

Simulation of the Mechanism of Gas Sorption in a Metal-Organic Framework with Open Metal Sites: Molecular Hydrogen in PCN-61

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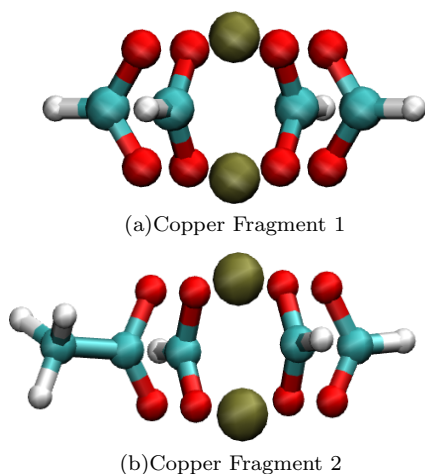
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Atomic Point Polarizability

Induced dipole energetics were modeled using known atomic point polarizabilities, α° , for hydrogen, carbon, & oxygen atoms.¹ For closed shell divalent copper, the polarizability tensor was determined for small copper containing fragments (Figure 1), using the Q-Chem² *ab initio* simulation package with the aug-cc-pVDZ basis set. The copper parameter was then selected to reproduce the tensor in conjunction with known atomic point polarizabilities in the fragment using the Massively Parallel Monte Carlo (MPMC) code.³ The polarizability tensors comparing *ab initio* results to those fit using the Thole-Applequist model⁴⁻⁶ are shown in Table 1. The fitted polarizability values are shown in Table 2.

Figure 1. Small fragments used for calculating the polarizability of closed shell Cu^{2+} . Atom colors: C = cyan, H = white, O = red, Cu = tan



Atomic Partial Charges

Atomic partial charges were fit to the electrostatic potential surface for a series of gas phase fragments (Figure 3) that were cut from the PCN-61 unit cell with the 6-31G* basis set. This basis set was chosen to account for over-polarized charges appropriate for condensed phase simula-

Table 1. Polarizability tensors for the copper fragments

Fragment	<i>ab initio</i>	Thole-Applequist
1	18.025 0.000 0.000	17.680 0.000 0.000
	0.000 17.671 0.000	0.000 17.478 0.000
	0.000 0.000 14.486	0.000 0.000 15.025
2	20.631 0.169 0.088	19.850 0.119 -0.014
	0.169 18.395 0.001	0.119 17.803 0.003
	0.088 0.001 14.905	-0.014 0.003 16.279

Table 2. The atomic point polarizabilities of copper from each fragment.

Fragment	$\alpha^\circ (\text{\AA}^3)$
1	2.3006
2	2.0920
Final	2.1963

tion. The electrostatic potential charges of each fragment were fitted to reproduce the electric potential calculated from *ab initio* methods at a sufficiently large number of grid points around a molecule such that a good approximation to the true charge distribution is obtained.⁷ The well-known CHELPG method^{8,9} was used to perform the least squared fit on the gas phase fragments. All calculations were performed using the NWChem¹⁰ *ab initio* simulation package. Final charges were taken from averaged fragment values, disregarding atoms with insufficient chemical insulation to approximate MOF conditions. Average partial charges for each fragment are shown in Table 3.

Figure 2. Label of chemically distinct atoms as referred to in Table 3. Atom colors: C = green, H = white, O = red, Cu = brown

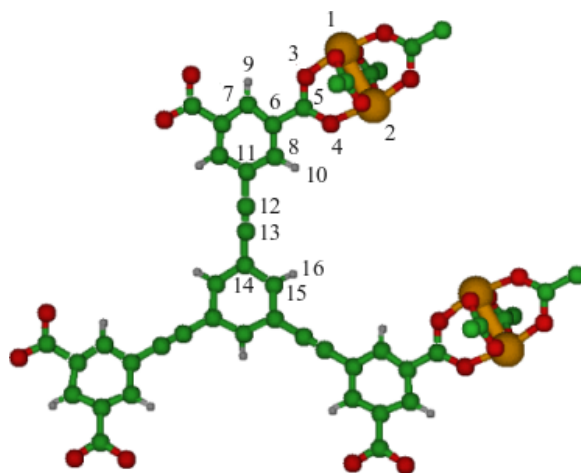
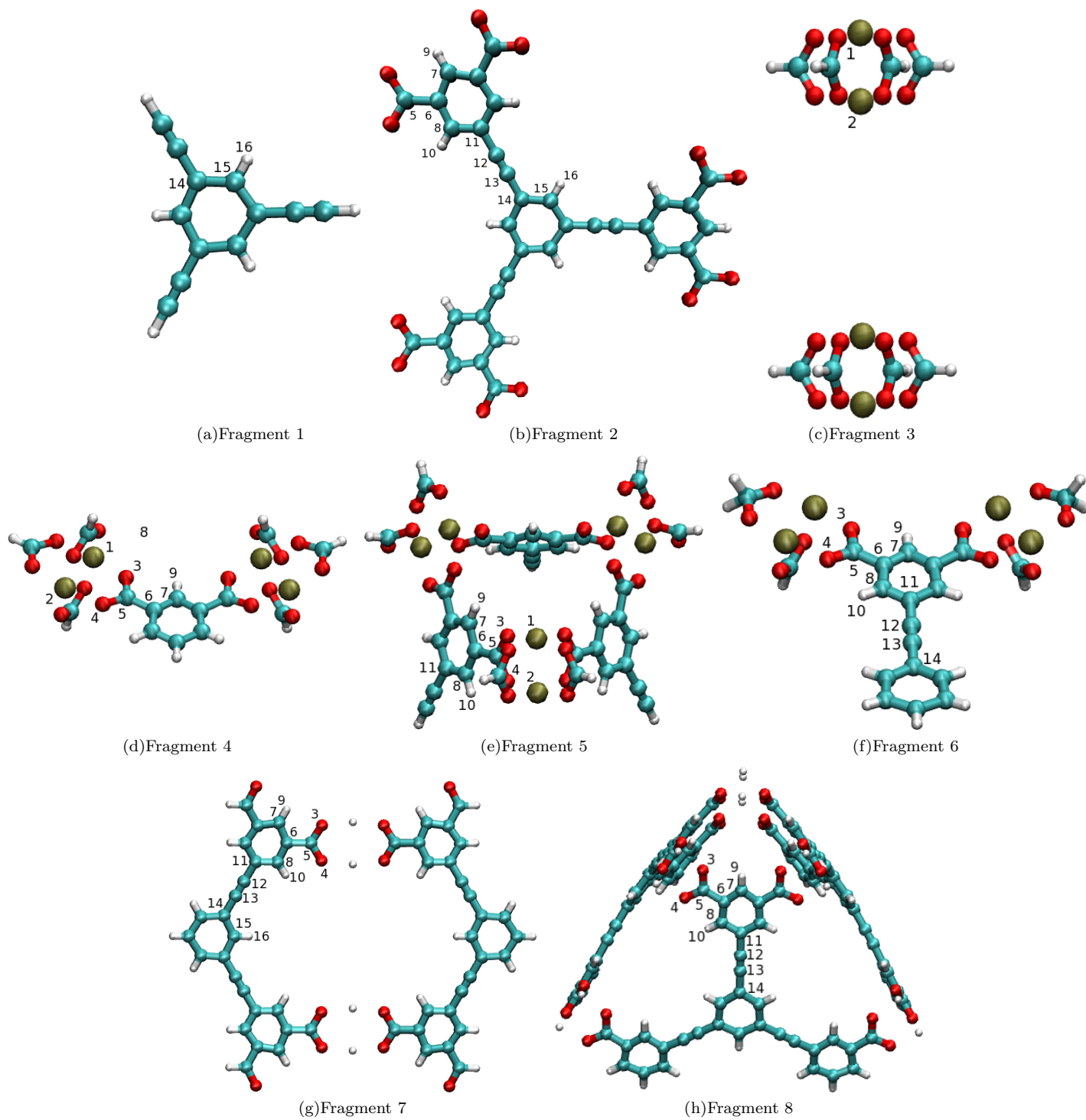


Table 3. Comparison of partial charges (e^-) for the series of fragments. Numbering of the atoms and fragments correlates to Figure 2.

Atom Label	Frag 1	Frag 2	Frag 3	Frag 4	Frag 5	Frag 6	Frag 7	Frag 8
Cu 1	-	-	1.7432	1.7261	1.7112	-	-	-
Cu 2	-	-	1.1143	1.0850	1.0397	-	-	-
O 3	-	-	-	-0.8559	-0.8454	-0.7425	-0.7583	-0.6968
O 4	-	-	-	-0.8386	-0.8271	-0.7267	-0.7493	-0.7178
C 5	-	0.8655	-	1.0237	1.0136	0.8217	0.8981	0.8984
C 6	-	-0.0773	-	-0.1808	-0.1948	0.0252	-0.0665	-0.1319
C 7	-	-0.0750	-	-0.0262	-0.0049	-0.2038	-0.0710	-0.0567
C 8	-	-0.2541	-	-	-0.1161	-0.3174	-0.2146	-0.1405
H 9	-	0.1289	-	0.1758	0.1800	0.2312	0.2161	0.1464
H 10	-	0.1717	-	-	0.1841	0.2285	0.2130	0.1798
C 11	-	0.2214	-	-	0.1941	0.3386	0.2526	0.2278
C 12	-	-0.1552	-	-	-	-0.1783	-0.1750	-0.1931
C 13	-	-0.0770	-	-	-	-0.0732	-0.0404	0.0101
C 14	0.0679	0.0545	-	-	-	0.1074	0.1067	0.0803
C 15	-0.1828	-0.1745	-	-	-	-	-0.2281	-0.1532
H 16	0.1644	0.1544	-	-	-	-	0.1791	0.1549

Figure 3. Fragments of PCN-61. Numerical labeling correspond to chemically distinct atoms evaluated. Atom colors: C = cyan, H = white, O = red, Cu = tan



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