Supporting information for:

Prediction of Beryllium Clusters (Be_n; n=3-25) from First Principles

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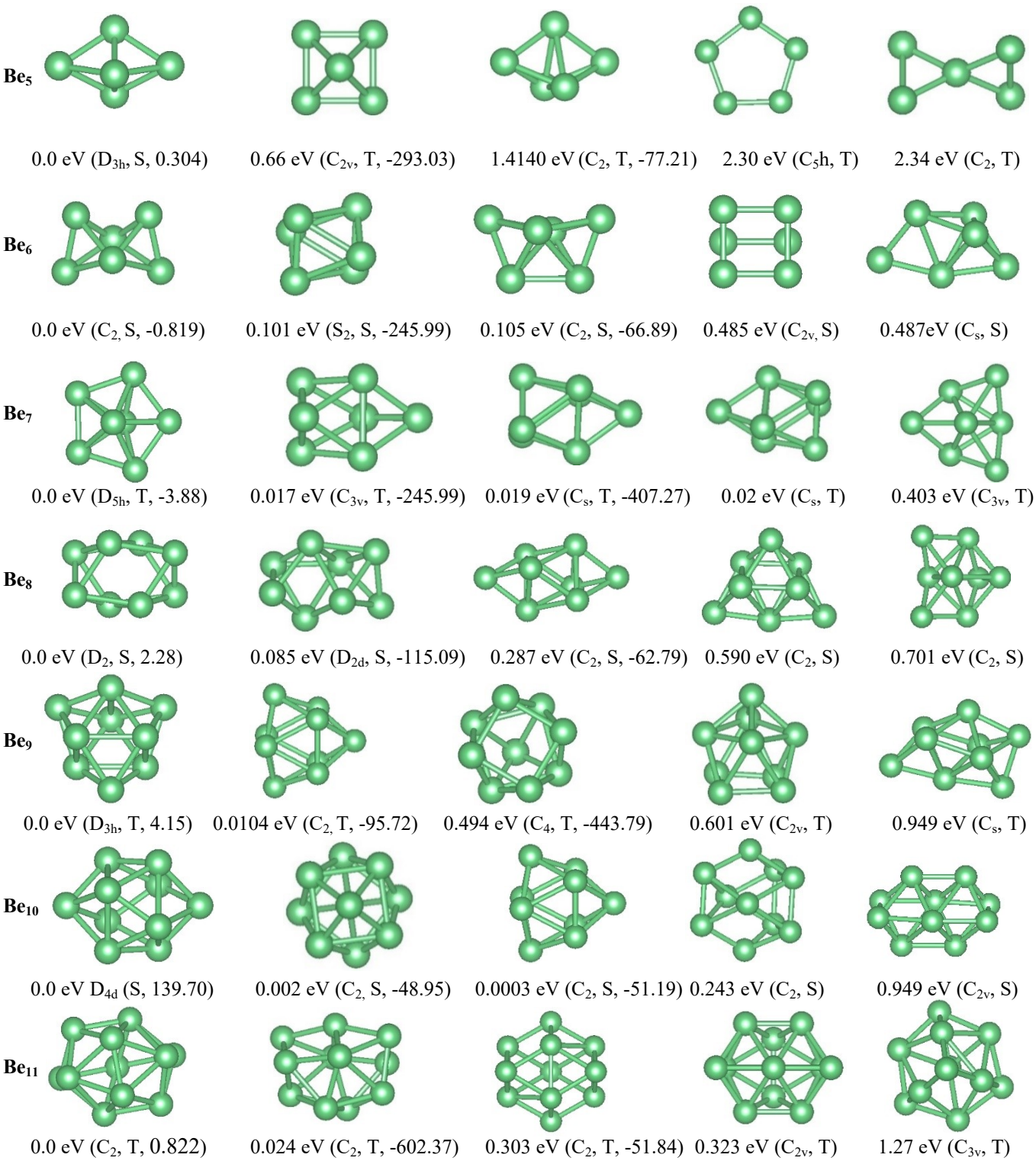


Figure S1. Low-lying isomers of Be_n (n = 3-25) clusters with relative energies, symmetries, states (S=singlet; T= triplet state) and minimum vibrational frequency (cm^{-1}) in parentheses.

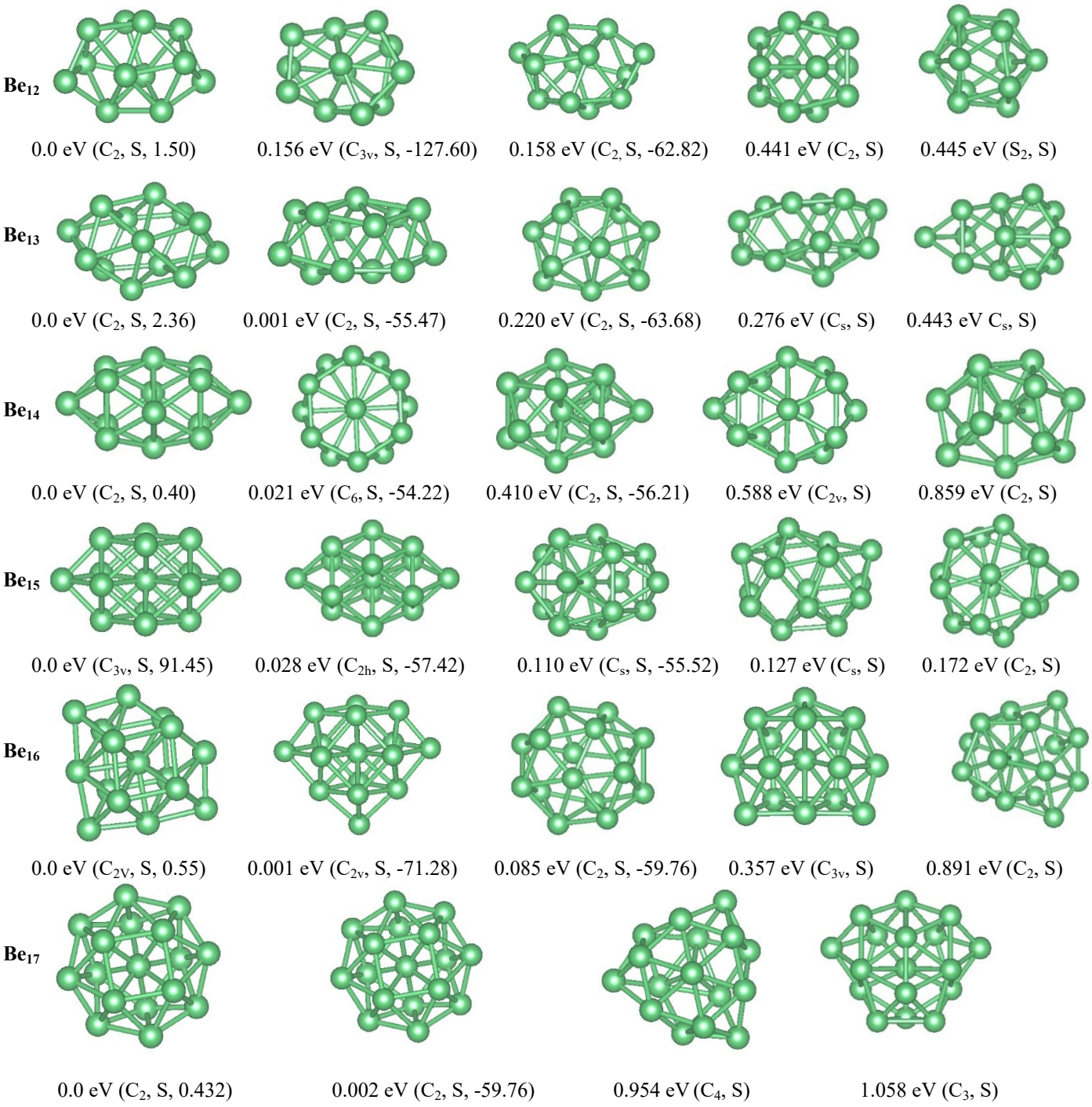


Figure S1. Continued

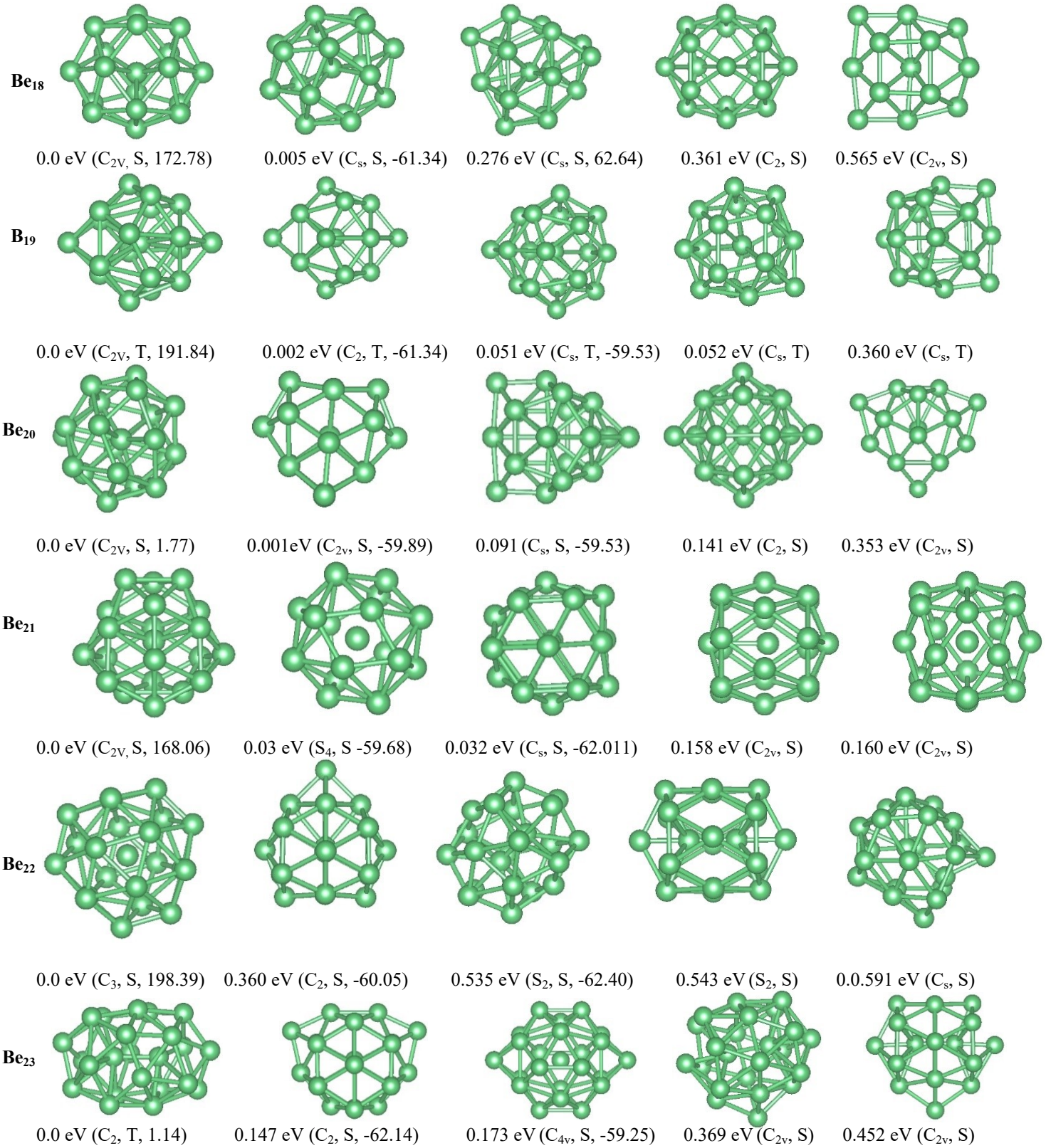
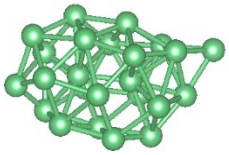
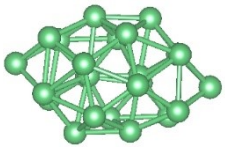
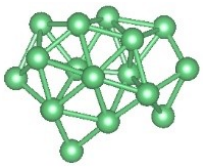
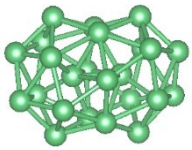


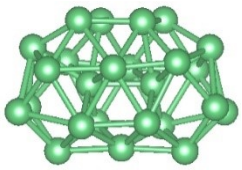
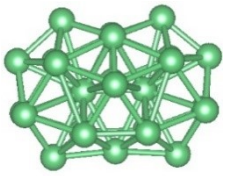
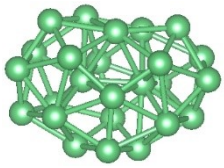
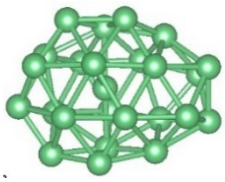
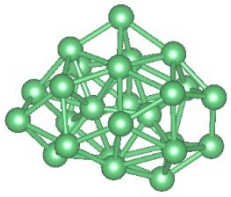
Figure S1. Continued

Be_{24}

0.0 eV (S_2, S, 137.62) 0.072 eV (C_2, S, -103.45) 0.541 eV (C_s, S, -62.31) 0.834 eV (C_2, S)

Be_{25}

0.0 eV (C_2, S, 1.12) 0.286 eV (C_{2v}, S, -60.19) 0.773 eV (C_{2v}, T, -77.23) 1.196 eV (C_s, S) 1.22 eV (C_2, S)

Figure S1. Continued.

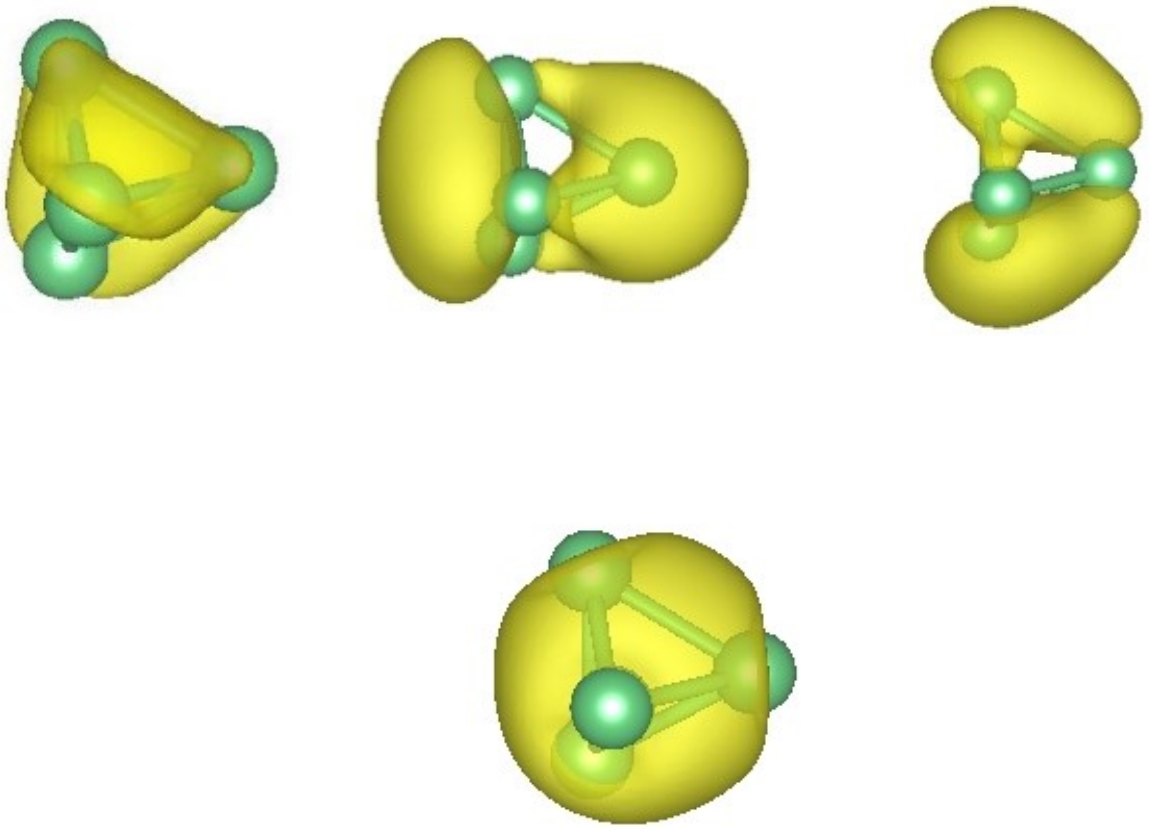


Figure S2. Occupied superatomic orbitals of Be_4 cluster.

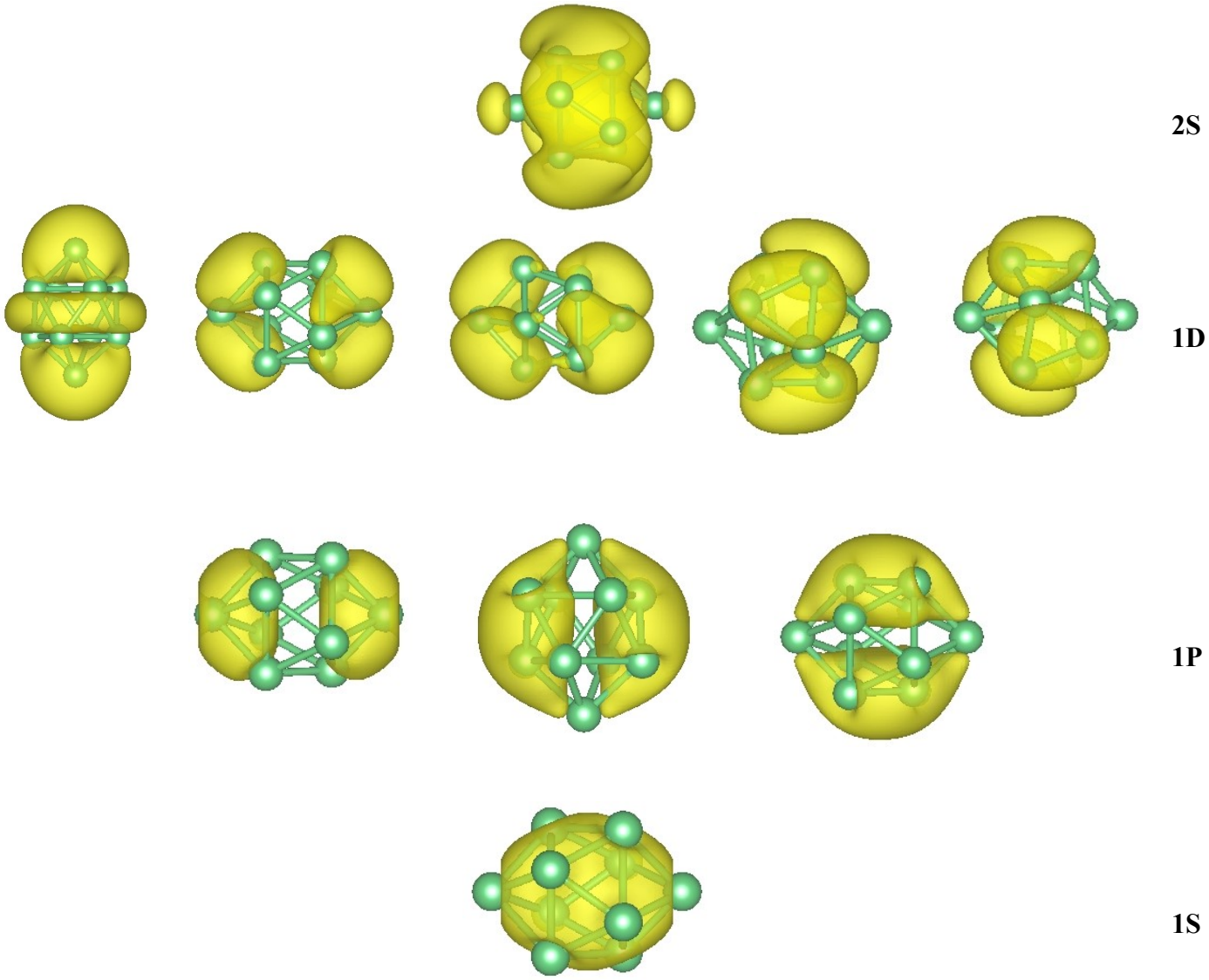


Figure S2. Continued. The occupied superatomic orbitals of Be_{10} cluster.

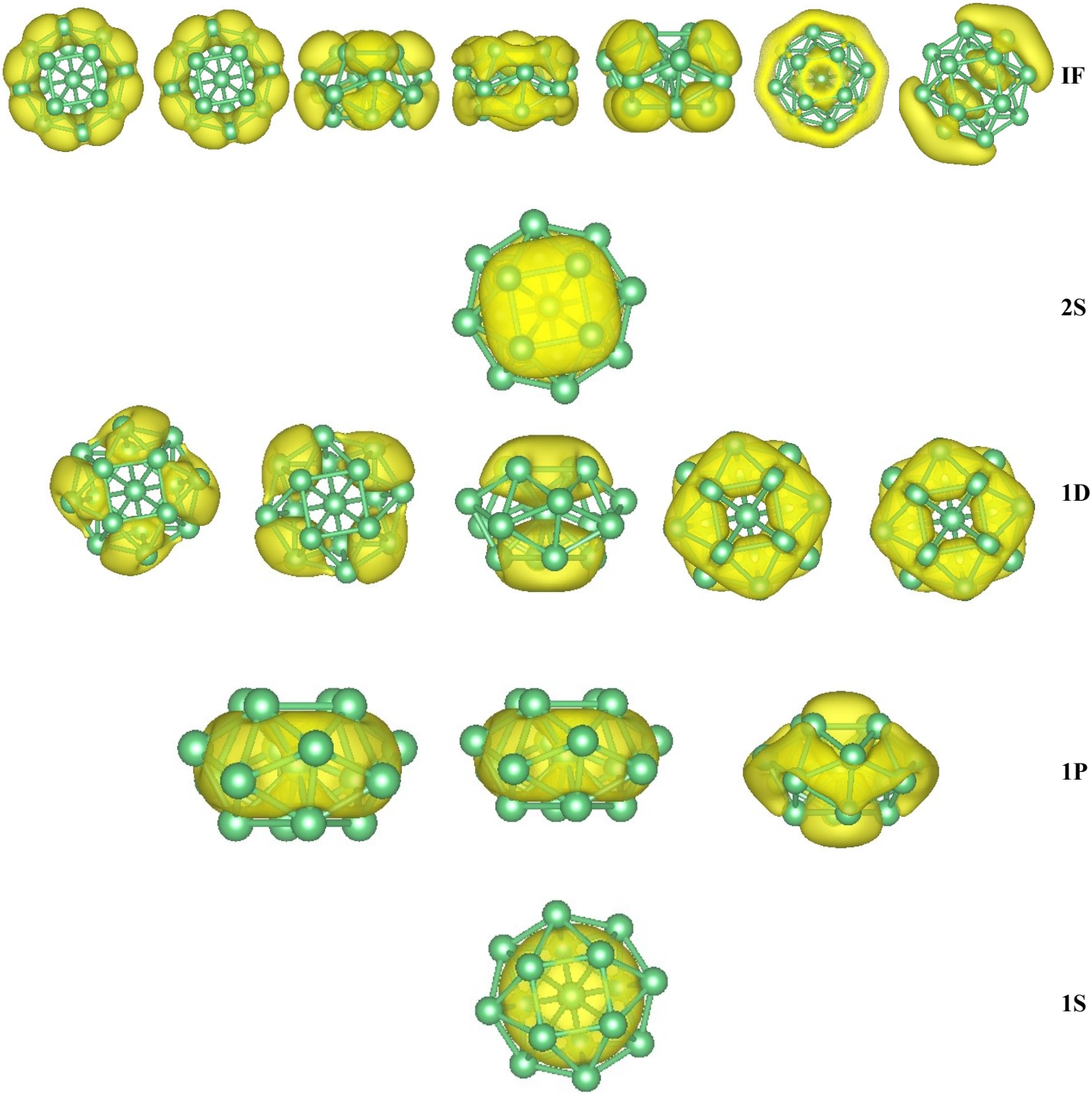


Figure S2. Continued. The occupied superatomic orbitals of Be_{17} cluster.

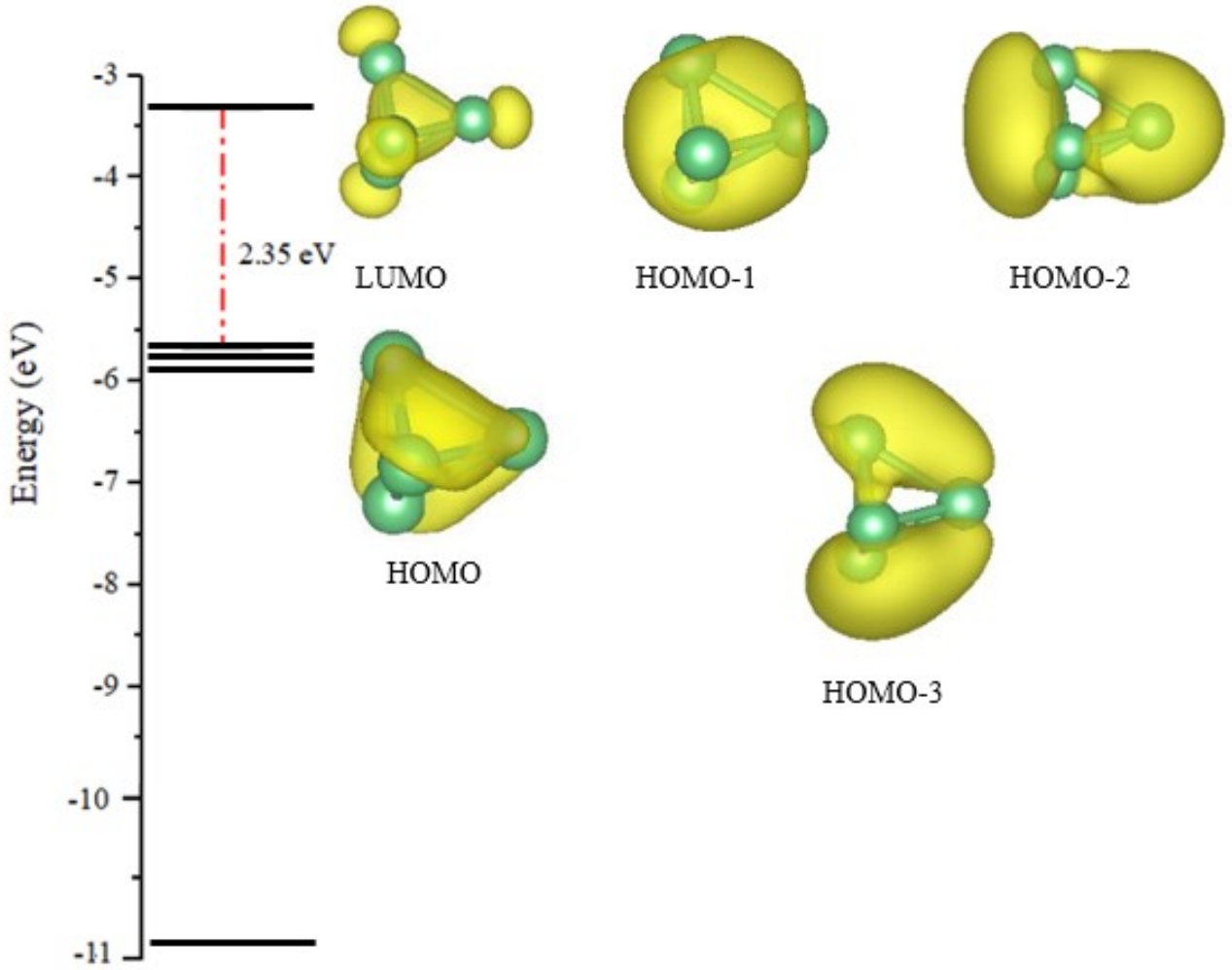


Figure S3. The charge density distributions of molecular orbitals for Be_4 cluster corresponding to different energy levels.

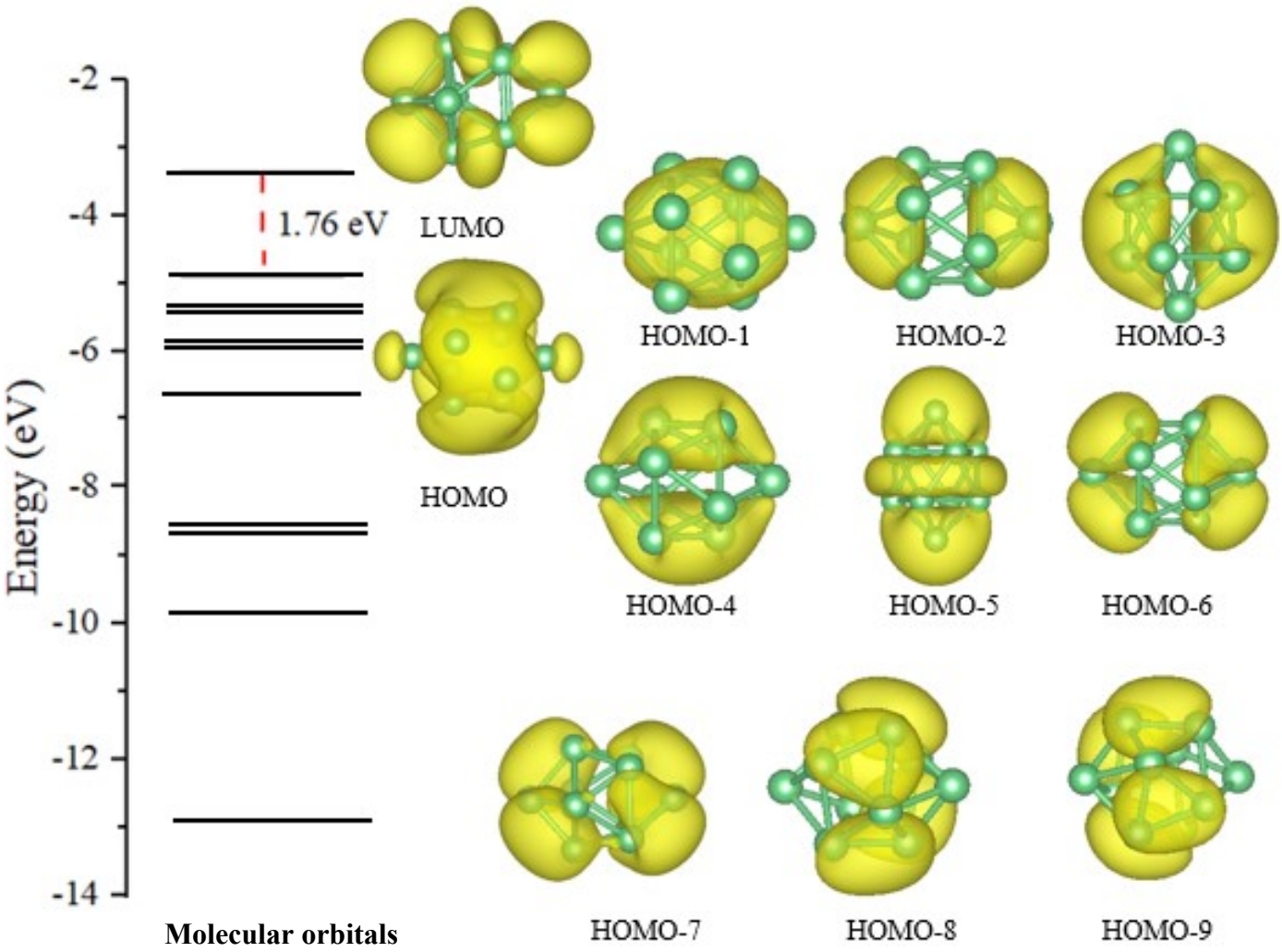


Figure S3. Continued. The charge density distributions of molecular orbitals for Be_{10} cluster corresponding to different energy levels.

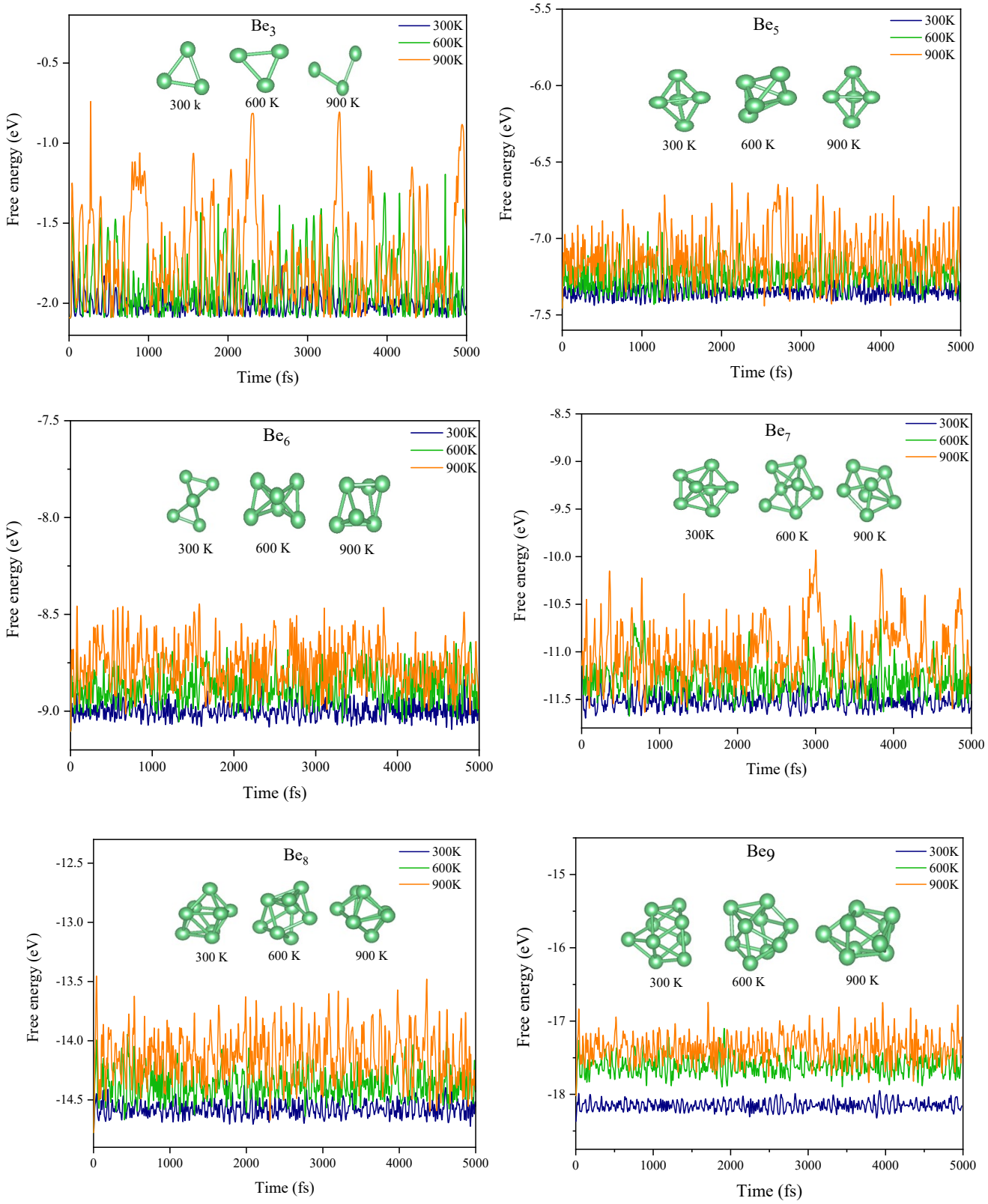


Figure S4. Images of the most stable structures of Be_n obtained for a time of 5 ps. The temperatures of the AIMD were set to 300 K, 600 K and 900 K.

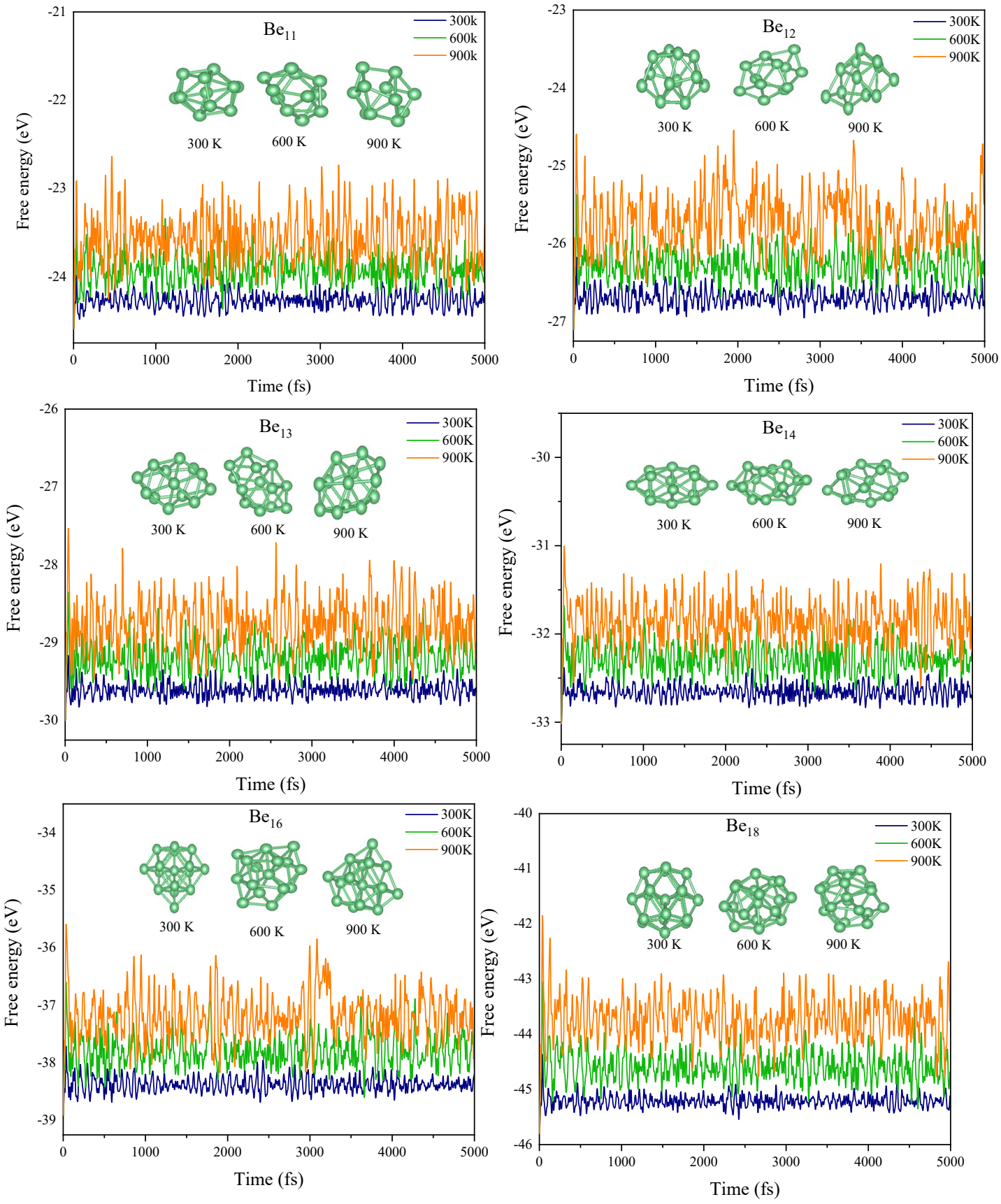
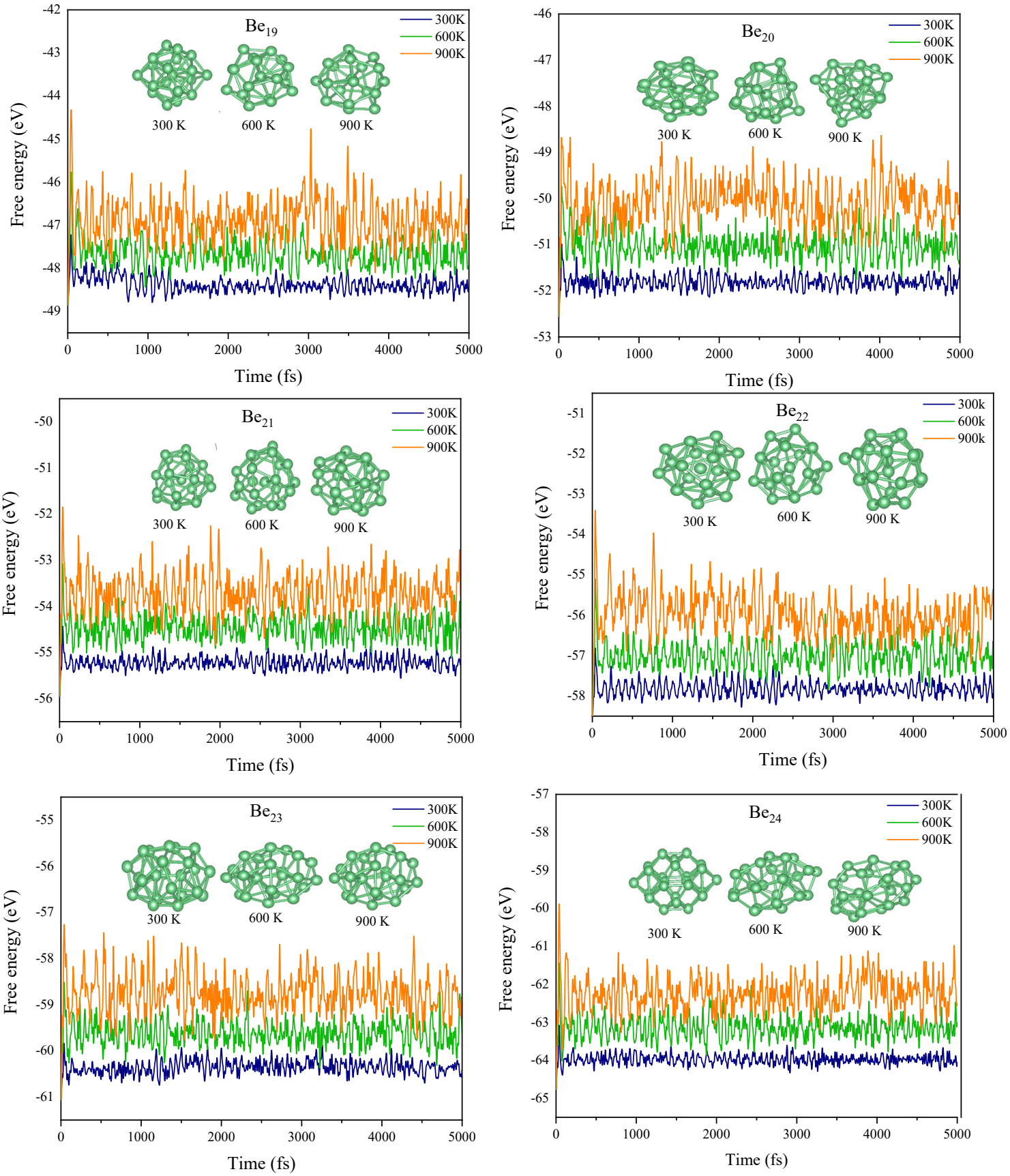


Figure S4. Continued



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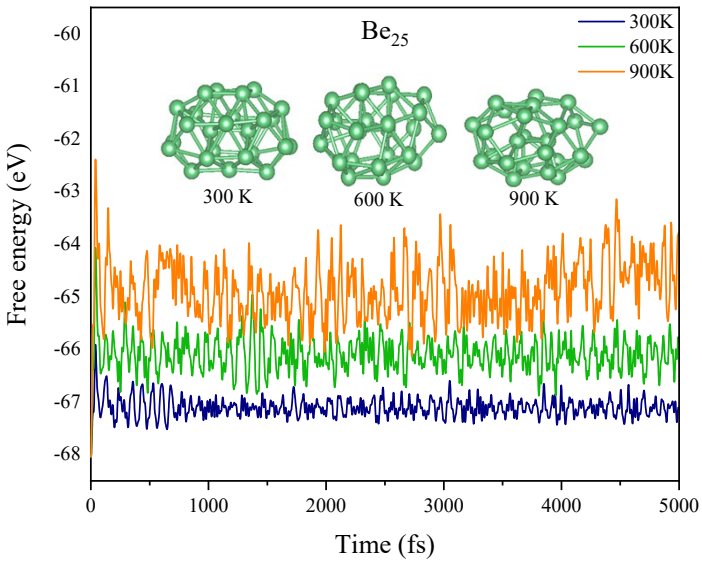


Figure S4. Continued

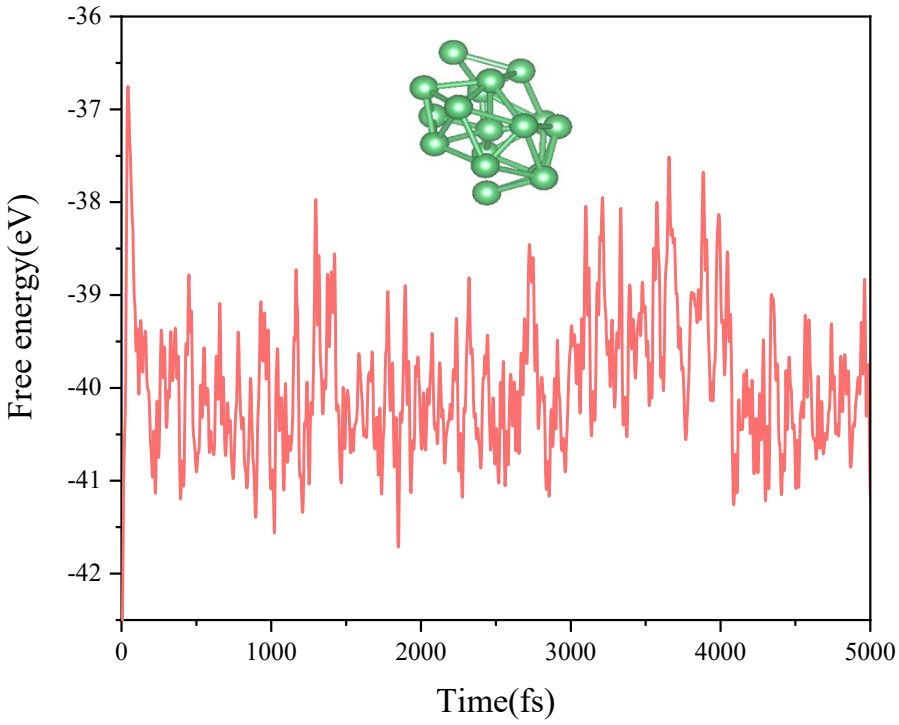
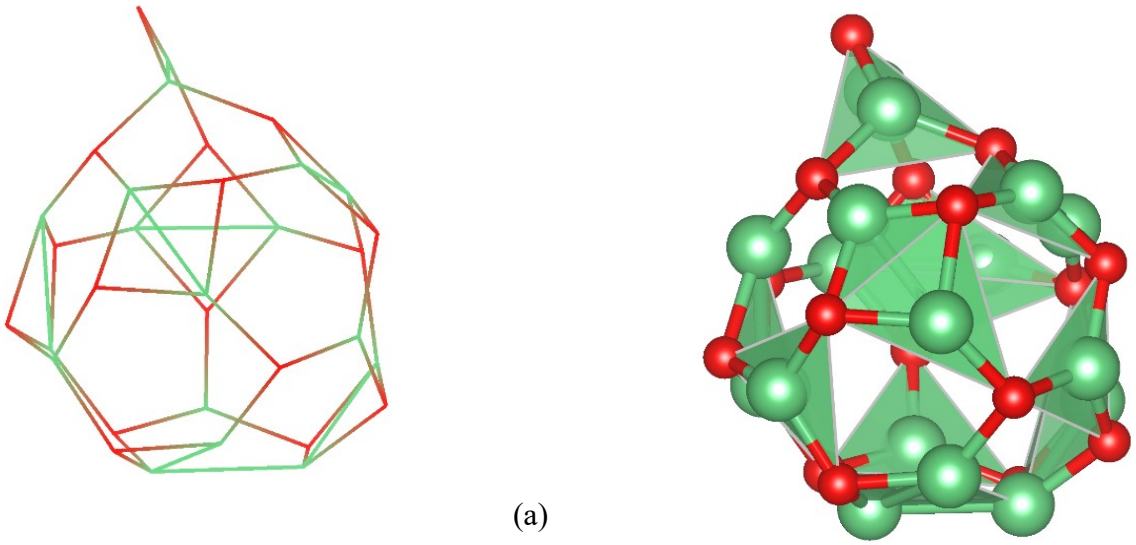
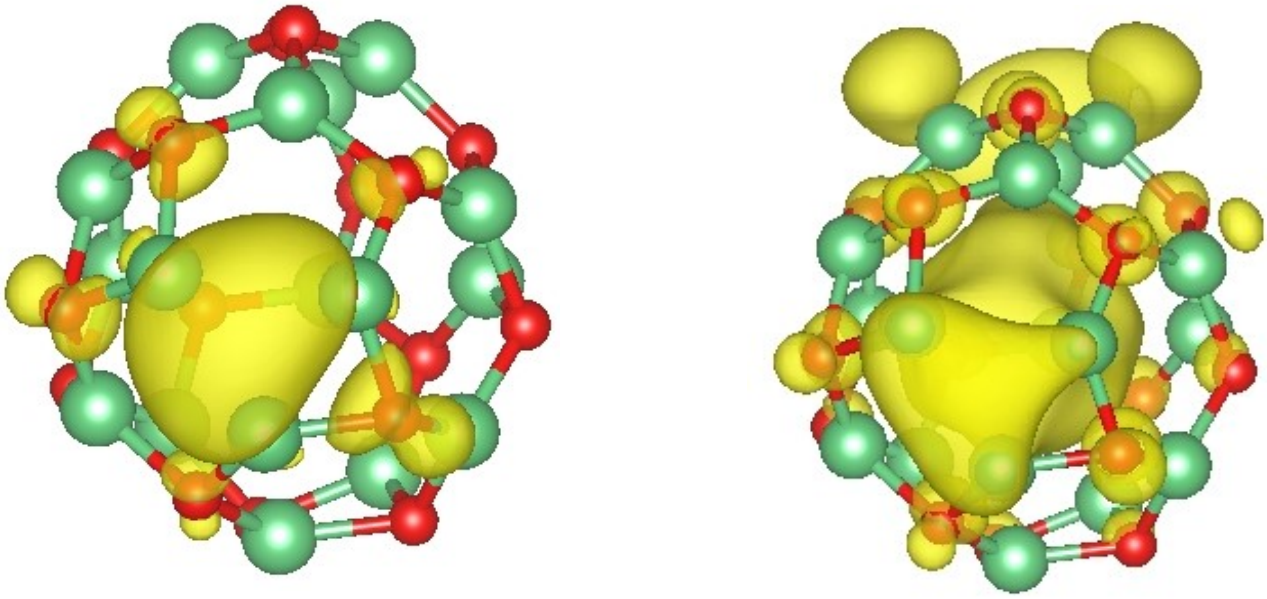


Figure S5. Images of the most stable structure of Be_{17} obtained for a simulation time of 5 ps. The temperatures of the AIMD was set to 1200 K. Bond breaking is observed.



(a)

HOMO LUMO



(b)

Figure S6. (a) Different view of the final relaxed geometry of $Be_{17}O_{16}$ clusters, (b) PBE contour plots of the HOMO and LUMO orbitals of the relaxed geometries of $Be_{17}O_{16}$ cluster. The green and red balls represent Be and O atoms, respectively.

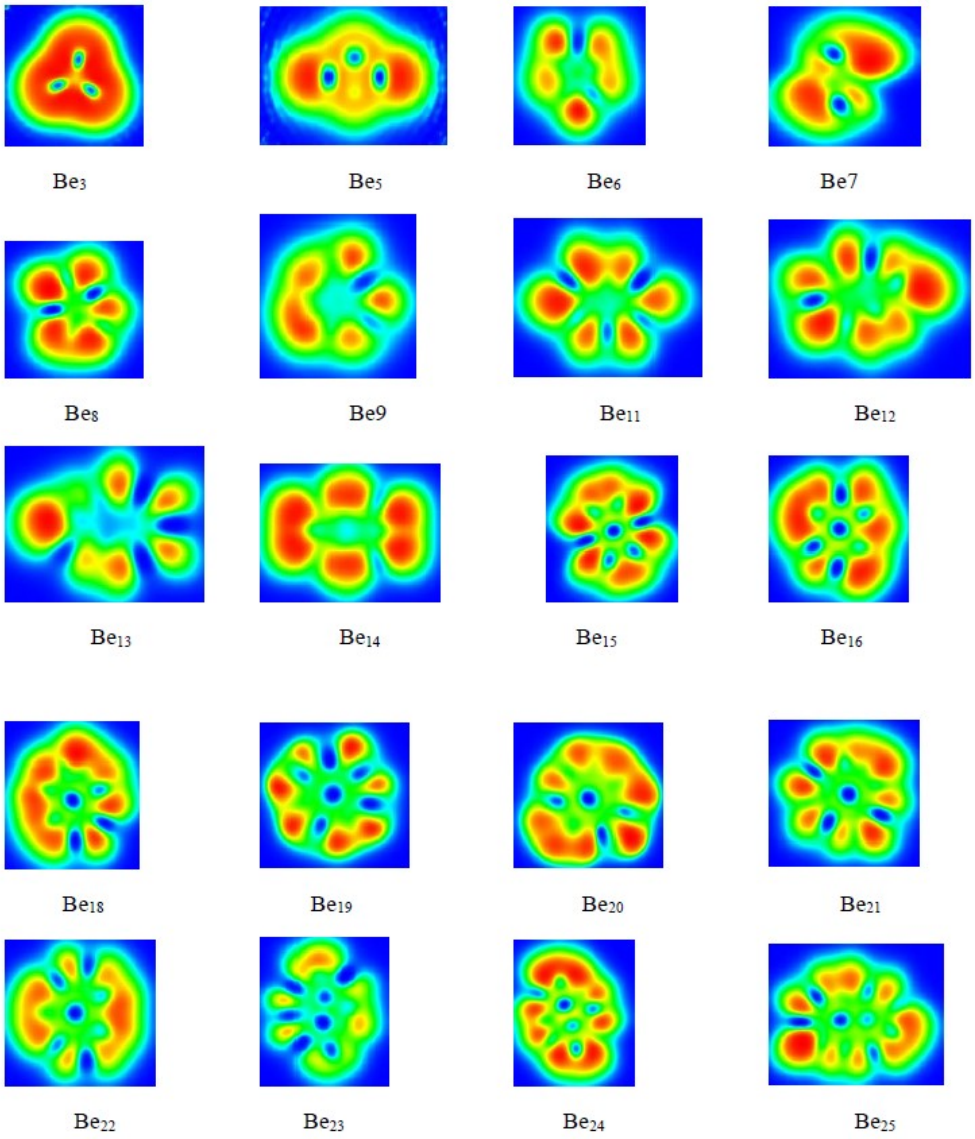


Figure S7. Contour plots of the electron localization function (ELF) (isovalue= 0.8 au) for the most stable structures of the Be_n clusters computed at the HSE06 level of theory.

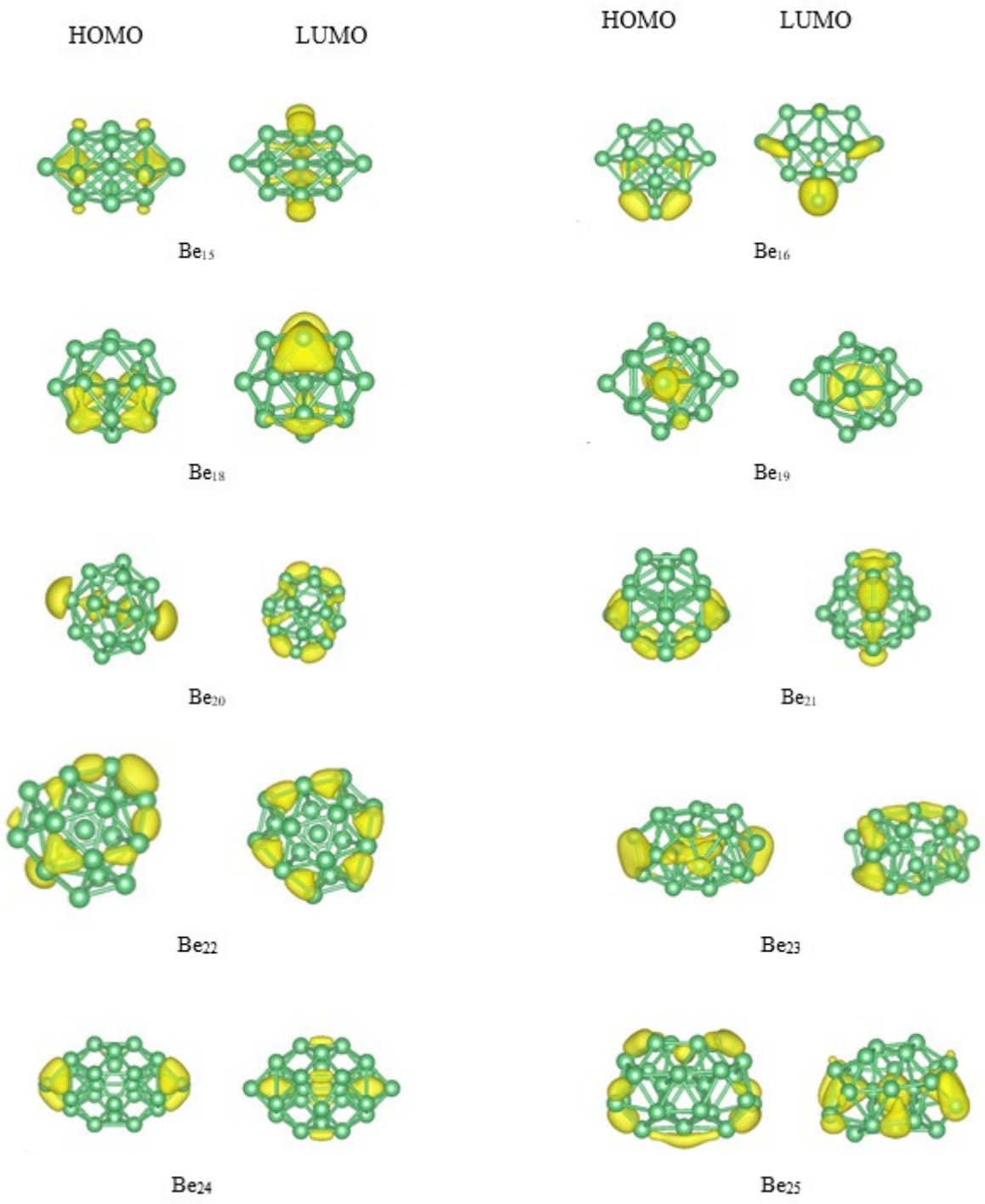


Figure S8. HSE06-contour plots of the HOMO and LUMO orbitals of the low-lying structures of Be_n clusters

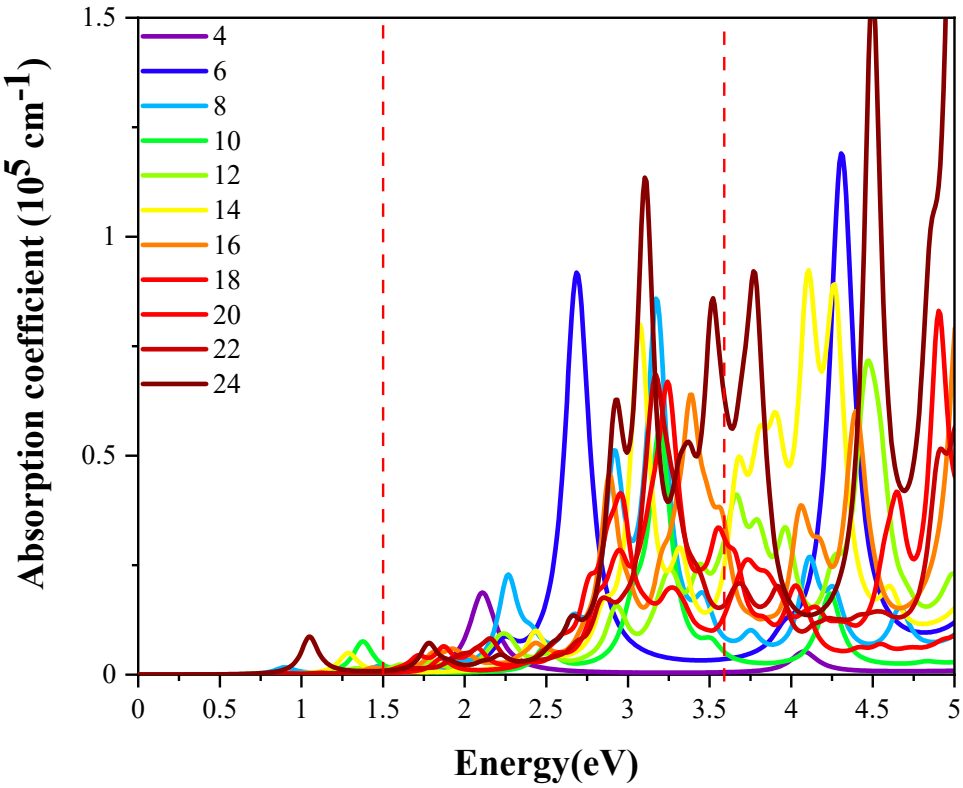


Figure S9. Optical absorption spectrum of Be_n clusters (even number) along xx direction from 0 eV to 5 eV calculated by the HSE06 functional. The energy range corresponding to visible light is indicated by vertical red-dashed lines

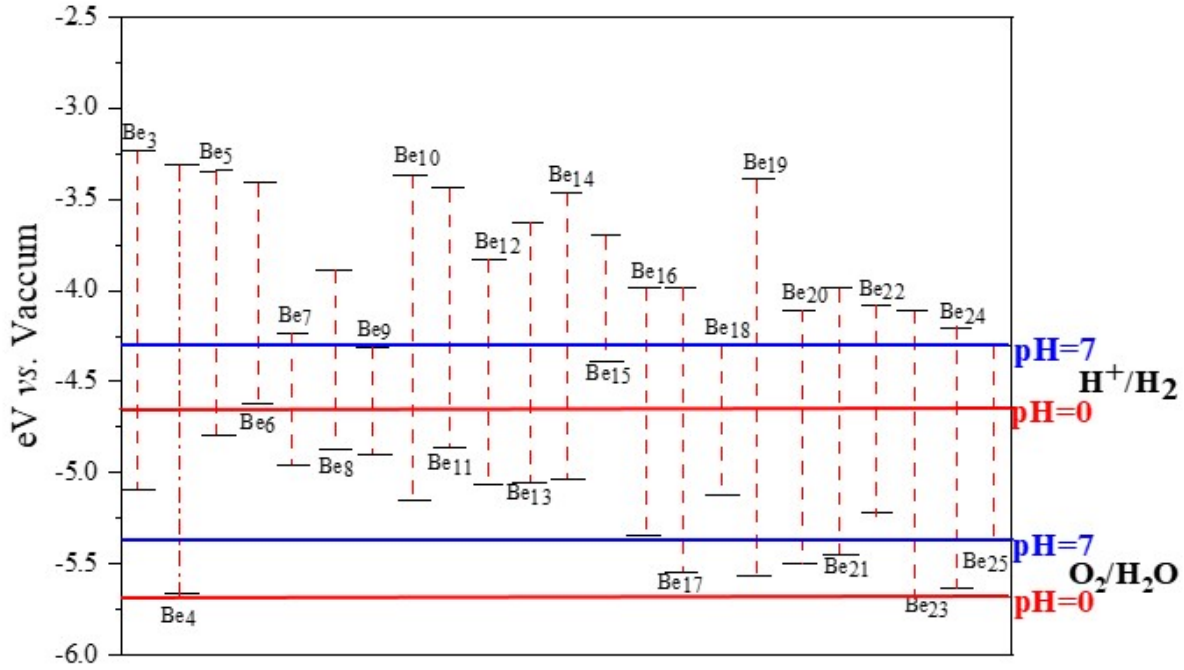


Figure S10. Band alignments of Be_n clusters with respect to the vacuum level, calculated with the HSE06 functional. The redox potentials of water splitting are plotted as red (pH=0) and blue (pH=7) solid lines.

S11. Optimized structures of Be_n clusters

The final relaxed *.xyz* format that could be opened by VESTA, Mercury or any other structure visualization program of the most stable structure of Be_n clusters

Be_3

```
3
EA840  14.080 13.923 11.920 90.00 90.00
Be    5.866960    6.505776    5.960000
Be    7.225995    8.191423    5.960000
Be    8.026917    6.188043    5.960000
```

Be_4

```
4
EA161  13.645 13.891 13.875 90.00 90.00
Be    6.343562    6.097822    6.155864
Be    6.326519    8.065033    6.691730
Be    6.557960    6.622790    8.114195
Be    8.061259    6.997093    6.788189
```

Be_5

```
5
EA1182 15.325 13.668 13.914 90.00 90.00
Be    7.662402    5.987992    6.175771
Be    7.662402    7.933300    6.614905
Be    9.364803    6.833905    6.956906
Be    7.662402    6.580340    8.080029
Be    5.960000    6.833905    6.956906
```

Be_6

```
6
EA206  14.964 13.758 14.351 90.00 90.00
Be    9.005635    6.031391    7.178213
Be    7.482776    6.739889    5.959505
Be    8.640505    7.865542    7.173635
Be    6.319511    7.864015    7.174984
Be    5.961908    6.028034    7.175644
Be    7.480846    6.743672    8.390248
```

Be_7

```
7
EA726  15.290 15.301 13.947 90.00 90.00
Be    7.828342    7.649016    5.801414
Be    8.208858    6.032987    7.068602
Be    6.261337    6.627779    6.750492
Be    9.376483    7.676504    7.249835
Be    8.155303    9.285446    7.057438
Be    6.228925    8.630562    6.743479
Be    7.455263    7.651103    8.144357
```

Be_8

```
8
EA377  15.298 13.986 13.685 90.00 90.00
Be    8.176930    8.025881    5.962583
Be    9.336291    7.698302    7.521617
Be    7.123554    5.964058    5.959778
Be    9.337593    6.288476    6.165425
Be    8.174942    5.959960    7.721969
Be    7.119913    8.023475    7.724980
Be    5.959772    7.699085    6.166233
Be    5.962296    6.284560    7.518291
```

Be_9

```
9
EA604  15.292 14.512 14.566 90.00 90.00
Be    7.645948    8.818212    7.673857
Be    7.645948    5.470530    8.243547
Be    7.645948    7.787718    5.760335
Be    8.778902    7.214190    8.490153
Be    8.781524    6.227867    6.654950
Be    9.385472    8.172755    6.789855
Be    6.512996    7.214190    8.490153
Be    6.510374    6.227867    6.654950
Be    5.906425    8.172755    6.789855
```

Be_{10}

```
10
EA646  16.268 14.873 14.869 90.00 90.00
Be    7.305027    6.939637    5.956648
Be    7.305027    7.933279    8.912444
Be    8.962486    8.129720    6.037926
Be    8.962634    8.833386    8.128352
Be    5.954252    7.436458    7.434546
Be    7.305060    8.915296    6.937518
```

```
Be    8.962486    6.743196    8.831166
Be   10.313392    7.436458    7.434546
Be    7.305060    5.957619    7.931574
Be    8.962634    6.039528    6.740740
```

Be_{11}

```
11
EA1343 15.920 15.265 14.839 90.00 90.00
Be    7.960552    7.634018    5.942116
Be    9.510305    6.308206    7.231419
Be    7.505785    5.955659    7.037812
Be    8.141979    6.621725    8.864327
Be    5.956144    7.227540    6.338032
Be    9.699201    8.011579    8.357094
Be    8.412522    9.309572    7.044002
Be    7.779145    8.637279    8.867595
Be    6.409714    8.958053    7.237829
Be    6.220903    7.249217    8.354867
Be    9.965228    8.042474    6.340714
```

Be_{12}

```
12
EA986  16.960 15.101 14.449 90.00 90.00
Be    8.807094    7.134876    5.958827
Be    8.144273    9.048863    6.220115
Be    8.152876    7.134119    8.490093
Be    6.651881    7.584292    6.044281
Be   11.002889    6.912934    6.661619
Be    6.808268    8.765851    7.785470
Be    5.955905    6.913149    7.786312
Be    8.816127    9.047938    8.229684
Be   10.308362    7.582601    8.403833
Be    7.495203    5.857072    6.943788
Be   10.152302    8.766126    6.664194
Be    9.464381    5.856788    7.504007
```

Be_{13}

```
13
EA1328 17.478 15.443 14.487 90.00 90.00
Be    5.955724    8.127604    6.694409
Be    8.111326    8.577024    6.087413
Be    7.187866    9.024773    8.062396
Be    8.310925    5.956426    7.639048
Be    7.251876    6.690297    6.072968
Be   10.289945    6.422535    8.068169
Be   10.224635    8.747455    6.067862
```

```
Be     6.627253     7.059504     8.210605
Be     8.738653     7.724636     8.639513
Be    11.520364     7.312758     6.693996
Be    10.851802     8.387301     8.208314
Be     9.366127     6.860240     6.088665
Be     9.168361     9.488021     7.632702
```

Be_{14}

```
14
EA314  18.135 15.264 14.962 90.00 90.00
Be     5.965139     7.634671     7.486557
Be     7.374045     8.709179     8.532270
Be     7.367892     6.559931     6.429925
Be     7.372260     6.576091     8.552224
Be     7.370369     8.687930     6.410167
Be     9.066175     6.007022     7.493078
Be     9.067215     7.646318     9.081857
Be    10.762370     8.706360     8.533024
Be    12.170045     7.629499     7.487338
Be    10.766005     6.556652     6.429836
Be    10.762232     6.573734     8.552361
Be    10.767609     8.685008     6.410463
Be     9.068638     9.256364     7.462945
Be     9.066972     7.617375     5.871671
```

Be_{15}

```
15
EA340  18.043 15.111 15.111 90.00 90.00
Be     9.021399     5.623114     8.112217
Be     9.021399     6.998943     5.623114
Be     9.021399     9.488046     6.998943
Be     9.021399     8.112217     9.488046
Be    10.641598     6.280960     6.851416
Be    10.641598     8.259744     6.280960
Be    10.641598     8.830199     8.259744
Be    10.641598     6.851416     8.830199
Be     7.401200     6.280960     6.851416
Be     7.401200     8.259744     6.280960
Be     7.401200     8.830199     8.259744
Be     7.401200     6.851416     8.830199
Be     5.958910     7.555580     7.555580
Be    12.083888     7.555580     7.555580
Be     9.021399     7.555580     7.555580
```

Be_{16}

```
16
EA843  16.651 16.476 15.009 90.00 90.00
Be     9.408313     9.669125     8.679878
Be    10.847309     6.645495     7.451529
Be     9.414823     9.786035     6.500331
```

```
Be     7.522078     7.199089     6.028247
Be     6.033910    10.142062     7.612558
Be     7.491558     7.033614     8.830419
Be     9.608994     7.475732     8.862382
Be    10.775587     8.663895     7.542869
Be     9.649351     7.615543     6.094976
Be     7.267813     9.351020     6.173426
Be     6.629236     5.912881     7.350478
Be     7.267882     9.181417     8.942096
Be     7.978498    10.697086     7.639128
Be     6.191725     7.997444     7.469852
Be     8.751505     6.135143     7.389760
Be     8.368724     8.303805     7.502615
```

Be_{17}

```
17
EA1192 16.553 16.462 15.871 90.00 90.00
Be     5.917097     7.176676     7.947508
Be     6.845037     8.195797     6.395555
Be     5.917097     9.285648     7.923257
Be     6.845037     8.266526     9.475209
Be     8.277319     8.231162     7.935382
Be     9.707347     7.162423     9.044580
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Be     9.707347     9.299901     6.826185
Be    10.635573     8.998951     8.655678
Be     9.251821     5.893087     7.445090
Be     8.868766     7.418757     6.091003
Be     9.251821    10.569237     8.425674
Be     8.868766     9.043567     9.779762
Be     7.300349    10.283254     9.157046
Be     7.684636     6.383944     8.742963
Be     7.300349     6.179070     6.713717
Be     7.684636    10.078381     7.127802
```

Be_{18}

```
18
EA711  17.346 16.442 15.638 90.00 90.00
Be     8.672706     8.228540     7.819718
Be    10.463270     6.754342     6.798667
Be     8.672385     7.062217     5.957816
Be     5.958772     8.267464     7.819286
Be     8.671780    10.436565     6.771393
Be     7.345498     8.756028     6.283897
Be     9.999169     8.757236     6.282597
Be     8.674023     5.915438     7.819257
Be     6.881950     6.752316     6.798524
Be     6.920117    10.131250     7.820556
Be     8.674102     7.062285     9.680181
```

```
Be    8.672784   10.434691    8.867734
Be   10.464859    6.752948    8.839233
Be   10.001850    8.755956    9.354132
Be   11.387507    8.269187    7.817978
Be   10.424864   10.132457    7.817946
Be    6.883465    6.752447    8.838720
Be    7.344922    8.755116    9.355785
```

Be_{19}

```
19
EA539  17.758 16.651 16.651 90.00 90.00
Be   11.809165    8.325657    8.325657
Be   10.515625    9.893523    8.084110
Be   10.515625    8.567204    9.893523
Be   10.515625    6.757791    8.567204
Be   10.515625    8.084110    6.757791
Be    7.242395    9.605887    9.264132
Be    7.242395    9.264132    7.045427
Be    7.242395    7.045427    7.387182
Be    7.242395    7.387182    9.605887
Be    8.444694    5.952240    8.690852
Be    8.444694    7.960461    5.952240
Be    8.444694   10.699074    7.960461
Be    8.444694    8.690852   10.699074
Be    9.312967    6.389601    6.905825
Be    9.312967    6.905825   10.261713
Be    9.312967   10.261713    9.745488
Be    9.312967    9.745488    6.389601
Be    8.878369    8.325657    8.325657
Be    5.950550    8.325657    8.325657
```

Be_{20}

```
20
EA1193 17.143 16.505 16.073 90.00 90.00
Be    6.345150    8.769501    8.062075
Be    7.055496    6.900950    7.206397
Be    8.303098    7.902566    5.806086
Be    7.706287    9.744673    6.682436
Be    9.174106   10.799214    7.801421
Be    7.691246    8.820418   10.016036
Be    8.019251    5.776227    8.727279
Be   10.354295    7.413740    5.702783
Be   10.709526    9.592226    8.414407
Be    9.201880   10.223918    9.751180
Be    8.439517    6.910999   10.360852
Be    9.965841    6.352628    9.011991
Be    8.574967    8.263238    8.095493
Be    6.636759    7.178004    9.291192
Be    9.145514    6.393083    7.033061
Be    9.797847    9.234366    6.506999
```

```
Be     7.374853   10.400141    8.699533
Be     6.267317    8.408017    6.033850
Be    10.752450    7.689614    7.701917
Be     9.917153    8.272058    9.821297
```

Be_{21}

```
21
EA218  17.288 16.443 16.534 90.00 90.00
Be    10.450712    7.198861   10.040964
Be    10.386972    9.161410    9.473545
Be     8.644238   10.185638    9.900240
Be     6.901506    9.161395    9.473545
Be     6.837749    7.198861   10.040946
Be     8.644238    6.222354   10.042315
Be    10.450728    7.198861    6.493183
Be     8.644238    6.222354    6.491816
Be     6.837766    7.198861    6.493167
Be     6.901506    9.161410    7.060585
Be     8.644238   10.185638    6.633890
Be    10.386972    9.161395    7.060585
Be    11.329935    7.789521    8.267065
Be     9.727118   10.746888    8.267065
Be     7.561358   10.746888    8.267065
Be     5.958543    7.789521    8.267065
Be     7.530122    6.291628    8.267065
Be     9.758354    6.291628    8.267065
Be     8.644238    8.206413    5.960053
Be     8.644238    8.206413   10.574079
Be     8.644238    8.324946    8.267065
```

Be_{22}

```
22
EA711  17.322 17.333 16.190 90.00 90.00
Be     8.333993    9.799889    5.701171
Be     9.226317    6.713067    6.863385
Be     9.805975    8.384967    5.700818
Be    10.361450    6.394010    8.568070
Be     7.100515    7.043539    7.490112
Be     5.842968    8.331543    8.570231
Be     7.844678    7.817751    5.700539
Be     8.437975    5.837790    8.569214
Be    10.846847    8.128248    7.490279
Be    10.070781   10.133314    6.865677
Be     8.010163   10.912679    9.520117
Be    11.222963    9.888263    8.571241
Be     8.036285   10.828901    7.490796
Be     6.322598   10.275690    8.568305
```

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Be     9.779611   11.274947    8.571259
Be     7.428650    8.969671    9.968947
Be     9.539976    9.580718    9.970090
Be    10.931993    8.105386    9.519735
Be     9.013422    7.446672    9.968798
Be     7.039205    6.978851    9.519095
Be     8.660933    8.666014    8.035323
Be     6.686551    9.153967    6.864172
```

Be_{23}

```
23
EA385  18.454 16.074 16.215 90.00 90.00
Be    12.454581    8.309685    8.459689
Be     8.951497    8.197420    6.020198
Be    11.271439    8.484856    6.285787
Be    11.293626    9.927704    7.980202
Be    10.790741    8.936098    9.814074
Be    11.480872    6.872284    9.483167
Be    11.899546    6.631327    7.483218
Be     9.966321    5.925464    8.280133
Be    10.263027    6.620975    6.247451
Be     9.764452    9.958827    6.627867
Be     9.302716   10.084891    8.646371
Be    10.211779    8.035405    7.988075
Be     7.758243    9.756417    7.088421
Be     6.921005    7.852528    6.379984
Be     7.186157    7.672337    9.946696
Be     9.473289    7.137725    9.996155
Be     8.793698    9.020391   10.353236
Be     8.347656    6.333899    6.927819
Be     6.453669    6.684414    8.007044
Be     8.248643    8.038789    8.224272
Be     7.292474    9.754478    9.178890
Be     6.031832    8.657921    8.000168
Be     8.063017    5.961201    9.049767
```

Be_{24}

```
24
EA633  19.348 16.372 16.373 90.00 90.00
Be    10.759240   10.413948    7.599832
Be     8.589083    5.957915    8.772800
Be     7.290836    6.815578    7.387845
Be    12.057486    9.556284    8.984789
Be     7.292566    9.556177    8.985017
Be    12.055757    6.815686    7.387617
Be    10.630472    8.186788    8.186741
Be     8.717849    8.185075    8.185893
Be    10.760393    5.957347    8.774714
Be     8.587929   10.414515    7.597919
Be    10.759897    7.599551    5.957463
```

```
Be     8.588426     8.772312    10.415170
Be     9.671547    10.050336     9.273236
Be     9.676774     6.321527     7.099396
Be     9.674480     7.099264    10.050776
Be     9.673841     9.272599     6.321856
Be     8.589149     7.597683     5.958907
Be    10.759174     8.774179    10.413727
Be    13.390104     8.184793     8.185674
Be     5.958218     8.187068     8.186959
Be     7.291774     7.386791     9.556354
Be    12.056548     8.985072     6.816279
Be     7.291825     8.984187     6.815859
Be    12.056496     7.387676     9.556774
```

Be_{25}

```
25
EA449  18.574 16.147 15.921 90.00 90.00
Be    10.666894    10.177158     6.887070
Be     9.551102     8.640869     5.961037
Be     6.893282     8.570636     9.755004
Be     6.254472     7.375075     6.641874
Be     9.961551    10.129359     8.801941
Be     9.023835     8.628214     9.959496
Be     8.252254     8.114470     7.933222
Be     7.484593     8.832934     6.000365
Be     8.618129    10.131792     7.133451
Be     6.425281     9.284148     7.794652
Be     5.959628     7.210338     8.622786
Be     7.910984    10.171709     9.046917
Be     7.232178     5.947896     7.696791
Be    11.338460     5.945253     8.208095
Be    12.615014     7.214426     7.296449
Be    12.316470     7.359890     9.277984
Be     9.285407     6.046468     7.952517
Be    11.682066     8.579014     6.169190
Be    11.088874     8.817037     9.925035
Be    10.110639     6.857565     9.731615
Be    10.577627     6.770446     6.343976
Be    12.149981     9.279234     8.135441
Be     7.994218     6.759860     9.568806
Be    10.316546     8.117801     7.986188
Be     8.461005     6.870655     6.178538
```