3960	3.6025	3.6025	3.6716	4.2926

Table 3. Pairwise exponents for Buckingham terms for CO_2-ZIF-8 interaction.

	C1	C2	C3	H2	H3	N	Zn
$\beta(Å^{-1})$							
C	2.9184	2.9184	2.9184	3.0722	3.0722	3.1225	3.5474
O	3.0758	3.0758	3.0758	3.2628	3.2628	3.3254	3.8879

Table 4. Pairwise parameters used in Tang-Toennies damping function for R^{-6}, R^{-8}, R^{-10} dispersion terms. These are equal to B_{ij} exponents in Table 3 scaled by 0.90571.

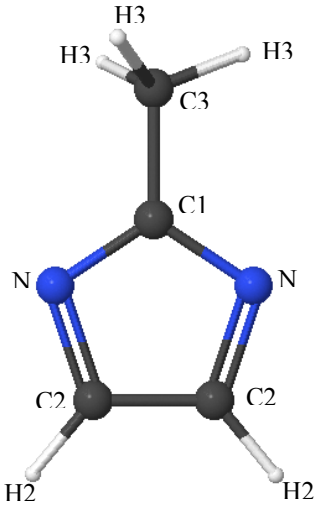

Figure 4: Methyl imidazolate atom types.

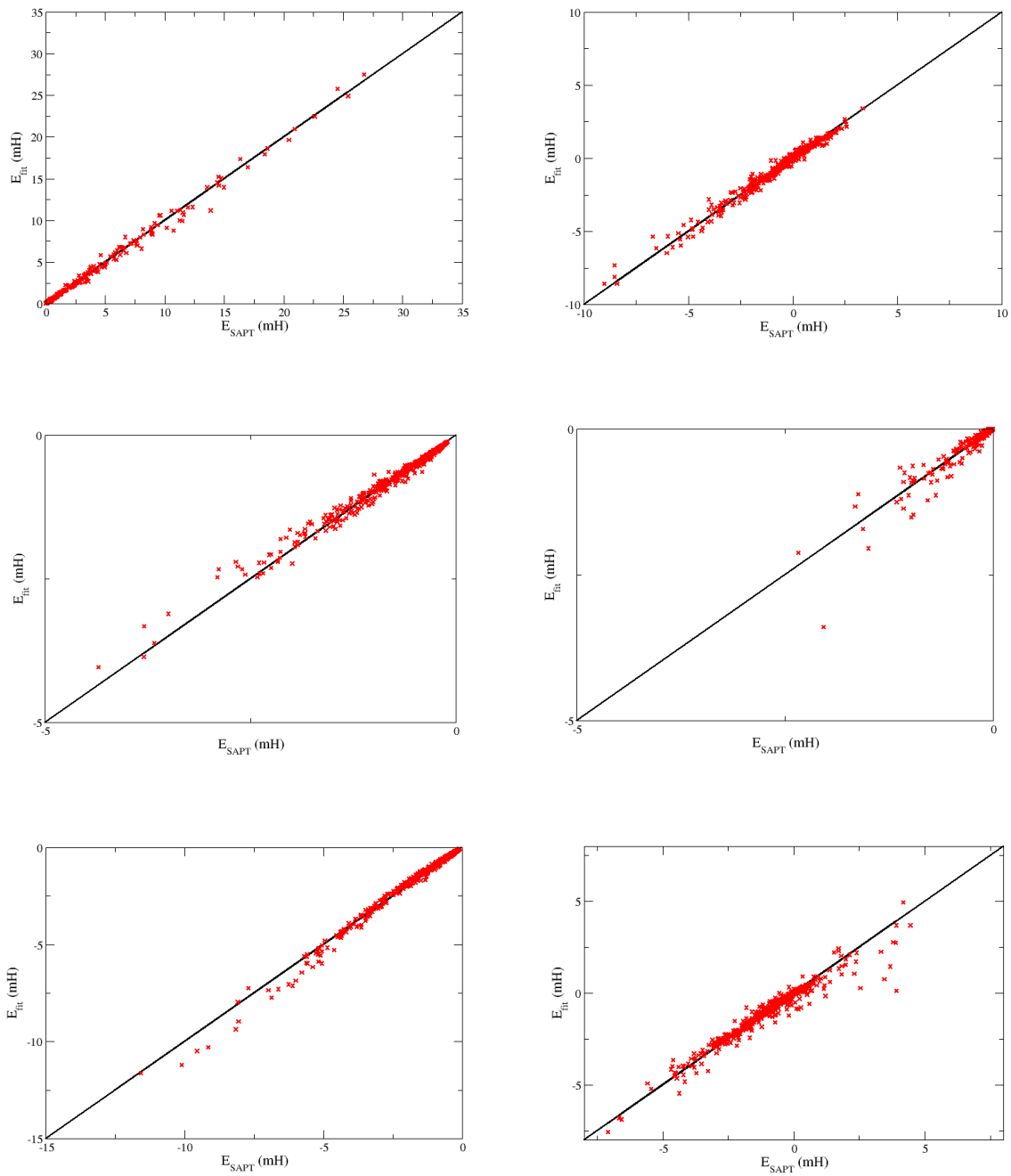

Figure 5. Fits of the SAPT interaction energies between a Li_2mIm ring and a CO_2 molecule. Left side top to bottom: Exchange, induction and dispersion energies. Right side top to bottom: Electrostatic, δhf, and total energies. For all plots, points shown are restricted to those in the modified data sets used to fit induction and dispersion energies. The rms error for the total energy fit is 0.36 mH.

Section 4

Parameters for the CO_2–ZIF-71 force field are given in Tables 5-8 (The CO_2 parameters are the same as those given in Table 1, except for the C6, C8, C10 parameters). The atom labels corresponding to the atoms of the dichloro-imidazolate linker rings are shown in Figure 6. Shown in Figure 7 are the fits for the SAPT interaction energies for the ~700 configurations of the Li_2dcIm ring and a CO_2 molecule. Again, note that the total energy was not explicitly fit, and the plot shown is the sum of all the individual components.

	C	O
q(e)	0.6574	-0.3287
q_{shell}(e)	-0.8971	-0.7797
A^{exch}(kJ/mol)/10^4	9.551	52.190
A^{elect}(kJ/mol)/10^4	-2.785	-16.391
A^{ind}(kJ/mol)/10^4	-1.343	-0.448
$A^{\delta hf}$(kJ/mol)/10^4	0.207	-2.604
A^{disp}(kJ/mol)/10^4	0	-9.783
C6[kJ/(mol*$Å^{-6}$)]/10^2	12.036	8.326
C8[kJ/(mol*$Å^{-8}$)]/10^3	10.985	3.454
C10[kJ/(mol*$Å^{10}$)]/10^4	5.015	0.672

Table 5. Atomic parameters of CO_2 used in the solute-framework interactions for ZIF-71. Note that the only difference between these and the parameters given in Table 1 for ZIF-8 are the C6, C8, and C10 parameters, where the difference comes from fitting a slightly different scaling factor.

	C1	C2	Cl	H1	N1	Zn
q(e)	0.5934	0.3886	-0.1139	0.0609	-0.9992	1.5894
A^{exch}(kJ/mol)/10^4	8.381	5.436	73.646	0.292	28.291	0
A^{elect}(kJ/mol)/10^4	-3.221	-2.392	-30.072	-0.061	-10.928	0
A^{ind}(kJ/mol)/10^4	0	0	-1.415	-0.036	-1.990	0
$A^{\delta hf}$(kJ/mol)/10^4	0.891	0.883	7.387	0.050	8.990	0
A^{disp}(kJ/mol)/10^4	0	0	-11.619	0	0	0
C6[kJ/(mol*$Å^{-6}$)]/10^2	9.162	25.270	46.752	2.645	7.164	0
C8[kJ/(mol*$Å^{-8}$)]/10^3	5.419	34.088	21.386	0	20.269	0
C10[kJ/(mol*$Å^{10}$)]/10^4	1.571	22.555	4.744	0	27.575	0

Table 6. Framework parameters for ZIF-71.

	C1	C2	Cl	H1	N1	Zn
B($Å^{-1}$)						
C	3.2222	3.2222	3.3514	3.3920	3.4476	3.9167
O	3.3960	3.3960	3.5537	3.6025	3.6716	4.2926

Table 7. Pairwise exponents for Buckingham terms for CO_2-ZIF-71 interaction.

	C1	C2	Cl	H1	N1	Zn
β(Å-1)						
C	2.9880	2.9880	3.1079	3.1455	3.1971	3.6321
O	3.1492	3.1492	3.2955	3.3407	3.4048	3.9807

Table 8. Pairwise parameters used in Tang-Toennies damping function for R^{-6}, R^{-8}, R^{-10} dispersion terms. These are equal to B_{ij} exponents in Table 7 scaled by 0.92733.

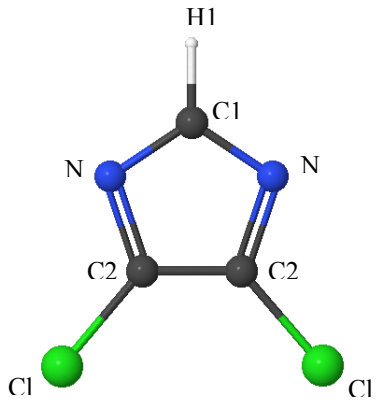

Figure 6. Dichloro-imidazolate atom types.

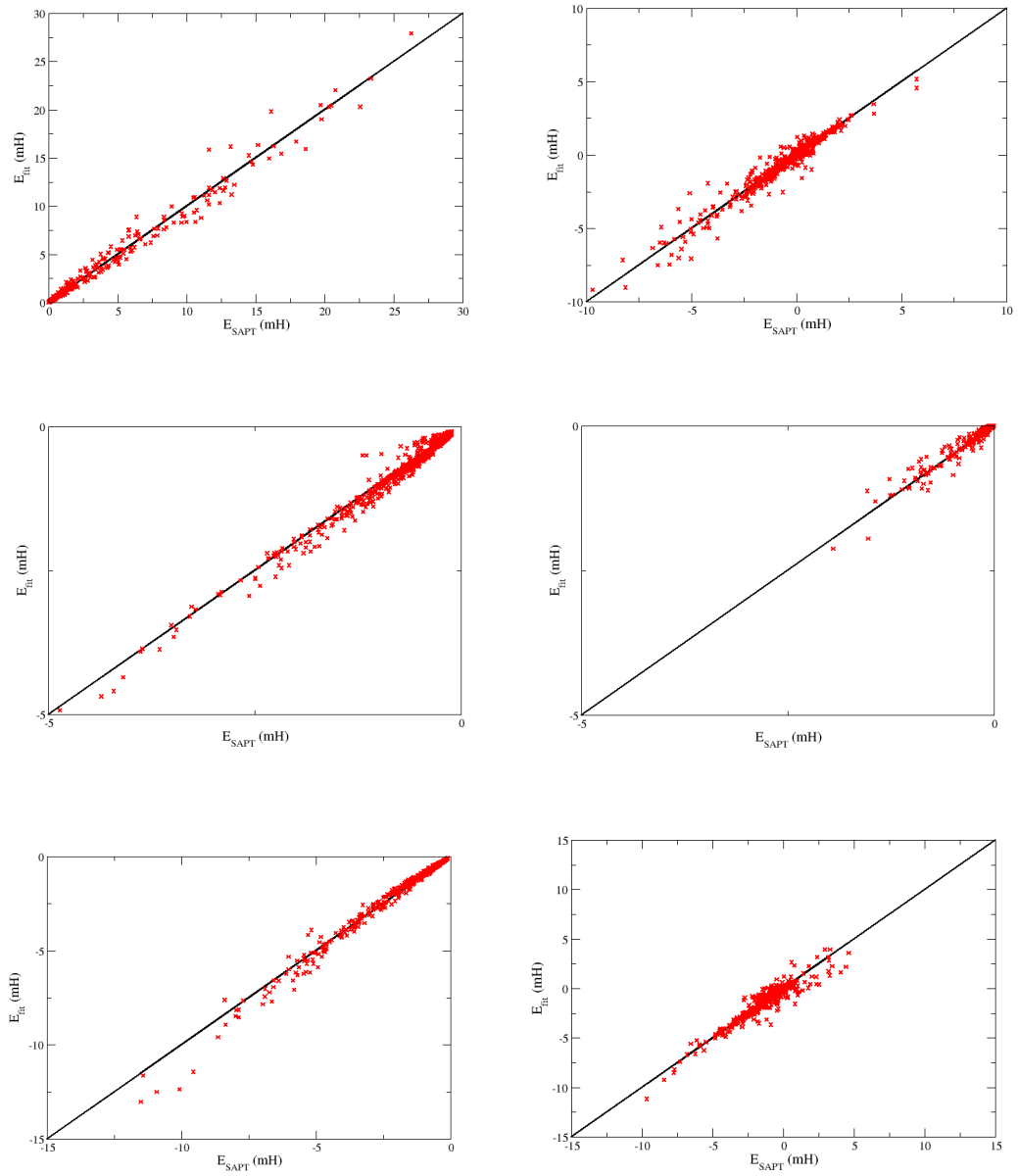

Figure 7: Fits of the SAPT interaction energies between a Li_2dcIm ring and a CO_2 molecule. Left side top to bottom: Exchange, induction and dispersion energies. Right side top to bottom: Electrostatic, δhf, and total energies. For all plots, points shown are restricted to those in the modified data sets used to fit induction and dispersion energies. The rms error for the total energy fit is 0.52 mH.

(1) Yu, K.; McDaniel, J. G.; Schmidt, J. R. *Journal of Physical Chemistry. B* **2011**, *115*, 10054.