Supporting Information

Understanding the role of carboxylic acid surfactants growth inhibition effect in the area selective atomic layer deposition: The case of ZnO growth on Cu and Cu_2O

L. E. López-González[1*], R. Ponce-Pérez[1], H. Tiznado[1*], J. Guerrero-Sánchez[1*]

[1]*Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, BC 22860, Mex.*

Figure captions

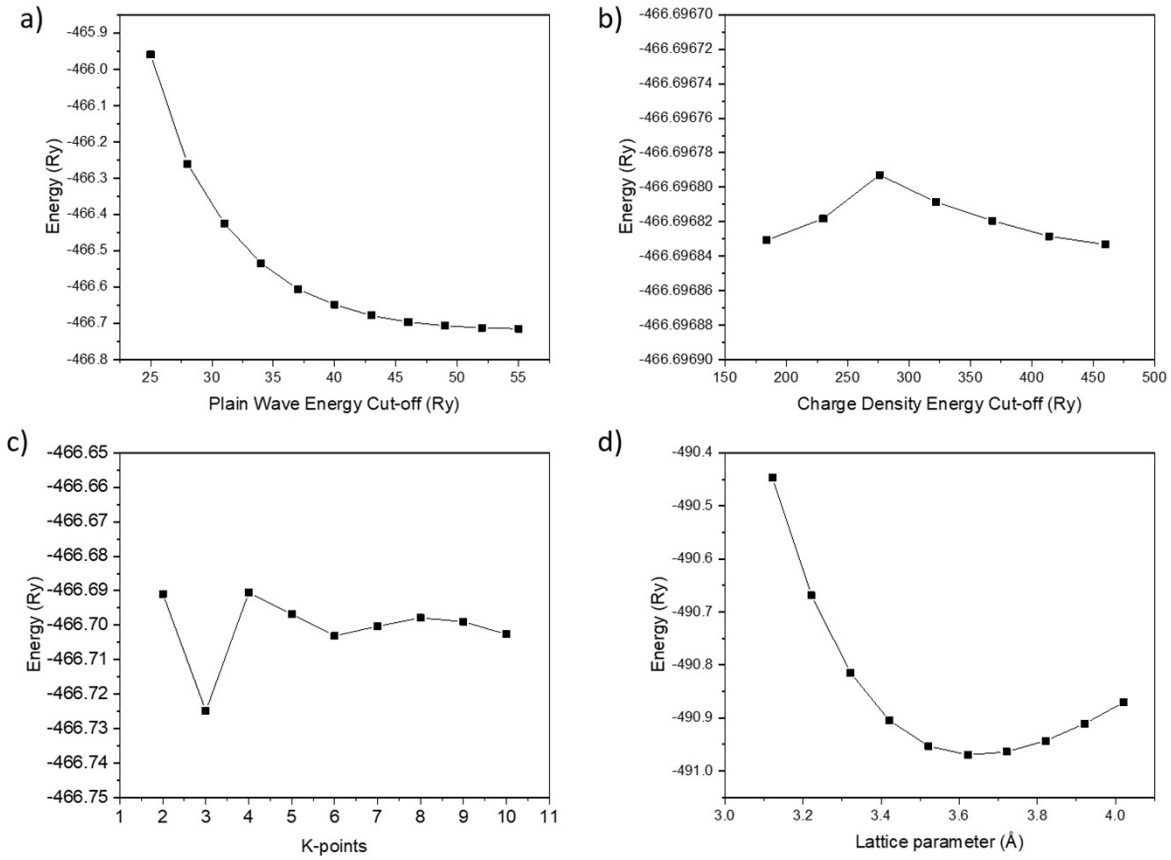

Figure S1. Optimization of computational parameters for bulk Copper. The total energy of the system as a function of (a) plain wave energy cut-off, (b) charge density energy cut-off, (c) k-points, (d) lattice parameter.

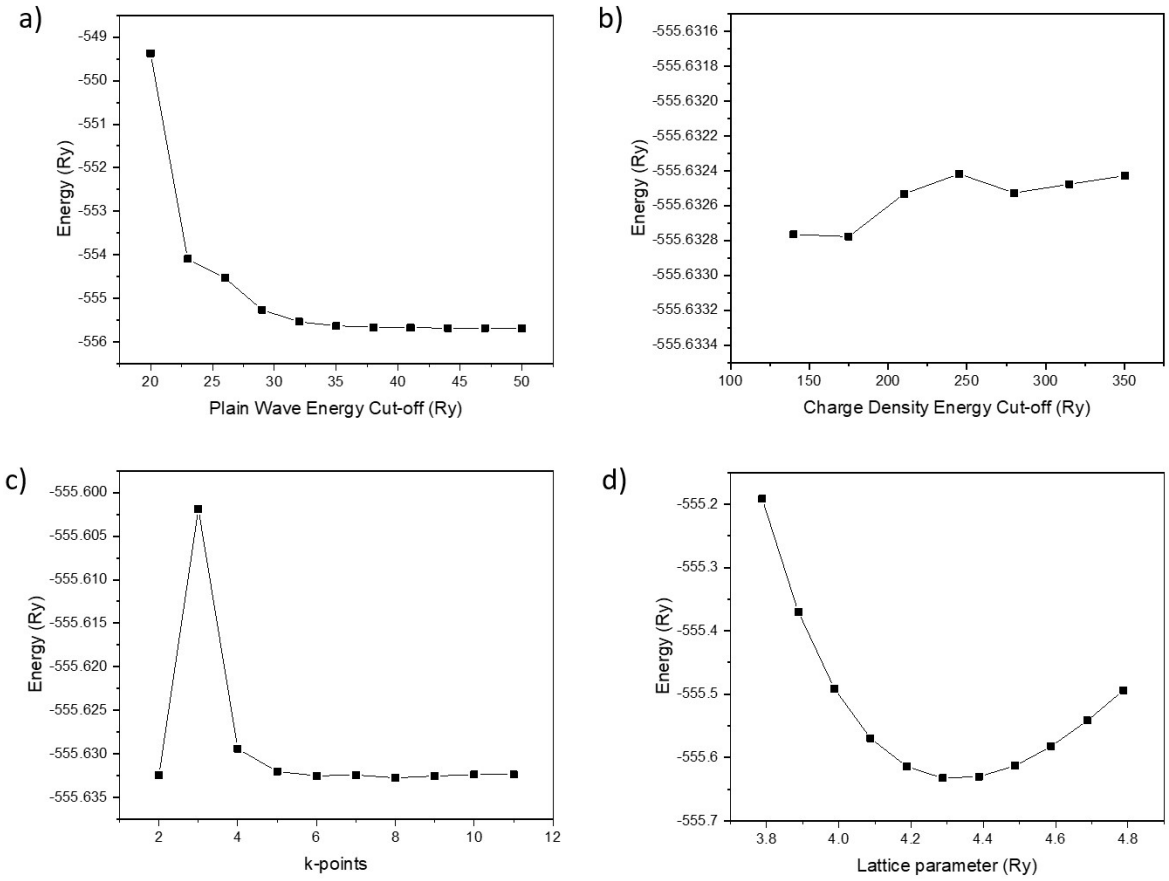

Figure S2. Optimization of computational parameters for bulk Cu_2O. The total energy of the system as a function of (a) plain wave energy cut-off, (b) charge density energy cut-off, (c) k-points, (d) lattice parameter.

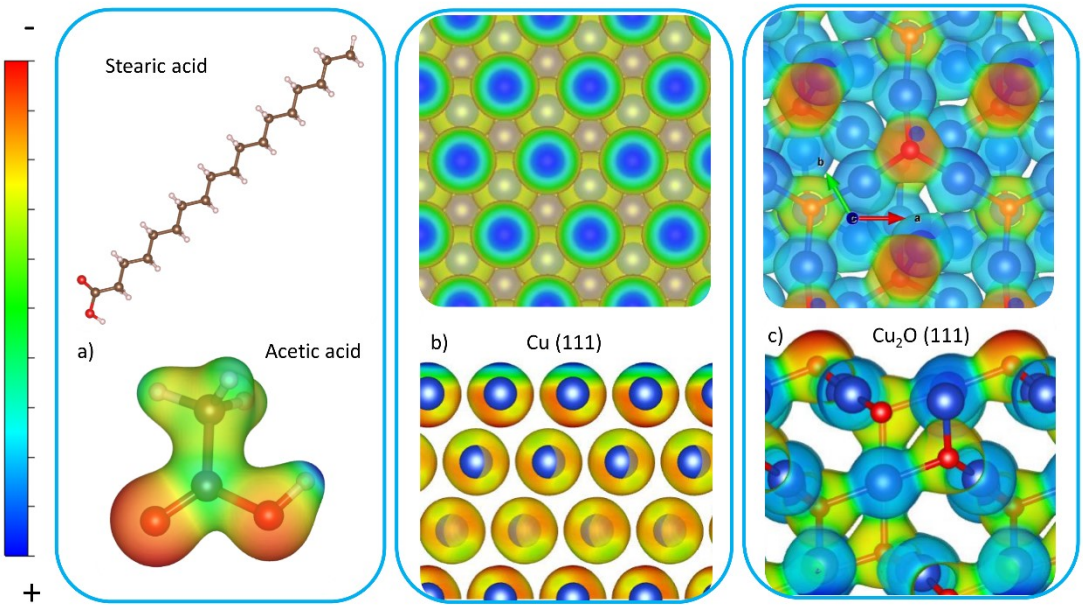

Figure S3. Charge density isosurfaces colored by electrostatic potential for a) acetic acid (AA), b) copper (111) surface top and side views, c) cuprous oxide (111) surface top and side views. Color scale indicates a positive electrostatic potential as blue and a negative one as red. Atom color code: Cu (blue), O (red), C (brown), H (white).

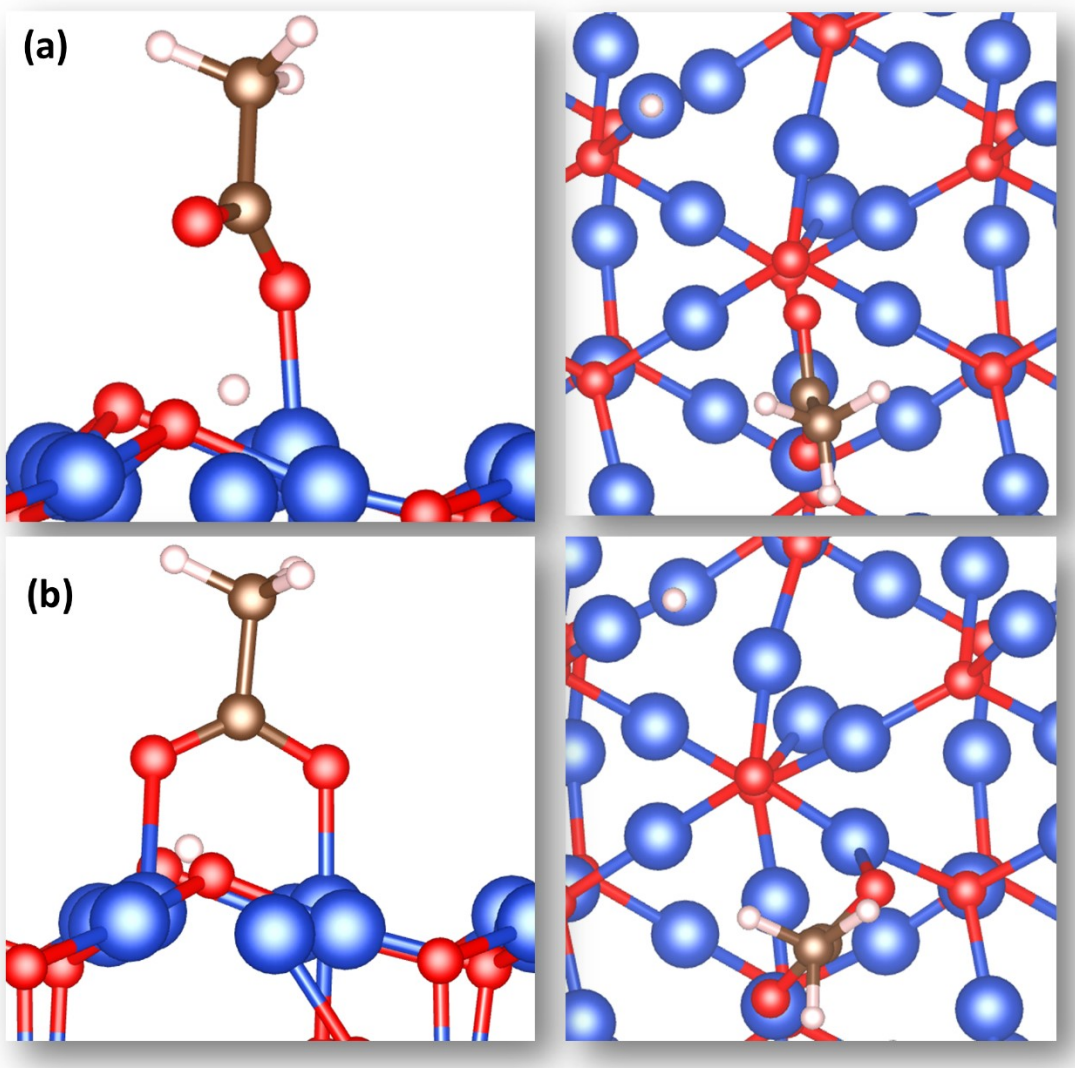

Figure S4. (a) Initial geometry in a monodentate manner (dissociative chemisorption binding with one COO oxygen to CUS Cu atom and H adsorbed to the surface) prior to relaxation, (b) optimized geometry (after relaxation) of (a) yielding spontaneous bidentate adsorption configuration.

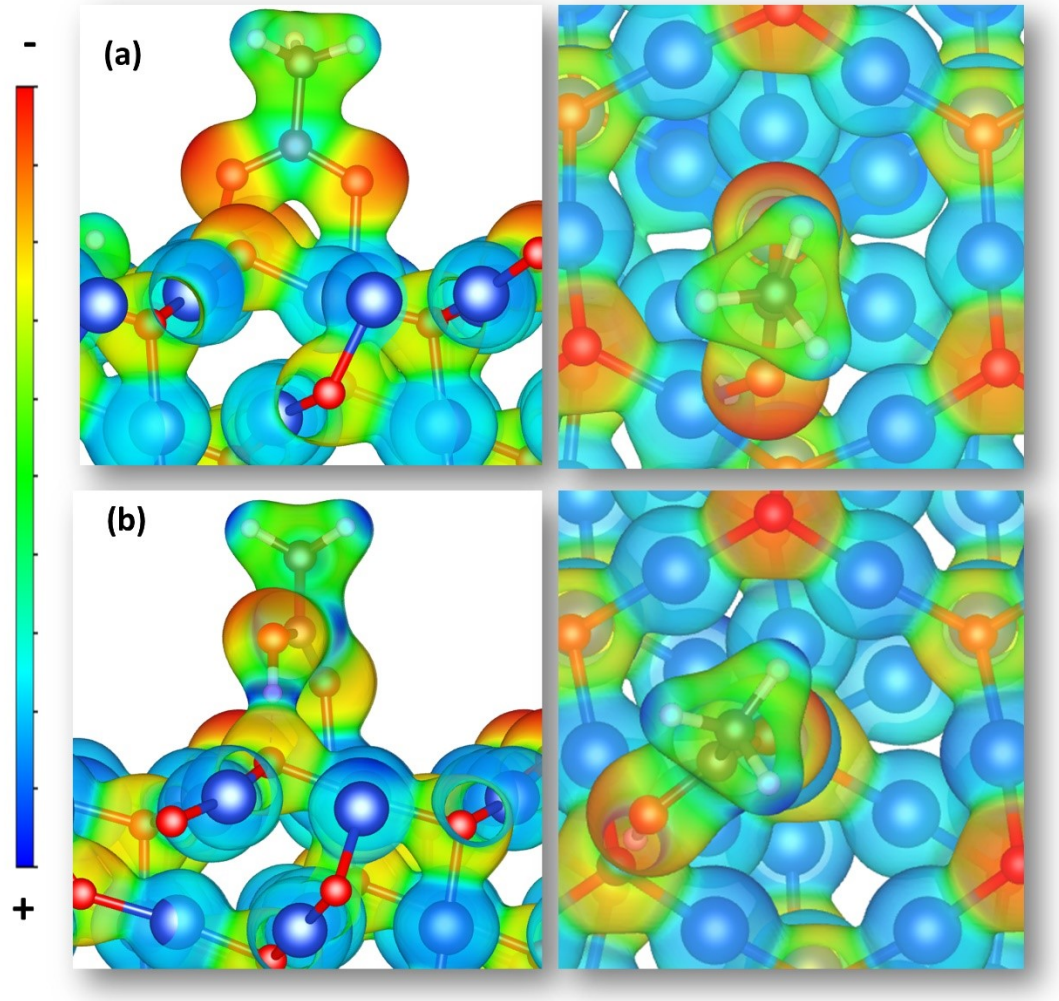

Figure S5. Charge density isosurfaces colored by the electrostatic potential for the most stable (most negative E_{ads}) configurations (carbonyl chemisorbed and bidentate) of AA adsorbed on Cu_2O (111).

Table S1. Bond lengths and angles for the acetic acid molecule in vacuum and adsorbed (each most stable obtained adsorption model).

Chemical species	**Bond**	**Length (Å)**	**Angle**	**Length (°)**
Free CH3COOH	C-C	1.51	C2-O1-H1	110.22
	C-O	1.37	H2-C1-H3	109.09
	C=O	1.21	C2-C1-H2	110.69
	C-H	1.10	H2-C1-H4	107.70
	C-H	1.10	C2-C1-H3	109.54
	C-H	1.10	H3-C1-H4	109.08
	O-H	0.97	C2-C1-H4	110.70
			O2-C2-C1	125.14
			O1-C2-C1	115.43
			O1-C2-O2	119.43
Carbonyl chemisorbed AA				
Cu (b)	C-C	1.50	C2-O1-H1	109.37
	C-O	1.36	H2-C1-H3	108.54
	C=O	1.22	C2-C1-H2	110.34
	C-H	1.10	H2-C1-H4	108.54
	C-H	1.10	C2-C1-H3	109.85
	C-H	1.10	H3-C1-H4	108.68
	O-H	0.97	C2-C1-H4	110.80
			O2-C2-C1	126.37
			O1-C2-C1	116.10
			O1-C2-O2	117.52
Cu (c)	C-C	1.50	C2-O1-H1	110.84
	C-O	1.37	H2-C1-H3	108.74
	C=O	1.22	C2-C1-H2	112.20
	C-H	1.10	H2-C1-H4	110.14
	C-H	1.10	C2-C1-H3	112.20
	C-H	1.09	H3-C1-H4	107.41
	O-H	0.98	C2-C1-H4	109.82
			O2-C2-C1	125.44
			O1-C2-C1	115.86
			O1-C2-O2	118.65
Cu (d)	C-C	1.50	C2-O1-H1	112.56
	C-O	1.37	H2-C1-H3	107.67
	C=O	1.21	C2-C1-H2	110.13
	C-H	1.10	H2-C1-H4	109.43
	C-H	1.10	C2-C1-H3	109.54
	C-H	1.10	H3-C1-H4	109.51
	O-H	0.98	C2-C1-H4	110.50
			O2-C2-C1	125.34
			O1-C2-C1	115.42
			O1-C2-O2	119.23
Cu_2O (a)	C-C	1.50	C2-O1-H1	108.70
	C-O	1.33	H2-C1-H3	107.19
	C=O	1.24	C2-C1-H2	109.88
	C-H	1.10	H2-C1-H4	109.43
	C-H	1.10	C2-C1-H3	109.21
	C-H	1.09	H3-C1-H4	107.19

	O-H	1.04	C2-C1-H4	109.21
			O2-C2-C1	122.34
			O1-C2-C1	114.22
			O1-C2-O2	123.43
Cu_2O (b)	C-C	1.49	C2-O1-H1	109.16
	C-O	1.32	H2-C1-H3	108.98
	C=O	1.25	C2-C1-H2	109.65
	C-H	1.10	H2-C1-H4	111.04
	C-H	1.10	C2-C1-H3	108.96
	C-H	1.09	H3-C1-H4	107.80
	O-H	1.00	C2-C1-H4	110.34
			O2-C2-C1	121.37
			O1-C2-C1	114.40
			O1-C2-O2	123.43
Cu_2O (c)	C-C	1.50	C2-O1-H1	116.63
	C-O	1.30	H2-C1-H3	110.15
	C=O	1.26	C2-C1-H2	110.67
	C-H	1.10	H2-C1-H4	110.24
	C-H	1.10	C2-C1-H3	109.35
	C-H	1.10	H3-C1-H4	106.95
	O-H	1.09	C2-C1-H4	109.37
			O2-C2-C1	118.75
			O1-C2-C1	114.74
			O1-C2-O2	126.43
Bidentate adsorption				
Cu (a)	C-C	1.51	O1-C1-O2	125.60
	C-O	1.28	O2-C1-C2	116.73
	C-O	1.28	O1-C1-C2	117.64
	C-H	1.10	H2-C2-H3	108.34
	C-H	1.10	C1-C2-H3	111.12
	C-H	1.09	H1-C2-H3	110.11
			C1-C2-H2	108.98
			H1-C2-H2	107.33
			C1-C2-H1	110.82
Cu_2O (d)	C-C	1.51	O1-C1-O2	124.67
	C-O	1.30	O2-C1-C2	115.61
	C-O	1.26	O1-C1-C2	119.69
	C-H	1.10	H2-C2-H3	107.83
	C-H	1.09	C1-C2-H3	111.16
	C-H	1.09	H1-C2-H3	110.33
			C1-C2-H2	108.37
			H1-C2-H2	107.90
			C1-C2-H1	111.10
Cu_2O (e)	C-C	1.51	O1-C1-O2	124.67
	C-O	1.30	O2-C1-C2	115.61
	C-O	1.26	O1-C1-C2	119.70
	C-H	1.10	H2-C2-H3	107.83
	C-H	1.09	C1-C2-H3	111.16
	C-H	1.09	H1-C2-H3	110.35
			C1-C2-H2	108.37
			H1-C2-H2	107.90
			C1-C2-H1	111.10

Table S2. The vibrational frequencies of the acetic acid molecule for each obtained stable adsorption model (last two models include vibrational frequencies corresponding to DEZ molecule).

Model	Cu- AA (a) E_{ads} =-2.08 eV			Model	Cu- AA (c) E_{ads}=-0.23 eV		
Frequency	*THz*	*cm^{-1}*	*meV*	Frequency	*THz*	*cm^{-1}*	*meV*
1	93.63577	3123.353	387.2462	1	110.9866	3702.114	459.0035
2	92.35676	3080.69	381.9567	2	93.45961	3117.477	386.5177
3	90.1771	3007.984	372.9423	3	91.84475	3063.611	379.8392
4	44.92466	1498.525	185.7934	4	89.88186	2998.136	371.7213
5	42.85611	1429.526	177.2385	5	53.72067	1791.929	222.1707
6	42.31338	1411.423	174.994	6	43.07634	1436.872	178.1493
7	41.28326	1377.061	170.7338	7	42.57201	1420.049	176.0636
8	39.84969	1329.243	164.805	8	40.19848	1340.877	166.2475
9	32.43058	1081.768	134.1221	9	36.93709	1232.089	152.7595
10	30.41438	1014.515	125.7837	10	34.71216	1157.873	143.5579
11	29.90211	997.4269	123.6651	11	30.35767	1012.623	125.5492
12	27.92085	931.3392	115.4713	12	28.53168	951.7144	117.9975
13	26.15271	872.3604	108.1589	13	25.04442	835.3918	103.5753
14	24.12593	804.7544	99.77678	14	17.42751	581.3191	72.07435
15	19.60588	653.9818	81.08337	15	17.05827	569.0025	70.54728
16	17.56589	585.9351	72.64667	16	13.84059	461.6724	57.24005
17	14.94088	498.374	61.79047	17	12.5206	417.6421	51.781
18	7.208008	240.4333	29.80991	18	1.283434	42.81077	5.307856
19	5.919126	197.4408	24.47953	19	0.757782	25.27689	3.133933
20	3.956991	131.991	16.36479	20	0.645444	21.52968	2.669339
21	3.035792	101.2631	12.55502				
22	2.77943	92.71182	11.4948				
23	1.66897	55.67085	6.902303				

Model	Cu_2O- AA (d) E_{ads} =-2.33			Model	Cu_2O- AA (e) E_{ads}=-2.45		
Frequency	*THz*	*cm^{-1}*	*meV*	Frequency	*THz*	*cm^{-1}*	*meV*
1	90.442609	3016.8407	374.040407	1	90.298434	3012.032	373.4441
2	89.333763	2979.854	369.454593	2	89.194986	2975.224	368.8807
3	86.877601	2897.925	359.296724	3	86.83427	2896.479	359.1175
4	53.15898	1773.193	219.847779	4	51.701821	1724.587	213.8215
5	42.863021	1429.756	177.267132	5	42.888787	1430.616	177.3737
6	42.226381	1408.52	174.634202	6	42.199647	1407.629	174.5236
7	41.653756	1389.42	172.266017	7	41.579384	1386.939	171.9584
8	39.549899	1319.243	163.565166	8	39.520129	1318.25	163.442
9	38.100454	1270.894	157.570747	9	38.239191	1275.522	158.1445
10	29.768757	992.9789	123.113632	10	29.673362	989.7968	122.7191
11	28.993238	967.1103	119.906344	11	29.084959	970.1698	120.2857
12	26.859266	895.9287	111.080948	12	27.013062	901.0588	111.717
13	19.478339	649.7275	80.555903	13	19.489468	650.0987	80.60193
14	16.995934	566.9233	70.289503	14	17.872072	596.1482	73.91292

15	16.91894	564.3551	69.971083	15	16.798863	560.3498	69.47448
16	14.566408	485.8831	60.241796	16	14.739343	491.6516	60.957
17	11.821705	394.3296	48.890623	17	12.006832	400.5048	49.65624
18	6.948245	231.7685	28.735621	18	8.239406	274.837	34.07543
19	4.287824	143.0264	17.733008	19	4.191201	139.8034	17.33341
20	4.079715	136.0846	16.872336	20	3.529914	117.7452	14.59854
21	2.44902	81.69052	10.128329	21	2.401854	80.11722	9.933265

Model	Cu_2O- AA (a) E_{ads} =-3.44 eV			Model	Cu_2O- AA (b) E_{ads}= -3.04 eV		
Frequency	*THz*	*cm-1*	*meV*	Frequency	*THz*	*cm-1*	*meV*
1	93.73462	3126.6503	387.6551	1	90.92049	3032.781	376.0168
2	92.16675	3074.352	381.1709	2	90.19185	3008.476	373.0034
3	90.15853	3007.365	372.8655	3	87.46195	2917.416	361.7134
4	50.87224	1696.915	210.3906	4	86.79026	2895.012	358.9355
5	43.85159	1462.731	181.3555	5	46.89696	1564.314	193.9502
6	42.74506	1425.822	176.7793	6	42.2539	1409.438	174.748
7	42.67633	1423.529	176.495	7	41.81762	1394.886	172.9437
8	41.84322	1395.739	173.0496	8	40.70582	1357.8	168.3457
9	40.00056	1334.275	165.429	9	38.97095	1299.931	161.1708
10	37.24331	1242.303	154.0259	10	35.59723	1187.396	147.2182
11	35.90921	1197.802	148.5085	11	29.83246	995.1038	123.3771
12	30.55648	1019.254	126.3714	12	28.98247	966.751	119.8618
13	30.08757	1003.613	124.4321	13	26.31794	877.872	108.8422
14	27.18113	906.6649	112.4121	14	20.56648	686.0239	85.05608
15	18.69198	623.4973	77.30378	15	17.72769	591.332	73.31579
16	17.59437	586.885	72.76443	16	15.60325	520.4684	64.52983
17	14.50579	483.8612	59.99111	17	13.92641	464.5352	57.595
18	6.600782	220.1784	27.29863	18	6.933456	231.2752	28.67446
19	5.584956	186.2941	23.09751	19	4.385572	146.2869	18.13726
20	4.194962	139.9289	17.34896	20	2.915636	97.25516	12.0581
21	2.710122	90.39993	11.20816	21	1.132998	37.79276	4.685703
22	2.52918	84.36437	10.45984				
23	1.511367	50.41379	6.25051				

Model	Cu_2O-AA-DEZ (a)			Model	Cu_2O-AA-DEZ (b)		
Frequency	*THz*	*cm-1*	*meV*	Frequency	*THz*	*cm-1*	*meV*
1	93.76896	3127.796	387.7971	1	93.40567	3115.678	386.2946
2	92.38959	3081.785	382.0925	2	92.23185	3076.523	381.4401
3	91.17279	3041.197	377.0602	3	91.77102	3061.152	379.5343
4	91.03838	3036.713	376.5043	4	91.74319	3060.223	379.4192
5	90.55262	3020.51	374.4954	5	91.0903	3038.445	376.719
6	90.4796	3018.074	374.1934	6	90.9259	3032.962	376.0392
7	90.0233	3002.854	372.3063	7	90.35604	3013.953	373.6824
8	88.70865	2959.002	366.8693	8	89.84365	2996.861	371.5633

9	88.65058	2957.065	366.6292	9	89.03369	2969.844	368.2136
10	88.58173	2954.769	366.3444	10	88.96335	2967.498	367.9227
11	87.76319	2927.465	362.9592	11	88.57513	2954.548	366.3171
12	82.16687	2740.792	339.8147	12	87.15652	2907.229	360.4502
13	78.70082	2625.177	325.4803	13	86.72939	2892.981	358.6838
14	56.00578	1868.152	231.6212	14	50.37408	1680.298	208.3304
15	45.4459	1515.912	187.9491	15	45.20946	1508.025	186.9712
16	45.37235	1513.459	187.6449	16	43.54186	1452.4	180.0746
17	43.79807	1460.946	181.1342	17	43.45318	1449.442	179.7078
18	43.60238	1454.419	180.3249	18	43.32666	1445.222	179.1846
19	43.41291	1448.099	179.5413	19	43.25771	1442.922	178.8994
20	42.54689	1419.211	175.9597	20	43.08225	1437.069	178.1738
21	42.48369	1417.103	175.6983	21	42.24978	1409.301	174.731
22	42.11331	1404.749	174.1666	22	42.12284	1405.067	174.206
23	42.01014	1401.307	173.7399	23	41.79069	1393.987	172.8323
24	41.9058	1397.827	173.3084	24	41.27889	1376.916	170.7157
25	40.70031	1357.616	168.3229	25	40.85443	1362.757	168.9603
26	40.01891	1334.887	165.5048	26	40.38811	1347.202	167.0317
27	38.90299	1297.664	160.8898	27	39.78934	1327.229	164.5554
28	38.32636	1278.43	158.505	28	36.1128	1204.593	149.3505
29	36.25184	1209.231	149.9255	29	35.62945	1188.471	147.3515
30	34.94798	1165.739	144.5332	30	34.40771	1147.718	142.2988
31	34.89099	1163.838	144.2975	31	34.10062	1137.474	141.0288
32	34.60606	1154.334	143.1191	32	30.41169	1014.425	125.7726
33	33.98285	1133.546	140.5417	33	30.05314	1002.465	124.2898
34	30.49559	1017.223	126.1196	34	29.97857	999.9776	123.9814
35	30.39111	1013.738	125.6875	35	29.94958	999.0104	123.8615
36	30.05254	1002.445	124.2873	36	28.29405	943.7878	117.0147
37	29.5942	987.1562	122.3917	37	28.05183	935.7082	116.013
38	28.68699	956.8951	118.6398	38	27.94284	932.0727	115.5622
39	27.94027	931.987	115.5516	39	27.303	910.73	112.9161
40	27.22433	908.1059	112.5907	40	26.1164	871.1492	108.0087
41	26.90847	897.57	111.2845	41	19.95188	665.5232	82.51432
42	25.49099	850.2879	105.4222	42	18.74735	625.3442	77.53277
43	18.83373	628.2256	77.89002	43	18.27991	609.7522	75.59961
44	18.11916	604.39	74.93478	44	17.286	576.5988	71.48911
45	17.39385	580.1964	71.93515	45	15.98043	533.0499	66.08974
46	17.22004	574.3987	71.21633	46	15.1746	506.17	62.75706
47	16.04365	535.1586	66.35118	47	14.88786	496.6054	61.57119
48	14.99904	500.3142	62.03103	48	13.86611	462.5235	57.34558
49	13.73022	457.9908	56.78359	49	12.47623	416.1621	51.5975
50	9.846472	328.4429	40.72172	50	8.252623	275.2779	34.13009
51	7.755985	258.7118	32.07616	51	8.011535	267.2361	33.13303
52	7.033157	234.6009	29.08679	52	6.978933	232.7921	28.86254