DFT study of H_2 adsorption at Cu-SSZ-13 zeolite: a cluster approach

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KEYWORDS
Zeolite, SSZ-13, Hydrogen Storage, DFT, δ-cluster.

SUPPLEMENTARY MATERIAL

Table S1. Cu-O1 distances (Å) for 6MR/H_2 and 8MR/H_2 with different functionals.

Cluster	B3LYP	B3LYP-D3	PBE	PBE-D3	M06L	ωB97XD
6MR/H_2	2.000	1.991	1.990	1.984	1.991	1.996
8MR/H_2	2.060	2.066	2.040	2.043	2.058	2.058

Table S2. Cu-H_2 distances (Å) for 6MR/H_2 and 8MR/H_2 with different functionals.

Cluster	B3LYP	B3LYP-D3	PBE	PBE-D3	M06L	ωB97XD
6MR/H_2	1.656	1.651	1.581	1.578	1.581	1.643
8MR/H_2	1.592	1.594	1.542	1.542	1.543	1.589

Table S3. H-H distances (Å) for 6MR/H_2 and 8MR/H_2 with different functionals.

Cluster	B3LYP	B3LYP-D3	PBE	PBE-D3	M06L	ωB97XD
6MR/H_2	0.810	0.810	0.850	0.851	0.845	0.810
8MR/H_2	0.822	0.822	0.862	0.862	0.854	0.822

Table S4. H_2 adsorption energies calculated with different functionals along with two different basis set: def2-SVP (geometry optimizations) and def-TZVP (single point calculations) for adsorption at 6MR and 8MR clusters.

		Basis set	
Functional	Cluster	def2-SVP	def2-TZVP
B3LYP	6MR	-4.12	-3.84
B3LYP	8MR	-16.03	-15.99
B3LYP-D3BJ	6MR	-6.79	-6.40
B3LYP-D3BJ	8MR	-18.18	-21.50
PBE	6MR	-7.23	-6.77
PBE	8MR	-24.28	-25.75
PBE-D3BJ	6MR	-9.24	-8.70
PBE-D3BJ	8MR	-26.45	-27.99
M06L	6MR	-8.85	-8.03
M06L	8MR	-26.35	-25.89
wB97X-D	6MR	-6.81	-6.83
wB97X-D	8MR	-18.00	-20.26

NBO ANALYSIS

The NBO analysis, developed by Weinhold[1–4] and coworkers, allows the bond description through the most accurate possible Lewis-like orbitals. Natural Bonding Orbitals are localized orbitals with maximum population beyond a molecular pattern preserving the exterior limits of the Natural Orbitals (NOs) and the interatomic orthogonality established by the Pauli Exclusion Principle. The NBOs are obtained by the linear combination of Natural Hybrid Orbitals (NHOs) which are generated through the hybridization of the Natural Atomic Orbitals (NAOs) that are optimized from the molecular wave function ψ_M, written on bases of Atomic Orbitals (AOs). The canonical delocalized Molecular Orbitals (MO) are obtained from a transformation of the semi-localized Natural Localized Molecular Orbitals (NLMOs) obtained through a unitary transformation in the NBOs. The sequence to obtain the MOs with the NBO theory it is showed in the eq. 1.

AOs → NAOs → NHOs → NBOs → NLMOs → MOs (eq. 1)

The NBO for 2-center bond (A-B) between atoms A and B can be write as a linear combination of two NHOs (h_A and h_B) with their respective polarization coefficients c_A and c_B. Thus, the Lewis-type bonding contribution σ_{AB} (NBO donator) can be write as in the eq. 2.

$$\sigma_{AB} = c_A h_A + c_B h_B \quad \text{(eq. 2)}$$

There is a corresponding non-Lewis-type anti-bonding σ^*_{AB} contribution (NBO acceptor) for each valence bonding NBO as in the eq. 3.

$$\sigma^*_{AB} = c_B h_A - c_A h_B \quad \text{(eq. 3)}$$

The unperturbed NBOs can be perturbed by mixing the coefficients to obtain the perturbed NLMOs. This perturbation can provide delocalization effects through the interaction between a filled Lewis-type orbital σ (NBO donator) and an unfilled orbital σ* resulting in a non-covalent polarization or charge transfer $\sigma_i \rightarrow \sigma^*_j$. The NBO analysis enable to estimate the stabilization energy of a donor-acceptor delocalization given by the second order perturbation theory (for 2-electron occupancy) showed in eq. 4.

$$\Delta E^{(2)}_{i \rightarrow j^*} = -2\frac{\langle \sigma_i | \hat{F} | \sigma^*_j \rangle^2}{\varepsilon_{j^*} - \varepsilon_i} \quad \text{(eq. 4)}$$

In which $\hat{F}$ is the Fock or Kohn-Shan operator (effective Hamiltonian for 1-electron), ε_i and ε_{j^*} are the NBO orbital energies.[1–4] Thus the delocalization energies $\Delta E^{(2)}_{i \rightarrow j^*}$ was used to evaluate the interaction between the Cu and H_2 through donator-acceptor interaction and back donation (Cu-H_2). Besides that, it was investigated the possibility of charge transfer from zeolite to the H_2 molecule, the NBO charge distribution in functional of the cluster size and different DFT functionals.

AIM analysis.

Table S5.AIM properties (in atomic units) for 6MR/H_2 obtained with ωB97XD/def2-SVP level of theory. Electronic density, ρ(r), Laplacian of density, $\nabla^2\rho(r)$, ellipticity, ε, and density of potential energy, *V*(r).

BCP	ρ(r)	$\nabla^2\rho(r)$	ε	*V*(r)	*H*(r)
a	0.2267	-0.9813	0.0273	-0.2708	-0.2581
b	0.0818	+0.3925	1.4997	-0.1226	-0.0122
c	0.0712	+0.5003	0.0488	-0.1118	0.0066
d	0.0681	+0.4733	0.0486	-0.1049	0.0067
e	0.0180	+0.0454	0.0168	-0.0184	-0.0035

Table S6. AIM properties (in atomic units) for 8MR/H_2 obtained with ωB97XD/def2-SVP level of theory. Electronic density, ρ(r), Laplacian of density, $\nabla^2\rho(r)$, ellipticity, ε, and density of potential energy, *V*(r).

BCP	ρ(r)	$\nabla^2\rho(r)$	ε	*V(r)*	*H*(r)
a	0.2225	-0.9338	0.0344	-0.2621	-0.2478
b	0.0921	+0.4387	1.8007	-0.1427	-0.0165
c	0.0614	+0.4038	0.0051	-0.0890	0.0060
d	0.0690	+0.4784	0.0161	-0.1064	0.0066
e	0.0060	+0.0199	0.0763	-0.0037	0.0006
f	0.0024	+0.0113	0.3472	-0.0012	0.0008
g	0.0024	+0.0103	0.3068	-0.0012	0.0007

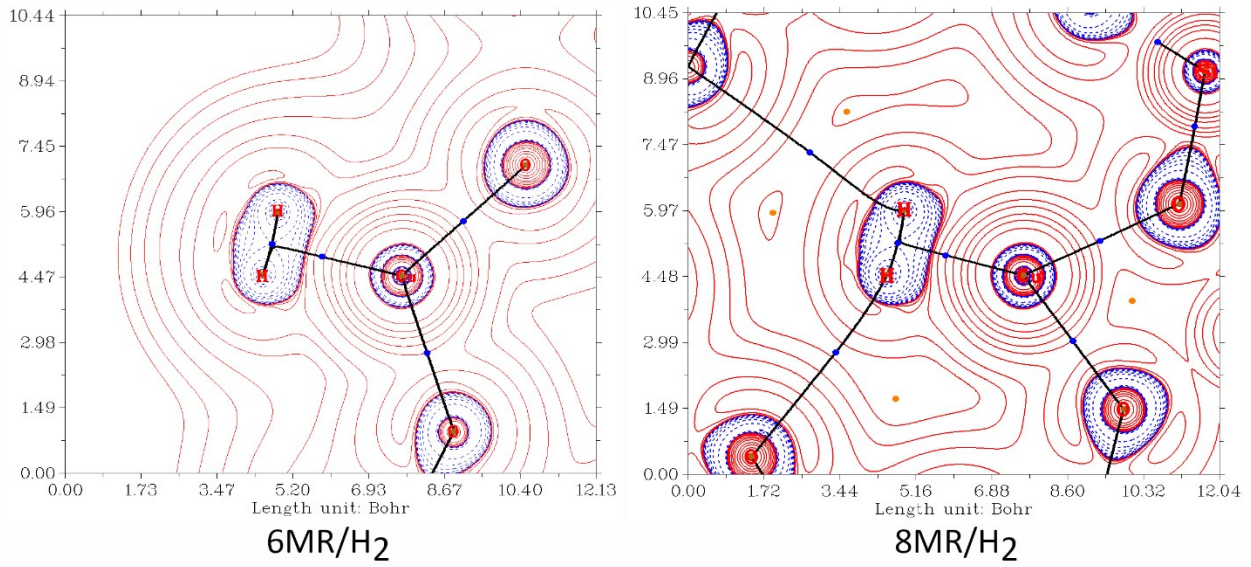

Figure S1. Contour line maps of Laplacian of electronic density, $\nabla^2\rho(r)$, for 6MR/H_2 and 8MR/H_2 with bond paths (BPs) and critical points CPs. Positive contours plotted as full red lines, negative contours as blue dotted lines, BPs as full black lines, bond critical points (BCPs) as blue dots and ring critical points (RCPs) as orange dots. Maps plotted for the planes defined by three atoms: Cu1-H1-H2 for both clusters.

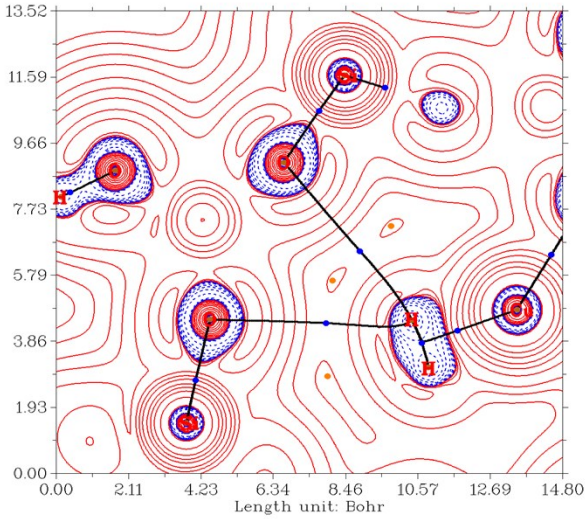

Figure S2. Contour line map of Laplacian of electronic density, $\nabla^2\rho(r)$, for 8MR/H_2 with bond paths (BPs) and critical points CPs. Positive contours plotted as full red lines, negative contours as blue dotted lines, BPs as full black lines, bond critical points (BCPs) as blue dots and ring critical points (RCPs) as orange dots. Map plotted for the plane defined by three atoms: H2-O6-O7.

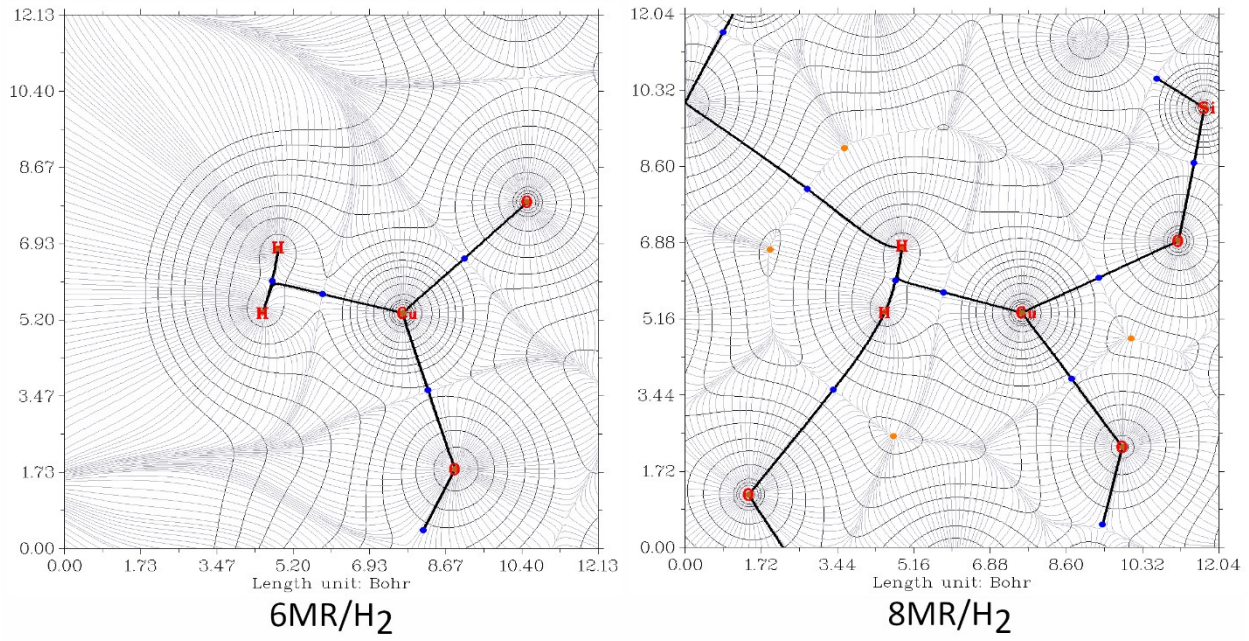

Figure S3. Gradient map of electron density, ρ(r), for 6MR/H_2 and 8MR/H_2 with bond paths (BPs) and critical points CPs. Electronic density contours plotted as full black lines, gradient line map for electron gray lines, BPs as full black lines, bond critical points (BCPs) as blue dots and ring critical points (RCPs) as orange dots. Map plotted for the plane defined by three atoms: Cu1-H1-H2 for both clusters.

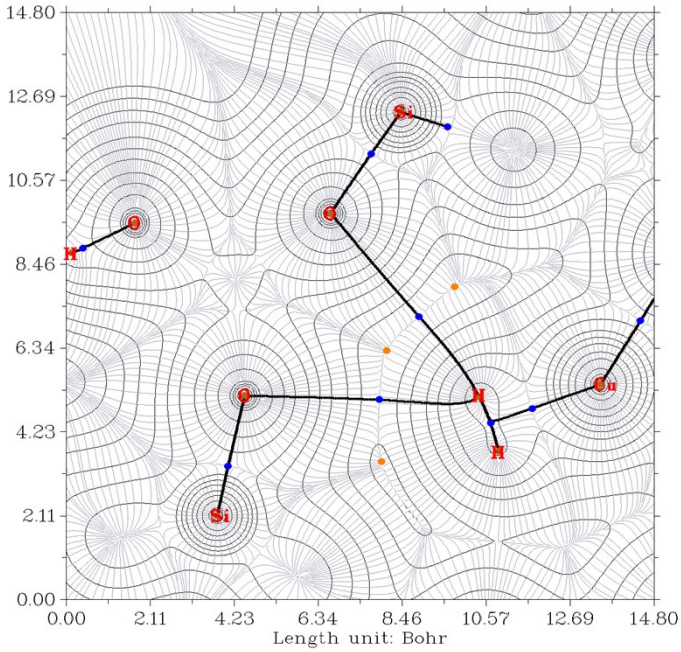

Figure S4. Gradient map of electron density, ρ(r), for 8MR/H_2 with bond paths (BPs) and critical points CPs. Electronic density contours plotted as full black lines, gradient line map for electron gray lines, BPs as full black lines, bond critical points (BCPs) as blue dots and ring critical points (RCPs) as orange dots. Map plotted for the plane defined by three atoms: H2-O6-O7.

Cartesian coordinates and sum of electronic and zero-point energies (in Hartree) for 6MR, 6MR/H_2, 8MR and 8MR/H_2 structures optimized with ωB97XD/def2SVP method.

6MR

Electronic + zero-point energies = -8899.404997

Si	8.412674	9.195475	13.584118
O	4.414134	7.596711	7.468641
O	5.258001	-0.027371	7.490681
O	11.182386	4.303920	7.316274
O	2.427347	4.205702	7.415802
Si	5.208905	9.213742	13.585940
O	9.241304	7.514441	7.672155
Si	5.249965	6.687833	6.397730
Si	5.404299	1.145445	6.409547
O	8.308934	-0.028274	7.456700
Si	9.871209	3.800151	6.496648
O	4.271793	8.395390	12.515164
Si	8.386854	1.215052	6.438554
Si	1.608358	5.204893	8.407879
O	6.805198	8.873306	13.423478
Si	8.292893	-1.291631	8.481737
Si	3.020259	7.902842	11.580578
Si	10.543559	7.992769	8.464347
Si	3.130692	7.971022	8.411047
O	6.806065	7.013196	6.288600
Si	10.654864	7.929215	11.676051
Si	12.021180	5.236963	8.407566
O	4.364865	2.299488	7.129083
Si	5.357960	-1.321577	8.497043
O	9.390179	2.314336	7.072902
O	8.558443	10.820911	13.331549
O	11.058079	6.397705	12.104811
O	2.597653	9.423340	7.867659
O	2.616839	6.381640	12.040263
O	5.075790	10.841156	13.341744
O	5.079111	5.078573	6.871264
O	11.056275	9.422933	7.835759
O	6.846650	1.940417	6.421762
O	8.956089	8.736092	15.075395
O	4.656326	8.754971	15.075557
O	8.646701	4.842858	6.785446
O	11.891072	8.974466	12.050465
O	1.989936	6.796006	8.209315
O	4.527067	6.765011	4.895930
O	8.631498	0.557909	4.965471
O	5.006122	0.546088	4.962990
O	6.823496	-2.017068	8.420445
O	9.185003	6.635003	4.775581
O	1.699355	8.891342	11.764366
O	10.092377	3.359481	4.922512
O	11.726640	6.835953	8.273681
O	3.824433	3.353224	4.831971
O	9.306372	8.326806	12.526392
O	3.519245	7.992796	10.004625

O	10.309004	8.125333	10.086570
Cu	6.824192	4.171968	6.914330
H	4.235698	11.299807	13.415997
H	5.148287	6.817209	4.157620
H	11.653797	10.000971	8.309693
H	5.145527	1.050023	4.157602
H	5.038801	-0.860901	9.816723
H	11.903712	9.847208	11.639306
H	3.482009	3.931312	4.157768
H	11.849805	4.794395	9.817137
H	9.387802	11.299806	13.415999
H	13.414696	5.007506	8.138656
H	5.148203	8.913897	15.886602
H	1.970100	10.000477	8.309585
H	4.440893	-2.323012	8.138687
H	1.969699	5.729902	11.734600
H	10.141281	3.931931	4.157197
H	0.209016	5.007806	8.138765
H	9.182712	-2.323821	8.139486
H	1.719789	9.847208	11.639303
H	8.475296	8.913897	15.886600
H	8.584793	-0.860500	9.816228
H	8.477880	1.050012	4.157612
H	11.653404	5.730600	11.734702
H	1.773603	4.794090	9.816936
H	8.475198	6.816977	4.157595
Al	8.513106	6.632430	6.384324
Al	3.801755	3.964735	6.438165
H	3.818076	1.962146	7.851113

6MR/H_2

Electronic + zero-point energies = -8900.572402

Si	8.412312	9.194691	13.587662
O	4.393074	7.575328	7.473671
O	5.207072	-0.004911	7.488485
O	11.101752	4.392646	7.329041
O	2.508031	4.304543	7.409193
Si	5.208185	9.213571	13.590195
O	9.271083	7.480170	7.694052
Si	5.289886	6.717991	6.407163
Si	5.389209	1.161010	6.397811
O	8.359941	0.004090	7.464356
Si	9.792434	3.866588	6.507743
O	4.270352	8.394226	12.522294
Si	8.390511	1.245329	6.432730
Si	1.614262	5.232769	8.408635
O	6.804586	8.872803	13.427715
Si	8.303995	-1.272375	8.469366
Si	3.023508	7.901171	11.582079
Si	10.558186	7.998000	8.481960
Si	3.128413	7.979721	8.423616
O	6.817868	7.149603	6.309542
Si	10.656115	7.930815	11.687065
Si	12.017741	5.260619	8.411576

O	4.401650	2.349921	7.144859
Si	5.346800	-1.302705	8.484113
O	9.334638	2.382083	7.105997
O	8.559297	10.819180	13.332276
O	11.059200	6.396520	12.109356
O	2.631920	9.447461	7.888624
O	2.618585	6.379406	12.041983
O	5.076304	10.841102	13.348389
O	5.211877	5.108862	6.897925
O	11.034819	9.437031	7.847532
O	6.841148	1.903651	6.377215
O	8.957926	8.734889	15.077512
O	4.654820	8.750895	15.077938
O	8.540098	4.889474	6.770360
O	11.887219	8.980832	12.064435
O	1.944818	6.841710	8.251269
O	4.548408	6.748232	4.913096
O	8.714204	0.596373	4.969387
O	4.941574	0.564108	4.961245
O	6.823243	-1.972291	8.378616
O	9.194109	6.695959	4.780825
O	1.701415	8.889890	11.754625
O	10.043458	3.402688	4.947639
O	11.775376	6.873091	8.317168
O	3.890930	3.414652	4.844142
O	9.303350	8.319149	12.534239
O	3.540872	7.985010	10.012873
O	10.304977	8.132811	10.101015
Cu	6.871099	4.278203	7.678862
H	4.235696	11.299807	13.416006
H	5.148281	6.817182	4.157620
H	11.653751	10.001033	8.309694
H	5.145535	1.050035	4.157650
H	5.038757	-0.860949	9.816722
H	11.903698	9.847215	11.639318
H	3.482038	3.931320	4.157796
H	11.849769	4.794372	9.817118
H	9.387802	11.299804	13.416000
H	13.414688	5.007492	8.138738
H	5.148199	8.913902	15.886602
H	1.970128	10.000465	8.309598
H	4.440925	-2.322958	8.138731
H	1.969693	5.729918	11.734600
H	10.141288	3.931902	4.157192
H	0.209000	5.007779	8.138836
H	9.182677	-2.323804	8.139467
H	1.719781	9.847210	11.639319
H	8.475290	8.913898	15.886601
H	8.584784	-0.860466	9.816225
H	8.477946	1.049986	4.157634
H	11.653390	5.730577	11.734695
H	1.773647	4.794115	9.816855
H	8.475237	6.816966	4.157579
Al	8.499737	6.681391	6.376762

Al	3.899143	4.035183	6.445989
H	3.764590	2.001260	7.782508
H	6.501738	3.438196	9.103988
H	7.305248	3.364541	9.033066

8MR

Electronic + zero-point energies = -8899.387315

Si	8.412220	9.300995	13.565549
O	4.442847	7.751567	7.565733
O	4.730020	0.081066	7.493598
O	11.106135	4.275367	7.495445
O	2.580762	4.385736	7.357487
Si	5.237544	9.198727	13.568891
O	9.369798	8.007142	7.742584
Si	5.430765	6.925161	6.540175
Si	5.236351	1.182133	6.416814
O	8.871027	0.188856	7.523419
Si	9.893988	4.156528	6.402879
O	4.306499	8.378705	12.501717
Si	8.443795	1.273780	6.383415
Si	1.640341	5.233850	8.388247
O	6.836667	8.914580	13.284374
Si	8.409528	-1.124341	8.399258
Si	3.005058	7.924050	11.607734
Si	10.600111	8.012486	8.814482
Si	3.106267	8.031377	8.431035
O	6.926821	7.470735	6.927736
Si	10.621766	7.825997	11.880402
Si	12.019997	5.237655	8.444240
O	4.435848	2.539155	7.071093
Si	5.261461	-1.179528	8.418153
O	9.163423	2.690309	6.618331
O	8.808253	10.748054	12.880471
O	11.243691	6.373839	12.328998
O	2.584852	9.460193	7.825530
O	2.623499	6.386229	12.020773
O	5.075159	10.833009	13.397518
O	5.306474	5.352335	6.913917
O	11.319085	9.477215	9.034297
O	6.806157	1.529677	6.445580
O	8.690258	9.523801	15.177795
O	4.766547	8.642122	15.047981
O	8.838333	5.341691	6.619617
O	11.801527	8.966048	12.025759
O	1.967197	6.854060	8.275173
O	4.978279	7.284296	4.989139
O	8.780056	0.576290	4.932940
O	4.683203	0.761109	4.947244
O	6.830608	-1.478135	8.064992
O	8.860273	7.476672	4.745025
O	1.710970	8.919281	11.901853
O	10.654449	4.137845	4.938350
O	11.677965	6.853827	8.361550
O	4.224524	4.028402	4.739443

O	9.350337	8.130906	12.889096
Cu	7.514530	8.111889	8.743057
O	3.466072	8.120546	10.036046
O	10.005201	7.714584	10.330495
H	4.235702	11.299788	13.415992
H	5.148221	6.817131	4.157672
H	11.653813	10.001083	8.309682
H	5.145655	1.049946	4.157755
H	5.038707	-0.860939	9.816767
H	11.903701	9.847222	11.639297
H	3.481784	3.931505	4.157548
H	11.849792	4.794081	9.816745
H	9.387809	11.299815	13.416000
H	13.414514	5.007711	8.138697
H	5.148205	8.913906	15.886608
H	1.970078	10.000462	8.309590
H	4.441283	-2.322861	8.138705
H	1.969701	5.729887	11.734584
H	10.141480	3.931303	4.157691
H	0.209056	5.007657	8.138791
H	9.182248	-2.322962	8.138913
H	1.719812	9.847203	11.639292
H	8.475300	8.913893	15.886592
H	8.584898	-0.860887	9.816723
H	8.477888	1.049914	4.157683
H	11.653391	5.730589	11.734727
H	1.773677	4.794122	9.816833
H	8.475285	6.817230	4.157712
Al	8.584368	7.056568	6.397076
Al	4.060094	4.277188	6.434365
H	3.811997	2.313826	7.775758

8MR/H_2

Electronic + zero-point energies = -8900.570596

Si	8.411602	9.196913	13.575412
O	4.263442	7.504866	7.492299
O	4.760726	0.056280	7.511151
O	11.079945	4.225807	7.497172
O	2.579308	4.456951	7.446820
Si	5.208891	9.210671	13.587015
O	9.112145	7.636119	7.858641
Si	5.279045	6.823615	6.402682
Si	5.299004	1.160918	6.456215
O	8.887170	0.129222	7.502099
Si	9.920937	4.056610	6.354544
O	4.294871	8.376079	12.516858
Si	8.433684	1.202037	6.367955
Si	1.598899	5.277959	8.435462
O	6.807178	8.877381	13.392391
Si	8.407418	-1.147762	8.408675
Si	3.025576	7.894310	11.593977
Si	10.551243	7.999542	8.519931
Si	3.066511	7.983071	8.464939
O	6.764352	7.222921	6.954888

Si	10.678705	7.926984	11.744003
Si	12.004918	5.208646	8.417179
O	4.449580	2.476792	7.157793
Si	5.272192	-1.202905	8.431397
O	9.333284	2.523582	6.466631
O	8.577558	10.807142	13.258162
O	11.114454	6.408671	12.167505
O	2.681090	9.483310	7.937953
O	2.614313	6.378682	12.053919
O	5.073155	10.836142	13.338090
O	5.131938	5.213989	6.354655
O	11.021892	9.429756	7.876023
O	6.845490	1.603398	6.612532
O	8.958892	8.774102	15.070194
O	4.669568	8.740974	15.072446
O	8.721207	5.103111	6.539392
O	11.854511	9.025660	12.143141
O	1.811428	6.924317	8.383320
O	4.956405	7.415852	4.889364
O	8.554410	0.458467	4.906423
O	4.902252	0.624109	4.982443
O	6.835918	-1.522432	8.086706
O	8.768090	7.420712	4.842655
O	1.717165	8.893445	11.779725
O	10.696745	4.169148	4.901157
O	11.643424	6.805946	8.218897
O	3.592723	3.299768	4.857124
O	9.275993	8.281414	12.525524
Cu	7.287309	7.883955	8.777349
O	3.577646	7.992190	10.036319
O	10.368952	8.116827	10.144543
H	4.235706	11.299786	13.415995
H	5.148174	6.817168	4.157671
H	11.653788	10.001078	8.309689
H	5.145578	1.049914	4.157739
H	5.038704	-0.860919	9.816753
H	11.903698	9.847211	11.639295
H	3.482093	3.931443	4.157570
H	11.849789	4.794081	9.816733
H	9.387811	11.299813	13.415999
H	13.414494	5.007706	8.138692
H	5.148197	8.913903	15.886592
H	1.970096	10.000484	8.309608
H	4.441287	-2.322843	8.138705
H	1.969697	5.729885	11.734588
H	10.141486	3.931298	4.157695
H	0.208954	5.007667	8.138850
H	9.182230	-2.322931	8.138904
H	1.719816	9.847195	11.639290
H	8.475303	8.913894	15.886583
H	8.584892	-0.860877	9.816704
H	8.477881	1.049905	4.157674
H	11.653384	5.730603	11.734728
H	1.773671	4.794117	9.816851

H	8.475272	6.817218	4.157691
Al	8.417894	6.816627	6.415405
Al	3.864339	4.061826	6.376886
H	3.911944	2.185629	7.906462
H	7.035671	8.295728	10.345974
H	6.280976	8.179141	10.041255

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