Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The Global Minimum of Ag_{30}: A Prolate Spheroidal Structure Predicted by the Genetic Algorithm with Incomplete Local Optimizations at a DFT Level

Wen Liu,[a] Lulu Huang,[a] Lei Meng,[a,#] Jin Hu,[a] Xiaopeng Xing[a,*]

[a]School of Chemical Science and Engineering, Shanghai Key Lab of Chemical Assessment and Sustainability, Tongji University, 1239 Siping Road, Shanghai, 200092, China

*Corresponding author. E-mails: xingxp@tongji.edu.cn

Present address:

YunShangQian Technology, 57 Jianger Road，Hangzhou, Zhejiang, 310051, China

S1. The definition of the structural similarity parameter

The structural similarity parameter (*SS*) of any two structures of a cluster is defined based on their bond types, their bond numbers, and the coordination numbers of their atoms. If the bond types are not identical, the SS is set to 0; otherwise, the *SS* is calculated using the following equation:

$$SS = 0.4 \times CNS + 0.6 \times \left(1 - \frac{|b1 - b2|}{\max\{b1, b2\}}\right). \quad (3)$$

The *CNS* shows the coordination number similarity, and the *b1* and *b2* are the total number of bonds in the two structures being compared. The *CNS* is calculated as follows:

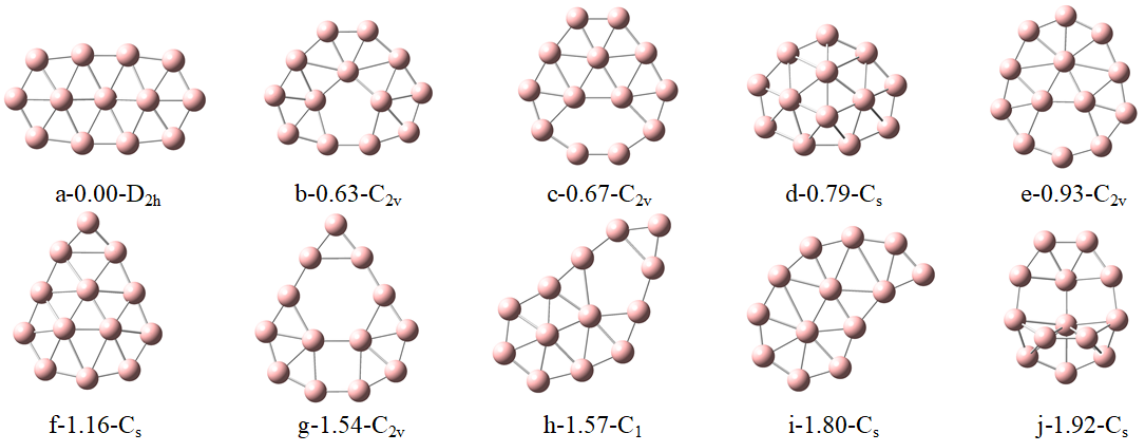
1) Separately input the coordination numbers of all atoms in the two structures into two integer arrays, whose size *n* is equal to the total atom number of the cluster.

2) Sequence the two integer arrays in ascending order. Set the *CNS* to 1 if the two integer arrays are equal to each other (i. e. the numerals at the corresponding locants of the two arrays are equal).

3) Otherwise, compare the numerals at the corresponding locants of the two arrays one by one, and determine the first locant (for example the *m*th) at which the numerals of the two arrays are different. Then, set the *CNS* to (*m*-1)/*n* if this value is larger than 1/2, otherwise, set the *CNS* to 1/2.

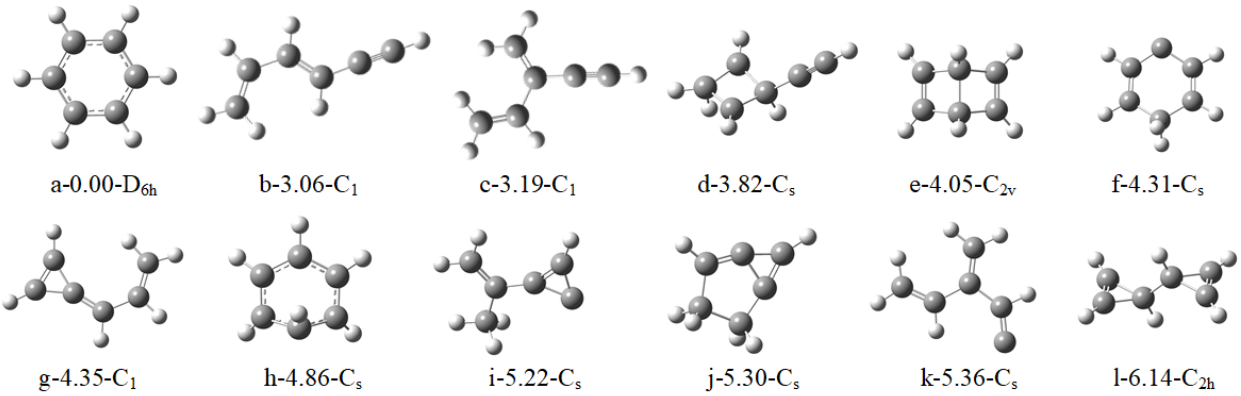
S2. The ten lowest-lying structures of B_{13}^-

The ten lowest-lying structures of B_{13}^- from the calculations at the PBE level with the basis set of 6-31G. All structures are in their singlet states. In the name of each structure, the lowercase letter indicates the energy order; the subsequent numeral indicates the energy (in eV) relative to the lowest-lying structure; the symmetry of the structure is shown in the last part.



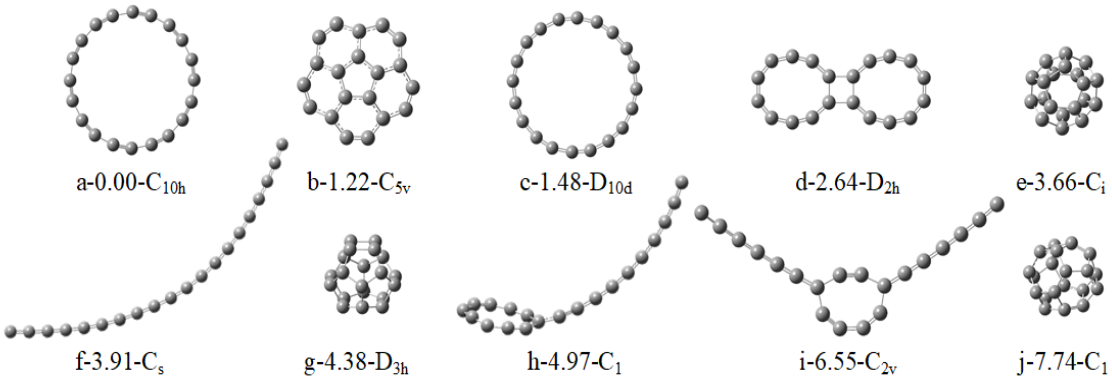
S3. The twelve lowest-lying structures of C_6H_6

The twelve lowest-lying structures of C_6H_6 from the calculations at the B3LYP level with the basis sets of 6-31G. All structures are in their singlet states. The meanings of the structures' names are the same as those in S2.



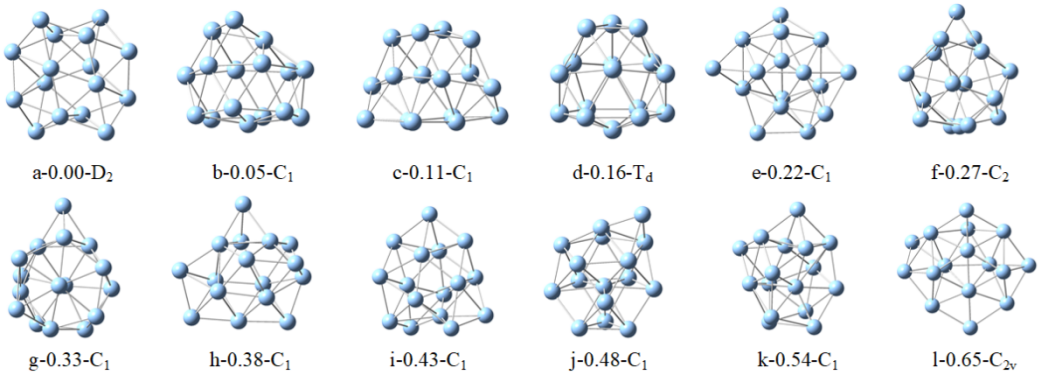
S4. The ten lowest-lying structures of C_{20}

The ten lowest-lying structures of C_{20} from the calculations at the B3LYP level with the basis set of 6-31G. All structures are in their singlet states. The meanings of the structures' names are the same as those in S2.



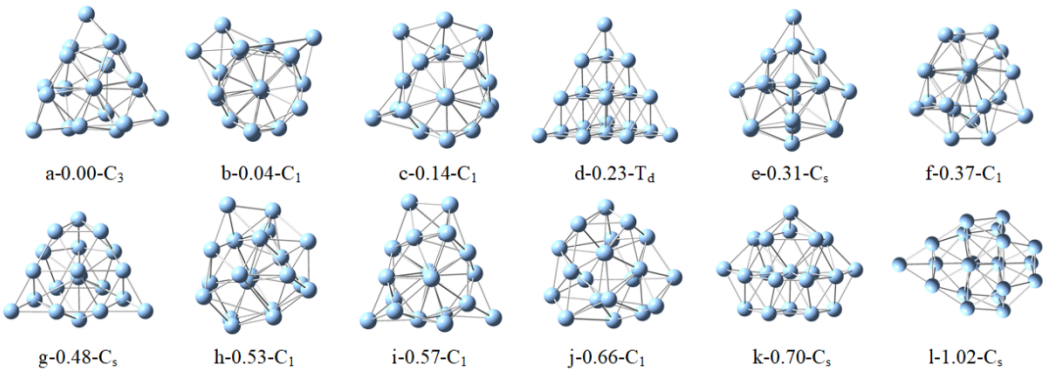
S5. The twelve lowest-lying structures of Ag_{16}^-

The twelve lowest-lying structures of Ag_{16}^- from the calculations at the PBE level with the basis set of lanl2dz. All structures are in their doublet states. The meanings of the structures' names are the same as those in S2.



S6. The twelve lowest-lying structures of Ag_{20}

The twelve lowest-lying structures of Ag_{20} from the calculations at the PBE level with the basis sets of lanl2dz. All structures are in their singlet states. The meanings of the structures' names are the same as those in S2.



S7. The atoms' coordinates (in Å) of the twelve lowest-lying structures of Ag_{30} listed in Fig. 3.

a-0.00-C_2

Ag	-1.61807803	3.18146701	0.48401671
Ag	0.67659412	3.46224217	-1.65743455
Ag	0.88247479	0.69386504	-2.49426411
Ag	-1.67109217	1.99318524	-2.36332911
Ag	2.36849435	-0.52915454	-0.23096972
Ag	0.53044655	1.43300140	0.33219895
Ag	3.93106806	-2.68486746	-0.89202076
Ag	3.16389178	2.07430359	-1.34543445
Ag	3.48577550	-0.48400333	-2.81025996
Ag	4.17939032	-1.33809584	1.80277634
Ag	1.19950314	2.40800622	2.92616913
Ag	3.52312155	1.48656950	1.53736042
Ag	2.27355466	3.84993290	0.68777072
Ag	1.55655393	-0.39414804	2.55834833
Ag	5.10127837	0.13378901	-0.50828606
Ag	1.61807803	-3.18146701	0.48401671
Ag	1.67109217	-1.99318524	-2.36332911
Ag	-2.36849435	0.52915454	-0.23096972
Ag	-0.53044655	-1.43300140	0.33219895
Ag	-3.93106806	2.68486746	-0.89202076
Ag	-0.88247479	-0.69386504	-2.49426411
Ag	-5.10127837	-0.13378901	-0.50828606
Ag	-1.55655393	0.39414804	2.55834833
Ag	-1.19950314	-2.40800622	2.92616913
Ag	-2.27355466	-3.84993290	0.68777072
Ag	-3.16389178	-2.07430359	-1.34543445
Ag	-0.67659412	-3.46224217	-1.65743455
Ag	-3.52312155	-1.48656950	1.53736042
Ag	-4.17939032	1.33809584	1.80277634
Ag	-3.48577550	0.48400333	-2.81025996

b-0.05-C_1

Ag	-1.618078	3.181467	0.484017
Ag	0.676594	3.462242	-1.657435
Ag	0.882475	0.693865	-2.494264
Ag	-1.671092	1.993185	-2.363329
Ag	2.368494	-0.529155	-0.23097
Ag	0.530447	1.433001	0.332199
Ag	3.931068	-2.684867	-0.892021
Ag	3.163892	2.074304	-1.345434
Ag	3.485775	-0.484003	-2.81026
Ag	4.17939	-1.338096	1.802776
Ag	1.199503	2.408006	2.926169
Ag	3.523122	1.48657	1.53736
Ag	2.273555	3.849933	0.687771
Ag	1.556554	-0.394148	2.558348
Ag	5.101278	0.133789	-0.508286
Ag	1.837591	-2.94379	1.195842
Ag	1.215674	-2.237733	-2.138238
Ag	-2.312986	0.501524	-0.100123
Ag	-0.369697	-1.472508	0.219386
Ag	-4.143851	2.544579	-0.716492
Ag	-1.393318	-0.970297	-2.540359
Ag	-5.102648	-0.108617	0.253552
Ag	-1.082081	0.641657	2.558248
Ag	-0.562262	-2.237378	2.950254
Ag	-2.12387	-3.726788	1.088327
Ag	-3.461359	-2.152518	-0.825246
Ag	-1.241454	-3.648978	-1.649591
Ag	-3.147515	-1.291391	2.017888
Ag	-3.716838	1.625013	2.072313
Ag	-3.978363	0.191131	-2.412402

c-0.11-C_1

Ag	-1.136112	-2.570908	2.664581
Ag	-1.653017	0.221761	2.621534
Ag	-0.500772	-3.433057	-2.59069
Ag	-3.904798	0.018213	-0.718639
Ag	-3.94857	2.809362	-0.479459
Ag	-4.200221	-2.752393	-0.932876
Ag	-1.481649	3.787247	-1.282533
Ag	-2.40036	1.490676	-2.646678
Ag	-1.768334	2.93917	1.534094
Ag	0.466362	-0.911819	-1.854011
Ag	-3.684424	-1.574315	1.691516
Ag	-4.141353	1.23585	1.861302
Ag	-0.981256	0.951646	-0.245952
Ag	-1.583678	-2.264142	-0.150873
Ag	-2.356398	-1.292234	-2.685707
Ag	1.983002	0.885074	-0.241439
Ag	0.608732	-1.025402	1.161612
Ag	3.35133	2.758812	-1.681895
Ag	0.806609	1.669138	2.299878
Ag	0.915342	3.487546	0.105319
Ag	4.8358	0.678173	-0.137685
Ag	2.425145	-2.825611	-2.649115
Ag	1.089917	-3.448741	-0.182439
Ag	2.428169	-2.852853	2.294158
Ag	3.230946	-0.070846	2.18714
Ag	0.96056	-0.781818	3.891711
Ag	3.402724	-1.788294	-0.162192
Ag	3.277563	-0.066798	-2.518373
Ag	3.39696	2.728352	1.31404
Ag	0.561782	1.99821	-2.466331

d-0.19-C_1

Ag	0.82827	1.49338	1.637551
Ag	2.014473	-1.076493	1.46309
Ag	3.248123	1.312692	-0.256894
Ag	0.734388	0.027228	-0.930644
Ag	-0.839911	-0.800426	1.189826
Ag	-1.516412	1.507766	-0.217897
Ag	-1.869069	-0.978892	-1.679401
Ag	-0.721374	1.361288	-2.96842
Ag	0.283783	-2.817822	-0.643567
Ag	2.900665	-1.681681	-1.457957
Ag	-3.725482	-0.171719	0.840919
Ag	0.198201	-0.453452	3.705492
Ag	0.942191	2.889806	-1.183214
Ag	2.383143	0.988265	-2.930301
Ag	0.169515	-3.220966	2.158325
Ag	3.581461	1.103382	2.452446
Ag	-2.547554	-2.90208	0.571072
Ag	-2.013471	1.397868	2.611242
Ag	-2.624581	-1.592989	3.111222
Ag	4.703145	-1.04546	0.645128
Ag	-3.839116	1.069338	-1.744564
Ag	-0.581949	3.894938	1.004118
Ag	5.055013	0.0742	-2.003738
Ag	-4.484074	-1.889679	-1.323854
Ag	-2.081866	3.859014	-1.485106
Ag	2.41828	3.70112	1.231434
Ag	-3.762378	2.781032	0.706623
Ag	2.784064	-3.604339	0.774313
Ag	0.5728	-1.519364	-3.214343
Ag	-2.210279	-3.705956	-2.0629

e-0.20-C_{2h}

Ag	2.541445	0.29316	2.60773
Ag	-0.107338	1.376308	2.601486
Ag	-0.222221	2.544373	0.0
Ag	1.395659	0.107041	0.0
Ag	-1.992201	4.712052	0.0
Ag	2.183706	2.90087	1.527347
Ag	-0.342997	4.154962	2.355091
Ag	-0.342997	4.154962	-2.355091
Ag	2.541445	0.29316	-2.60773
Ag	2.183706	2.90087	-1.527347
Ag	3.954718	1.347808	0.0
Ag	-0.107338	1.376308	-2.601486
Ag	1.110739	5.065852	0.0
Ag	-2.602613	2.337521	-1.51784
Ag	-2.602613	2.337521	1.51784
Ag	-2.541445	-0.29316	2.60773
Ag	0.107338	-1.376308	2.601486
Ag	0.222221	-2.544373	0.0
Ag	-1.395659	-0.107041	0.0
Ag	1.992201	-4.712052	0.0
Ag	-2.183706	-2.90087	1.527347
Ag	0.342997	-4.154962	2.355091
Ag	0.342997	-4.154962	-2.355091
Ag	-2.541445	-0.29316	-2.60773
Ag	-2.183706	-2.90087	-1.527347
Ag	-3.954718	-1.347808	0.0
Ag	0.107338	-1.376308	-2.601486
Ag	-1.110739	-5.065852	0.0
Ag	2.602613	-2.337521	-1.51784
Ag	2.602613	-2.337521	1.51784

f-0.31-C_1

Ag	-2.657011	1.75423	2.798158
Ag	3.937385	-1.073911	2.035761
Ag	2.831344	-0.132655	-2.509331
Ag	2.61132	2.617187	-1.921522
Ag	1.377499	-1.182464	3.095381
Ag	-2.941667	-3.35265	0.307952
Ag	2.097764	-3.259335	1.031927
Ag	-1.568896	-0.963633	-0.424079
Ag	2.679368	1.345805	2.780894
Ag	2.153767	-2.950341	-2.101795
Ag	0.948045	1.395071	-3.919303
Ag	1.565757	2.80069	0.670073
Ag	-0.678443	-2.518967	1.821335
Ag	-2.478137	-2.534693	-2.544716
Ag	4.195979	-1.716994	-0.644263
Ag	-2.41827	3.123652	-1.931214
Ag	0.262127	4.15111	-1.504454
Ag	3.769412	1.018155	0.078978
Ag	0.049623	-1.172207	-2.805822
Ag	-1.347664	-0.627327	3.934732
Ag	-2.70392	0.368853	-2.631657
Ag	-1.315373	3.202297	0.733358
Ag	-0.130819	1.368925	-1.270291
Ag	1.383023	-0.862543	-0.109699
Ag	-3.440607	1.361209	0.046071
Ag	-3.303123	-0.874558	1.846388
Ag	-0.254879	-3.497718	-0.815829
Ag	-0.34753	0.586078	1.58209
Ag	0.127612	2.751983	3.193627
Ag	-4.403687	-1.125248	-0.822751

g-0.38-C_1

Ag	2.138934	-0.10798	0.30594
Ag	-2.032795	1.751692	2.181716
Ag	4.749073	0.480359	-1.088144
Ag	-4.417172	-2.144876	0.988186
Ag	4.695246	-0.053386	1.677414
Ag	-1.653526	-2.927332	1.22022
Ag	-1.436884	3.907882	0.428472
Ag	2.530338	1.945992	-1.976826
Ag	0.393279	0.753311	-3.331581
Ag	-0.071028	-1.32512	-1.38573
Ag	1.140875	-2.902694	0.706146
Ag	-4.636838	0.74763	1.537077
Ag	0.655348	2.644118	1.955115
Ag	2.796981	-1.903242	2.646069
Ag	-2.307373	0.317723	-2.553234
Ag	3.923255	-2.240365	-0.116749
Ag	-0.196797	1.368478	-0.457229
Ag	-2.855137	-2.382565	-1.59898
Ag	-3.373415	2.195901	-0.636583
Ag	2.402239	0.860509	3.107238
Ag	-2.318571	-0.370283	0.275233
Ag	1.249092	3.935924	-0.565259
Ag	2.074791	-3.462837	-1.902406
Ag	-0.006404	-0.502367	2.122406
Ag	3.323417	2.410219	0.77047
Ag	-4.768165	-0.233373	-1.242096
Ag	-0.620199	-4.106123	-1.184232
Ag	-1.347212	3.033869	-2.404528
Ag	-2.712534	-0.890725	3.027187
Ag	2.681179	-0.800338	-2.505312

h-0.42-C_1

Ag	2.912957	1.219496	2.055651
Ag	0.945032	3.270417	2.281178
Ag	-2.182261	2.185831	2.6686
Ag	0.287918	0.558831	3.074
Ag	-2.909379	3.777082	0.401515
Ag	-0.453772	1.55216	0.510551
Ag	-4.015864	1.208616	0.571235
Ag	-2.532319	2.014717	-1.793573
Ag	2.214702	0.071624	-0.46849
Ag	0.236983	1.316183	-2.24276
Ag	2.073652	2.893988	-0.347705
Ag	-4.254124	-0.205368	-2.203418
Ag	3.066407	1.530806	-2.705312
Ag	-0.494494	3.889942	-1.059782
Ag	4.629833	1.559579	-0.278054
Ag	1.615667	-1.041848	-3.06998
Ag	-1.374778	-0.759032	-3.345323
Ag	4.579967	-1.002071	0.928389
Ag	4.359469	-0.977871	-1.965725
Ag	2.331407	-1.618651	2.503344
Ag	2.68248	-2.693503	-0.380515
Ag	-2.017937	-0.53182	-0.641084
Ag	0.174392	-1.207122	0.866497
Ag	-0.165519	-2.678044	-1.505366
Ag	-4.449054	-1.620661	0.40666
Ag	-0.47662	-2.339253	3.319767
Ag	-2.010935	-3.058313	0.844863
Ag	0.782148	-3.927314	1.224216
Ag	-2.491206	-0.565673	2.263986
Ag	-3.064751	-2.822734	-1.913364

i-0.47-C_1

Ag	-0.765096	-1.643646	2.060029
Ag	1.74006	-0.658019	0.941904
Ag	-0.132565	-1.727869	-0.795409
Ag	-0.575221	0.751806	0.391003
Ag	1.33646	0.608501	-1.756794
Ag	1.858586	2.290521	1.004344
Ag	0.467814	0.870248	3.047679
Ag	-2.796939	-1.062235	-0.054374
Ag	-2.605322	0.7252	2.300128
Ag	-1.472504	0.437924	-2.3379
Ag	-2.976845	2.127381	-0.344441
Ag	1.823742	-1.874393	3.378823
Ag	-0.322157	2.899346	-1.44645
Ag	2.785587	-1.859039	-1.432381
Ag	3.979751	0.609328	-0.197004
Ag	3.519974	0.461076	2.675241
Ag	-1.739998	-3.768121	0.458446
Ag	1.430767	-3.492215	0.774248
Ag	-3.568183	-2.282701	2.257825
Ag	0.629416	-1.639511	-3.429146
Ag	-0.825684	3.149392	1.709541
Ag	-2.198191	-2.285365	-2.59006
Ag	4.054956	-2.156594	1.176111
Ag	2.750308	3.060432	-1.565759
Ag	0.072744	-4.247382	-1.763762
Ag	3.806202	0.590788	-2.958721
Ag	0.979855	4.83561	0.050802
Ag	-4.327675	7.29E-4	-2.073501
Ag	-1.936212	4.876506	-0.217511
Ag	-4.993631	0.4023	0.73709

j-0.49-Cs

Ag	-0.765096	-1.643646	2.060029
Ag	1.74006	-0.658019	0.941904
Ag	-0.132565	-1.727869	-0.795409
Ag	-0.575221	0.751806	0.391003
Ag	1.33646	0.608501	-1.756794
Ag	1.858586	2.290521	1.004344
Ag	0.467814	0.870248	3.047679
Ag	-2.796939	-1.062235	-0.054374
Ag	-2.605322	0.7252	2.300128
Ag	-1.472504	0.437924	-2.3379
Ag	-2.976845	2.127381	-0.344441
Ag	1.823742	-1.874393	3.378823
Ag	-0.322157	2.899346	-1.44645
Ag	2.785587	-1.859039	-1.432381
Ag	3.979751	0.609328	-0.197004
Ag	3.519974	0.461076	2.675241
Ag	-1.739998	-3.768121	0.458446
Ag	1.430767	-3.492215	0.774248
Ag	-3.568183	-2.282701	2.257825
Ag	0.629416	-1.639511	-3.429146
Ag	-0.825684	3.149392	1.709541
Ag	-2.198191	-2.285365	-2.59006
Ag	4.054956	-2.156594	1.176111
Ag	2.750308	3.060432	-1.565759
Ag	0.072744	-4.247382	-1.763762
Ag	3.806202	0.590788	-2.958721
Ag	0.979855	4.83561	0.050802
Ag	-4.327675	7.29E-4	-2.073501
Ag	-1.936212	4.876506	-0.217511
Ag	-4.993631	0.4023	0.73709

k-0.52-C_{2h}

Ag	-0.84053119	4.36282702	0.00000000
Ag	-0.95695910	2.18042419	-1.87459981
Ag	2.06514108	-0.28147881	0.00000000
Ag	4.95886309	-0.44419765	0.00000000
Ag	1.27810498	0.56267939	-2.63769101
Ag	3.54566008	-1.11998450	-2.35940322
Ag	3.66230800	1.69223614	1.47076505
Ag	1.56555293	3.40662091	2.61970226
Ag	1.27348992	2.46987614	0.00000000
Ag	1.56555293	3.40662091	-2.61970226
Ag	1.27810498	0.56267939	2.63769101
Ag	3.66230800	1.69223614	-1.47076505
Ag	3.54566008	-1.11998450	2.35940322
Ag	3.25002423	-2.86440974	0.00000000
Ag	-0.95695910	2.18042419	1.87459981
Ag	0.84053119	-4.36282702	0.00000000
Ag	0.95695910	-2.18042419	-1.87459981
Ag	-2.06514108	0.28147881	0.00000000
Ag	-4.95886309	0.44419765	0.00000000
Ag	-1.27810498	-0.56267939	-2.63769101
Ag	-3.54566008	1.11998450	-2.35940322
Ag	-3.66230800	-1.69223614	1.47076505
Ag	-1.56555293	-3.40662091	2.61970226
Ag	-1.27348992	-2.46987614	0.00000000
Ag	-1.56555293	-3.40662091	-2.61970226
Ag	-1.27810498	-0.56267939	2.63769101
Ag	-3.66230800	-1.69223614	-1.47076505
Ag	-3.54566008	1.11998450	2.35940322
Ag	-3.25002423	2.86440974	0.00000000
Ag	0.95695910	-2.18042419	1.87459981

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Ag	-3.265716	1.510192	-0.724426
Ag	-1.087677	0.101742	0.721315
Ag	0.976342	-0.768489	2.901016
Ag	-0.601285	1.525224	3.17359
Ag	-0.673518	-2.809014	1.148622
Ag	-3.350227	-1.671322	0.997285
Ag	-1.816482	3.056188	1.180589
Ag	-3.471871	0.93643	2.13689
Ag	-3.765542	-1.113838	-1.752672
Ag	-5.470582	0.068166	0.229358
Ag	2.366688	1.763294	3.180532
Ag	-3.091976	4.275455	-1.020096
Ag	-2.874349	-3.681855	-0.856107
Ag	-1.805377	-1.154292	3.29392
Ag	2.331743	-3.085479	1.992262
Ag	-0.919354	-1.76588	-1.544984
Ag	1.428717	-3.967489	-0.611995
Ag	3.919202	-2.481253	-0.375959
Ag	1.416495	-1.226284	0.114303
Ag	3.615149	-0.43942	1.729998
Ag	3.532594	0.285039	-1.145978
Ag	1.154272	1.728519	0.698191
Ag	-0.686712	2.879411	-1.429717
Ag	3.992511	2.29069	0.918507
Ag	0.72993	0.557765	-1.982704
Ag	2.239928	2.915152	-1.601572
Ag	-0.040676	-1.091296	-4.163528
Ag	5.01581	2.609383	-1.680839
Ag	-1.919336	0.674605	-2.996978
Ag	2.121302	-1.921343	-2.528824

S8. The simulated photoelectron spectra of Ag_{30}^-.

The structures of Ag_{30}^- were optimized starting from the a-f structures of Ag_{30} listed in Fig. 3. The PBE density functional method and the def2-SVP basis set were used for these optimizations. The bars in each spectrum showed the positions of the Kohn-Sham orbitals in the optimized Ag_{30}^-, and the spectra curves were obtained by broadening each orbital to a peak with the FWHM of 0.2 eV and then adding all peaks together.