Electronic Supplementary Information: Identifying Systematic DFT Errors in Catalytic Reactions

R. Christensen, H. A. Hansen, and T. Vegge[*]

Department of Energy Conversion and Storage, Technical University of Denmark, Fysikvej bld. 309, DK-2800 Kgs. Lyngby, Denmark

E-mail: teve@dtu.dk

S1 Computational method

Calculations have been performed using the VASP code with the projector augmented-wave (PAW) method.[1–4] In general, calculational parameters have been chosen very cautiously to avoid inducing errors unrelated to the choice of functional, e.g. by using more accurate PAW potentials and higher plane wave energy cut-off than usually needed. The hard PAW potentials distributed with the code have been used for C, H and O atoms and default potential for Cu. The potentials have been generated with the PBE functional and are used for all functionals. This is expected to give negligible errors. An energy cut-off at 650 eV has been used. The high cut-off value is required for convergence with the hard PAW potentials. For gas phase species, Γ-point calculations were performed. For adsorption energies, a (4,4,1) Monkhorst-Pack k-point mesh was applied. Although not expected to be of importance, spin polarization has been included. Atomic configurations were optimized to a maximum force of 0.05 eV/Å. Vibrational ground state energies have been calculated for geometries with a maximum force of 0.01 eV/Å using the RPBE functional and extrapolated to the other functionals. Vibrational energies match well with those found by Peterson et al.[5] The approach for conversion to free energies has also been adapted from Peterson et al.[5]

For the Cu surface, a cell with three closed-pack layers with 9 atoms in each was used with periodic boundary conditions in the surface plane dimensions. Perpendicular to the surface a vacuum region of 12 Å has been used with dipole corrections at the cell boundaries. The two lower layers have been constrained to simulate a large underlying bulk structure. The lattice constant has been optimized for each functional.

S1.1 Examined reactions

Previously,[5–7] reactions similar to reactions (1)-(10) in Table 1 of the main text with CO as reactant instead of CO_2 have also been used. As they couple with those in the Primary Set through the reverse water-gas shift reaction, i.e. reaction (0), they do not add any additional

experimental data and have thus been omitted for simplicity.

S2   Functional dependence on reactions

An extended analysis is conducted to confirm that the dominating functional dependence can be attributed to the carbon-oxygen double (C=O) bonds. With the assumption that C=O bonds dominate functional dependence, the slope when plotting two reactions versus each other can be predicted by dividing the change in C=O bonds in the reaction plotted on the y-axis with the change in C=O bonds in the reaction plotted on the x-axis. All possible combinations of reactions (1)-(16) have been examined. In 66 % of the cases the predicted slope will be different from 1. Slopes found through linear regression on the ensemble functionals are compared with predicted slopes. The differences between predicted and fitted slopes relative to the fitted slopes are depicted in Figure S1a.
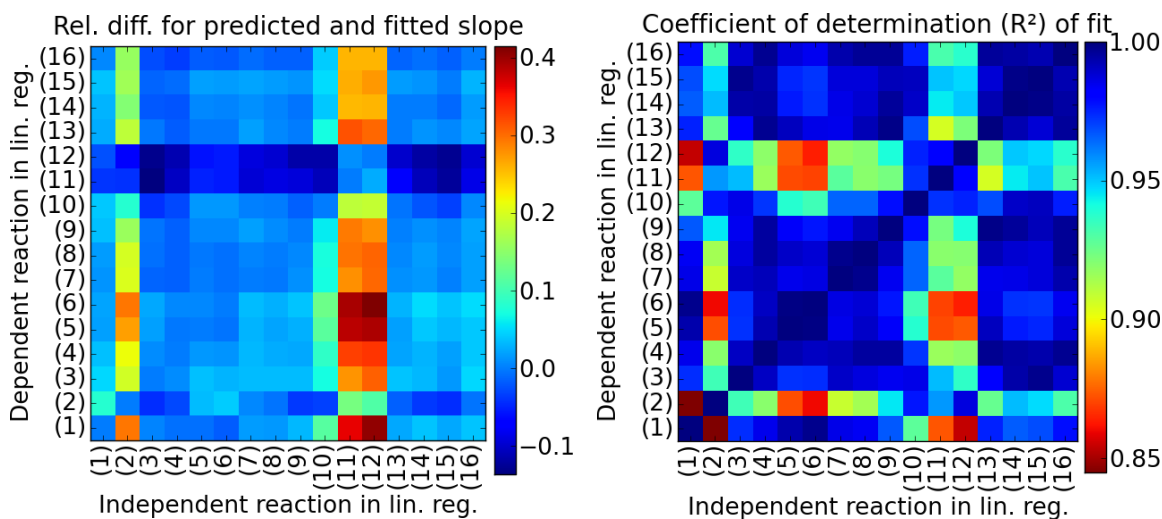
(a) Relative difference between fitted and predicted slopes.

(b) R^2 values of linear regressions on ensemble functionals.

Figure S1: Overview of analysis.

The difference between fitted and predicted slopes is at most 5 % with few exceptions discussed below. The good agreement confirms that C=O bonds are the major functional dependent molecular components. The exceptions are cases where reactions (2), (11) or

(12) are involved and most notably when they are used as independent reaction. In the products of these three reactions, the ratio of C=O bonds to carbon atoms is 1. Thus only one of the C=O bonds present in the reactant CO_2 is broken resulting in less functional dependent reaction enthalpies than for the other reactions. As the level of data noise is not reduced correspondingly, the slope of the line is less well-defined. This is exemplified in Figure S2. The linear regression for reaction (2) and (3) will give a slope of 1.67, where the predicted is 2.0. As can be seen, the fitted slope is not significantly better in terms of describing functional dependence than a slope with 2.0, which actually fits better with the 5 main functionals. The coefficient of determination (R^2) of the linear regressions (Figure S1b) can be used as an indicator for cases, where the slope found from linear regression is a sub-optimal measure for functional dependence. It is noteworthy, that cases where the fitted and predicted slopes differ the most all have relatively low R^2 value. I.e., these cases are less well described by a linear relation.
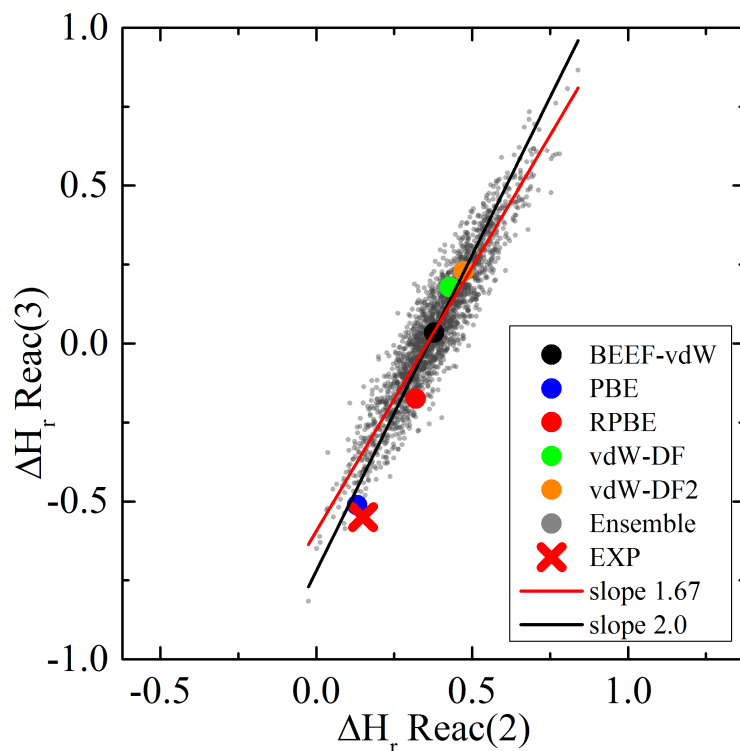

Figure S2: Example of how the slope obtained through linear regression is not given to be a good description of functional dependence.

In addition to C=O bonds, carbon-carbon double (C=C) bonds present in the C_2H_4 and C_4H_6 products of reactions (7) and (8), respectively, also display significant functional dependence. This can be found in a similar way as for C=O bonds by considering the slope of reactions. To remove CO_2 functional dependence from reactions, methane is used as reactant. H_2 and hydrocarbons with different amounts of C=C bonds are used as products. Two such cases are illustrated in Figure S3. In Figure S3(a), the reaction plotted on the x-axis displays little functional dependence as no C=C bonds are formed. The reaction plotted on the y-axis displays significant functional dependence as one C=C bond is formed. In Figure S3(b), two C=C bonds are formed in the reaction on the x-axis and one in the reaction on the y-axis. The slope is observed to agree with the expected 0.5.
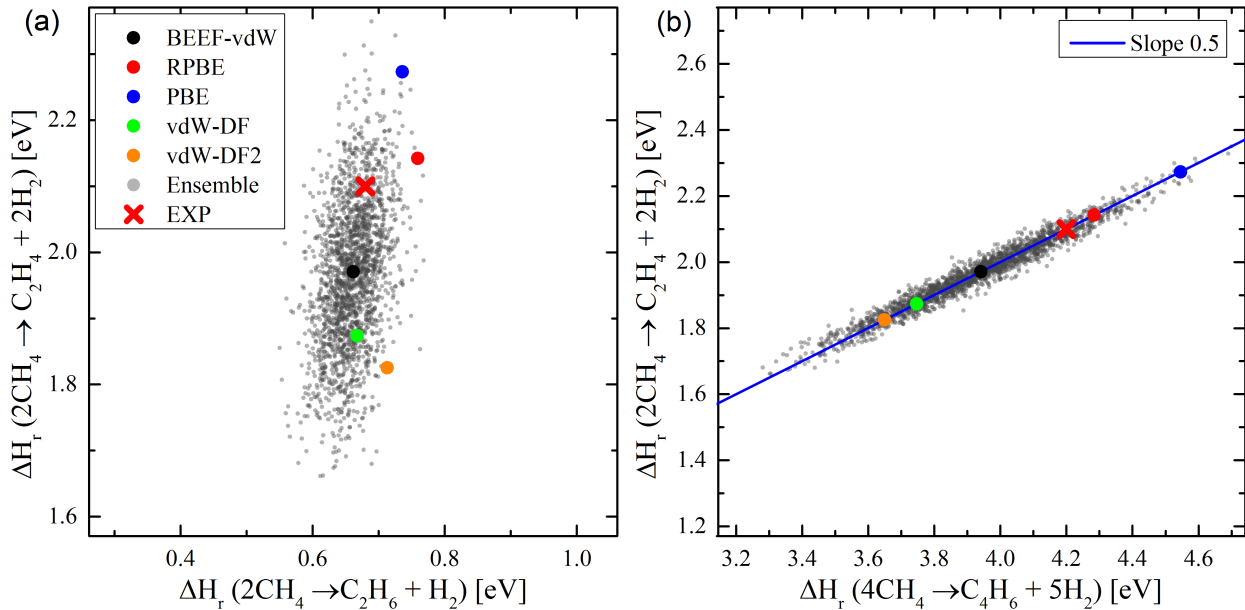
Figure S3: Correlations between reactions with different number of C=C bonds formed.

The functional dependence of the C=C bond scales linearly with the C=O bond, i.e. the error in C=O and C=C energy will for a given functional correlate. If this was not the case the presence of both C=O and C=C bonds in reactions (7) and (8) would result in an increasingly scattered ensemble pattern when plotted against other reactions. However, the R^2 values for the linear regressions involving reactions (7) and (8) are similar to those for other reactions. The functional dependence on C=C bonds is included in prediction of

slopes. The functional dependence relative to C=O bonds are determined by minimizing the mean of the relative differences shown in Figure S1a. It is found to be 0.72, which corresponds to a correction of approximately 0.1 eV per C=C bond. When determining optimal corrections for C=O bonds and H_2, addition of corrections specifically applied to C=C bonds will with the used reactions not change the optimal corrections found for H_2 and C=O bonds. As C=C bonds are less functional dependent and generally present in smaller numbers than C=O bonds when considering CO_2 reduction catalysts, e.g. 2 C=O bonds to 1/2 C=C bond in reaction (7) (formation of ethylene), the potential error associated with the C=C bonds will in most cases be insignificant in comparison to other sources of error. It might, however, be important in studies of larger organic species.

S3   Energies

Table S1 shows used electronic, ZPE, and $\int C_p \mathrm{d}T$ energies.

Table S1: List of energies in eV. ZPE and $\int C_p \mathrm{d}T$ computed from frequencies obtained with RPBE.

Specie	BEEF-vdW	PBE	RPBE	vdW-DF	vdW-DF2	ZPE	$\int C_p \mathrm{d}T$
CO_2	-18.52	-23.10	-22.51	-17.20	-17.79	0.31	0.10
H_2	-7.46	-6.76	-7.04	-7.37	-7.55	0.32	0.09
CO	-12.14	-14.89	-14.59	-11.37	-11.82	0.14	0.09
H_2O	-13.12	-14.23	-14.26	-12.52	-12.89	0.60	0.10
CH_4	-23.77	-23.99	-24.14	-23.12	-23.65	1.17	0.10
HCOOH	-25.80	-29.92	-29.42	-24.34	-25.07	0.90	0.11
CH_3OH	-28.27	-30.19	-30.08	-27.16	-27.86	1.36	0.11
CH_3CH_2OH	-44.07	-46.84	-46.54	-42.38	-43.40	2.12	0.11
C_3H_8	-55.05	-56.94	-56.75	-53.25	-54.39	2.73	0.11
C_2H_6	-39.37	-40.43	-40.42	-38.15	-38.98	1.96	0.11
C_2H_4	-30.40	-31.93	-31.79	-29.36	-30.11	1.34	0.11
C_4H_6	-53.24	-56.94	-56.33	-51.23	-52.51	2.24	0.11
CH_3COOH	-41.76	-46.75	-46.07	-39.74	-40.77	1.62	0.11
$HCOOCH_3$	-41.10	-46.02	-45.36	-39.13	-40.21	1.63	0.11
CH_2O	-19.82	-22.15	-21.91	-18.88	-19.40	0.70	0.10
OCHCHO	-32.04	-37.37	-36.59	-30.24	-31.07	0.96	0.11
C_2H_5COOH	-57.43	-63.25	-62.30	-54.84	-56.03	2.38	0.11
CH_3COOCH_3	-57.04	-62.82	-61.88	-54.50	-55.75	2.35	0.11
CH_3OCH_3	-43.61	-46.33	-45.99	-41.96	-42.92	2.10	0.11
CH_3CHO	-35.90	-39.11	-38.67	-34.37	-35.17	1.47	0.11
Cu(111) surf	-9.00	-	-	-	-	-	-
COOH*	-30.54	-118.30	-105.77	-15.12	-24.69	0.59	0.10
CH_3*	-27.81	-111.75	-99.91	-13.23	-22.61	0.92	0.10

S4 Atomic configurations

Below (Section S5) the applied atomic configurations used with the BEEF-vdW functional, and thus also for the ensemble, are written in Cartesian coordinates in units of Å. For the other functionals, the atomic configurations are similar, but have been relaxed resulting in slightly different bond lengths (Table S3). It also includes the bond lengths in COOH* and HCOOH between the non-hydrogenated oxygen atom and the carbon atom. For the surface calculations different interatomic distances for the Cu atoms simulating bulk have been used.

Table S3: Distance in Å between atoms for various bonds with the used functionals.

Bond	Specie	BEEF-vdW	PBE	RPBE	vdW-DF	vdW-DF2
H–H	H_2	0.738	0.752	0.749	0.740	0.736
O–H	H_2O	0.963	0.969	0.970	0.969	0.968
C=O	CO_2	1.167	1.170	1.174	1.174	1.170
C=O	COOH*	1.211	1.214	1.219	1.217	1.212
C=O	HCOOH	1.202	1.206	1.210	1.209	1.206
C≡O	CO	1.133	1.135	1.139	1.136	1.132
C–O	CH_3OH	1.435	1.433	1.441	1.445	1.453
C–H	CH_3OH	1.096	1.103	1.104	1.099	1.095
C–C	C_2H_6	1.528	1.527	1.536	1.538	1.539
C=C	C_2H_4	1.332	1.334	1.339	1.336	1.331
Cu–Cu	bulk Cu	2.595	2.567	2.602	2.623	2.645

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S5 Positions

CO_2

C	6.0000	6.0000	6.0000
O	6.0000	6.0000	7.1666
O	6.0000	6.0000	4.8334

H_2

H	6.0000	6.0000	6.3689
H	6.0000	6.0000	5.6311

CO

C	6.0000	6.0000	5.3515
O	6.0000	6.0000	6.4842

H_2O

H	6.0000	6.7594	5.5245
H	6.0000	5.2406	5.5245
O	6.0000	6.0000	6.1162

CH_4

H	6.6288	6.6288	6.6288
H	5.3712	5.3712	6.6288
H	6.6288	5.3712	5.3712
H	5.3712	6.6288	5.3712
C	6.0000	6.0000	6.0000

HCOOH

H	5.3377	4.6609	6.0000
H	5.6218	7.4528	6.0000
C	6.0091	6.4250	6.0000
O	4.9625	5.5569	6.0000
O	7.1700	6.1134	6.0000

CH$_3$OH

H	4.9058	6.9725	6.0000
H	6.8758	4.9443	6.0000
H	6.4363	7.0821	6.8932
H	6.4363	7.0821	5.1068
C	5.9525	6.6712	6.0000
O	5.9589	5.2358	6.0000

CH$_3$CH$_2$OH

H	4.0448	6.3950	6.0000
H	6.0395	7.2020	6.8883
H	6.0395	7.2020	5.1117
H	8.1131	6.1500	6.0000
H	7.1456	4.9574	6.8857
H	7.1456	4.9574	5.1143
C	7.1724	5.5950	6.0000
C	6.0024	6.5577	6.0000
O	4.7868	5.7817	6.0000

C$_3$H$_8$

H	5.1239	6.0000	7.2378
H	6.8761	6.0000	7.2378
H	6.0000	8.1683	6.3724
H	6.0000	3.8317	6.3724
H	6.8831	7.3261	5.0958
H	5.1169	7.3261	5.0958
H	5.1169	4.6739	5.0958
H	6.8831	4.6739	5.0958
C	6.0000	6.0000	6.5801
C	6.0000	7.2775	5.7398
C	6.0000	4.7225	5.7398

C$_2$H$_6$

H	6.0000	7.0185	7.1603
H	5.1185	5.4915	7.1609
H	6.8815	5.4915	7.1609
H	6.0000	4.9815	4.8397
H	5.1185	6.5085	4.8391
H	6.8815	6.5085	4.8391
C	6.0000	6.0004	6.7640
C	6.0000	5.9996	5.2360

C$_2$H$_4$

H	6.0000	6.9211	7.2365

H	6.0000	5.0789	7.2365
H	6.0000	6.9211	4.7635
H	6.0000	5.0789	4.7635
C	6.0000	6.0000	6.6660
C	6.0000	6.0000	5.3340

C_4H_6

H	5.5118	7.4739	6.0001
H	6.4884	4.5262	6.0001
H	3.2724	6.5050	6.0000
H	3.9885	4.8018	6.0000
H	8.7277	5.4954	6.0000
H	8.0113	7.1985	6.0000
C	5.3899	6.3934	6.0000
C	6.6102	5.6066	6.0000
C	4.1511	5.8737	6.0000
C	7.8489	6.1265	6.0000

CH_3COOH

H	4.1215	6.3310	6.0000
H	8.0522	5.5861	6.0000
H	6.9732	4.4692	6.8791
H	6.9732	4.4692	5.1209
C	6.0017	6.1613	6.0000
C	7.0775	5.1075	6.0000

	O	6.1712	7.3577	6.0000
	O	4.7510	5.5935	6.0000

HCOOCH$_3$

	H	4.0646	6.3909	6.0000
	H	7.9848	7.2948	6.0000
	H	7.5638	5.7972	6.8900
	H	7.5638	5.7972	5.1100
	C	5.0516	5.9065	6.0000
	C	7.3746	6.3963	6.0000
	O	5.2457	4.7178	6.0000
	O	6.0000	6.8718	6.0000

CH$_2$O

	H	5.0604	5.1014	6.0000
	H	6.9396	5.1014	6.0000
	C	6.0000	5.6927	6.0000
	O	6.0000	6.8977	6.0000

OCHCHO

	H	5.5272	6.8970	5.3120
	H	6.9387	4.4871	6.8353
	C	5.5410	6.0275	6.0041
	C	6.8762	5.2769	6.0564
	O	4.5912	5.6744	6.6605

O	7.7716	5.5194	5.2833	

C₂H₅COOH

H	6.4888	4.6500	5.1198
H	6.4854	4.6308	6.8620
H	8.6739	5.5088	6.0065
H	7.8351	6.8018	5.1359
H	7.8298	6.7853	6.8961
H	3.3780	5.9013	6.0120
C	6.5256	5.3026	5.9984
C	7.7918	6.1510	6.0098
C	5.2537	6.1221	6.0040
O	4.1457	5.3092	6.0108
O	5.1715	7.3279	6.0025

CH₃COOCH₃

H	3.9182	5.6801	6.9354
H	3.8746	5.5965	5.1790
H	4.0385	4.0946	6.1217
H	8.0221	6.4186	5.0583
H	8.1238	6.3627	6.8329
H	7.7244	7.9050	6.0136
C	5.8157	5.2683	6.0157
C	4.3130	5.1445	6.0711
C	7.6171	6.8240	5.9854

O	6.1891	6.5827	6.0595
O	6.6013	4.3518	5.9337

CH_3OCH_3

H	7.8506	5.6162	6.8688
H	6.6866	4.7439	5.8339
H	7.3992	6.2828	5.2754
H	4.1428	7.2206	6.5709
H	5.1461	7.2599	5.0948
H	4.4367	5.7189	5.6516
C	7.0352	5.7352	6.1561
C	4.8762	6.6704	5.9823
O	6.0042	6.4547	6.8223

CH_3CHO

H	4.7169	5.4698	6.7716
H	4.8623	6.6386	5.4228
H	5.2867	4.9112	5.2094
H	7.2390	5.1702	6.8003
C	5.3047	5.7639	5.8959
C	6.7231	6.0334	6.3183
O	7.3014	7.0852	6.1687

Empty

Cu	7.7854	0.0009	7.8820

Cu	2.5955	0.0013	7.8835
Cu	5.1900	0.0013	7.8834
Cu	9.0830	2.2483	7.8833
Cu	3.8928	2.2489	7.8854
Cu	6.4879	2.2483	7.8834
Cu	10.3805	4.4963	7.8834
Cu	5.1904	4.4963	7.8834
Cu	7.7854	4.4954	7.8821
Cu	1.2975	0.7491	5.7949
Cu	3.8926	0.7491	5.7949
Cu	6.4877	0.7491	5.7949
Cu	2.5951	2.9965	5.7949
Cu	5.1902	2.9965	5.7949
Cu	7.7852	2.9965	5.7949
Cu	3.8926	5.2439	5.7949
Cu	6.4877	5.2439	5.7949
Cu	9.0828	5.2439	5.7949
Cu	2.5951	1.4983	3.6760
Cu	5.1902	1.4983	3.6760
Cu	7.7852	1.4983	3.6760
Cu	3.8926	3.7457	3.6760
Cu	6.4877	3.7457	3.6760
Cu	9.0828	3.7457	3.6760
Cu	5.1902	5.9931	3.6760
Cu	7.7852	5.9931	3.6760

	Cu	10.3803	5.9931	3.6760

COOH*

	H	3.8056	3.3725	11.5115
	C	3.9555	2.2465	9.9666
	O	4.1381	1.2682	10.6568
	O	3.7623	3.4928	10.5422
	Cu	7.7854	0.0051	7.8786
	Cu	6.4728	6.7263	7.8639
	Cu	9.0956	6.7215	7.8675
	Cu	9.0724	2.2448	7.8723
	Cu	3.8934	2.2555	7.9743
	Cu	6.5008	2.2476	7.8697
	Cu	10.3696	4.5091	7.8707
	Cu	5.1999	4.5080	7.8685
	Cu	7.7843	4.4926	7.8770
	Cu	1.2975	0.7491	5.7949
	Cu	3.8926	0.7491	5.7949
	Cu	6.4877	0.7491	5.7949
	Cu	2.5951	2.9965	5.7949
	Cu	5.1902	2.9965	5.7949
	Cu	7.7852	2.9965	5.7949
	Cu	3.8926	5.2439	5.7949
	Cu	6.4877	5.2439	5.7949
	Cu	9.0828	5.2439	5.7949

Cu	2.5951	1.4983	3.6760
Cu	5.1902	1.4983	3.6760
Cu	7.7852	1.4983	3.6760
Cu	3.8926	3.7457	3.6760
Cu	6.4877	3.7457	3.6760
Cu	9.0828	3.7457	3.6760
Cu	5.1902	5.9931	3.6760
Cu	7.7852	5.9931	3.6760
Cu	10.3803	5.9931	3.6760

CH$_3$*

H	4.8252	2.5275	10.3552
H	3.7204	1.1325	10.2975
H	3.0611	2.7857	10.3590
C	3.8701	2.1634	9.9737
Cu	7.7861	0.0059	7.8358
Cu	6.4728	6.7253	7.8247
Cu	9.0964	6.7217	7.8282
Cu	9.0719	2.2455	7.8316
Cu	3.8914	2.2637	7.9397
Cu	6.5025	2.2486	7.8287
Cu	10.3688	4.5113	7.8302
Cu	5.2024	4.5098	7.8290
Cu	7.7849	4.4932	7.8329
Cu	1.2975	0.7491	5.7949

Cu	3.8926	0.7491	5.7949
Cu	6.4877	0.7491	5.7949
Cu	2.5951	2.9965	5.7949
Cu	5.1902	2.9965	5.7949
Cu	7.7852	2.9965	5.7949
Cu	3.8926	5.2439	5.7949
Cu	6.4877	5.2439	5.7949
Cu	9.0828	5.2439	5.7949
Cu	2.5951	1.4983	3.6760
Cu	5.1902	1.4983	3.6760
Cu	7.7852	1.4983	3.6760
Cu	3.8926	3.7457	3.6760
Cu	6.4877	3.7457	3.6760
Cu	9.0828	3.7457	3.6760
Cu	5.1902	5.9931	3.6760
Cu	7.7852	5.9931	3.6760
Cu	10.3803	5.9931	3.6760