

## Supporting Information for:

### Comparative DFT Study of the van der Waals Complexes of the Rare-Gas Dimers, Alkaline-Earth Dimers, Zinc Dimers, and Zinc-Rare-Gas Dimers

Yan Zhao and Donald G. Truhlar

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Table S1: Bond lengths (in Å) of rare-gas dimers with counterpoise correction for BSSE. <sup>a b</sup>

Method	He <sub>2</sub>	Ne <sub>2</sub>	Ar <sub>2</sub>	Kr <sub>2</sub>	HeNe	HeAr	HeKr	NeAr	NeKr	ArKr	MSE	MUE
Reference	2.97 <sup>b</sup>	3.09 <sup>b</sup>	3.76 <sup>b</sup>	4.01 <sup>b</sup>	3.03 <sup>c</sup>	3.48 <sup>c</sup>	3.69 <sup>c</sup>	3.49 <sup>c</sup>	3.62 <sup>c</sup>	3.88 <sup>c</sup>		
B97-1	2.70	3.04	3.90	4.22	2.86	3.35	3.53	3.48	3.66	4.07	<b>-0.02</b>	<b>0.14</b>
M05-2X	2.74	2.86	3.82	4.11	2.80	3.32	3.57	3.38	3.54	3.97	-0.09	<b>0.14</b>
PBEPW91	2.74	3.11	3.99	4.31	2.92	3.41	3.61	3.54	3.72	4.16	<b>0.05</b>	<b>0.15</b>
B98	2.80	3.16	4.02	4.34	2.97	3.48	3.67	3.61	3.78	4.18	0.10	<b>0.15</b>
PBE	2.75	3.13	4.01	4.34	2.94	3.43	3.63	3.56	3.73	4.18	<b>0.07</b>	<b>0.15</b>
PW6B95	3.04	3.22	3.72	4.27	3.00	3.39	3.83	3.58	4.08	4.15	0.13	0.16
PW91	2.65	3.03	3.96	4.31	2.83	3.33	3.52	3.49	3.66	4.14	<b>-0.01</b>	0.17
PBE1W	2.75	3.13	4.06	4.40	2.93	3.44	3.65	3.58	3.76	4.23	0.09	0.17
PWB6K	2.77	2.94	3.71	4.26	2.98	3.38	3.81	3.56	4.08	4.14	<b>0.06</b>	0.17
PBE0	2.81	3.18	4.05	4.39	2.98	3.49	3.95	3.62	3.79	4.22	0.15	0.19
MPW1B95	3.05	3.23	3.73	4.28	3.01	3.40	4.18	3.60	4.09	4.16	0.17	0.20
MPWB1K	3.05	3.23	3.72	4.28	3.01	3.40	4.18	3.60	4.10	4.16	0.17	0.20
M05	2.63	2.86	3.74	4.24	2.73	3.28	3.46	3.30	3.45	3.97	-0.14	0.20
TPSS	2.95	3.27	4.38	4.66	3.05	3.67	3.83	3.84	4.02	4.52	0.32	0.32
TPSSh	2.96	3.27	4.38	4.66	3.06	3.68	3.99	3.85	4.03	4.52	0.34	0.34
LSDA	2.40	2.62	3.41	3.70	2.48	2.95	3.13	3.02	3.17	3.56	-0.46	0.46
MPW1K	3.10	3.51	4.74	5.04	3.29	3.95	4.15	3.98	4.15	4.89	0.58	0.58
mPW1PW91	3.10	3.50	4.74	5.06	3.29	3.94	4.14	3.99	4.16	4.90	0.58	0.58
Average											0.12	0.25

<sup>a</sup> The aug-cc-pVTZ basis set are employed in all calculations in this table.

<sup>b</sup> Ref. <sup>1</sup> <sup>c</sup> Ref. <sup>2</sup>

Table S2: Bond lengths (in Å) of alkaline metal dimers, Zn<sub>2</sub>, and Zn-rare-gas dimers with counterpoise correction for BSSE <sup>a</sup>

Method	Be <sub>2</sub>	Mg <sub>2</sub>	Ca <sub>2</sub>	Zn <sub>2</sub>	ZnNe	ZnAr	ZnKr	MSE	MUE
Reference	2.45	3.89	4.28	4.19	4.42	4.38	4.20		
PWB6K	2.62	3.79	4.30	3.68	4.00	4.26	4.29	-0.12	<b>0.20</b>
M05-2X	2.66	3.86	4.42	3.86	3.94	4.28	4.39	<b>-0.06</b>	<b>0.21</b>
B98	2.54	3.68	4.26	3.36	4.03	4.36	4.47	-0.16	<b>0.26</b>
PW6B95	2.53	3.74	4.24	3.59	4.03	4.63	4.55	<b>-0.07</b>	<b>0.27</b>
B97-1	2.53	3.64	4.24	3.48	3.87	4.22	4.33	-0.21	<b>0.28</b>
MPWB1K	2.62	3.76	4.28	3.63	4.20	4.66	4.79	<b>0.02</b>	0.28
PBE0	2.51	3.59	4.21	3.32	4.07	4.45	4.54	-0.16	0.29
MPW1B95	2.55	3.70	4.24	3.53	4.17	4.66	4.78	<b>-0.03</b>	0.30
M05	2.54	3.64	4.23	3.57	3.60	4.12	4.25	-0.27	0.31
PBE1W	2.43	3.57	4.13	3.31	3.91	4.38	4.50	-0.22	0.31
PBE	2.43	3.51	4.10	3.17	3.88	4.30	4.40	-0.29	0.34
PBEPW91	2.43	3.52	4.10	3.19	3.86	4.27	4.37	-0.30	0.35
PW91	2.43	3.51	4.09	3.14	3.76	4.25	4.37	-0.32	0.37
TPSS	2.45	3.53	4.11	3.11	4.17	4.74	4.90	-0.12	0.42
TPSSh	2.48	3.57	4.15	3.18	4.23	4.78	5.07	<b>-0.05</b>	0.42
mPW1PW91	2.51	3.61	4.21	3.34	4.48	5.14	5.50	0.14	0.48
MPW1K	2.59	3.67	4.27	3.45	4.58	5.17	5.54	0.21	0.49
LSDA	2.40	3.41	3.99	2.85	3.20	3.53	3.61	-0.69	0.69
Average								-0.15	0.35

<sup>a</sup> The aug-CV(T+2d)Z (see text) is employed for Ca, and the aug-cc-pVTZ basis set is employed for all other elements.

<sup>b</sup> The reference data for Be<sub>2</sub>: ref.<sup>3</sup>; Mg<sub>2</sub>: ref.<sup>4</sup>; Ca<sub>2</sub>: ref.<sup>5</sup>; Zn<sub>2</sub>:<sup>6</sup>; ZnNe: ref.<sup>7</sup>; ZnAr: ref.<sup>8</sup>; ZnKr: ref.<sup>9</sup>

## The aug-cc-pVTZ Basis Set for helium

HE 0

```
S 4 1.00
  234.000000    0.258700000E-02
  35.1600000    0.195330000E-01
  7.98900000    0.909980000E-01
  2.21200000    0.272050000
S 1 1.00
  0.666900000    1.000000000
S 1 1.00
  0.208900000    1.000000000
P 1 1.00
  3.04400000    1.000000000
P 1 1.00
  0.758000000    1.000000000
D 1 1.00
  1.96500000    1.000000000
S 1 1.00
  0.513800000E-01    1.000000000
P 1 1.00
  0.199300000    1.000000000
D 1 1.00
  0.459200000    1.000000000
****
```

## The aug-cc-pVTZ Basis Set for zinc

-Zn 0

S 20 1.00

5.820021E+06	8.549241E-06
8.715234E+05	6.647410E-05
1.983350E+05	3.494962E-04
5.617631E+04	1.473832E-03
1.832582E+04	5.338330E-03
6.614955E+03	1.712708E-02
2.579199E+03	4.894085E-02
1.068849E+03	1.217934E-01
4.651045E+02	2.476589E-01
2.104130E+02	3.582431E-01
9.761629E+01	2.798174E-01
4.438020E+01	6.857491E-02
2.142308E+01	-1.311092E-03
1.030891E+01	1.914001E-03
4.553645E+00	-8.759220E-04
2.132821E+00	3.740096E-04
9.296970E-01	-1.401399E-04
1.921470E-01	4.757132E-05
8.759500E-02	-3.642711E-05
3.770200E-02	1.153248E-05

S 20 1.00

5.820021E+06	-2.640069E-06
8.715234E+05	-2.052720E-05
1.983350E+05	-1.079859E-04
5.617631E+04	-4.558577E-04
1.832582E+04	-1.657758E-03
6.614955E+03	-5.368492E-03
2.579199E+03	-1.571249E-02
1.068849E+03	-4.122558E-02
4.651045E+02	-9.406459E-02
2.104130E+02	-1.719954E-01
9.761629E+01	-1.958523E-01
4.438020E+01	4.532907E-02
2.142308E+01	5.244442E-01
1.030891E+01	5.006142E-01
4.553645E+00	8.945527E-02
2.132821E+00	-2.146262E-03
9.296970E-01	2.112113E-03
1.921470E-01	-4.133980E-04
8.759500E-02	3.209752E-04
3.770200E-02	-1.016140E-04

S 20 1.00

5.820021E+06	9.967103E-07
8.715234E+05	7.754163E-06
1.983350E+05	4.076019E-05
5.617631E+04	1.722811E-04
1.832582E+04	6.259370E-04
6.614955E+03	2.032855E-03
2.579199E+03	5.954646E-03
1.068849E+03	1.576640E-02
4.651045E+02	3.637638E-02
2.104130E+02	6.892343E-02
9.761629E+01	8.238093E-02
4.438020E+01	-2.011360E-02
2.142308E+01	-3.252526E-01
1.030891E+01	-4.602899E-01
4.553645E+00	1.635546E-01
2.132821E+00	7.297118E-01
9.296970E-01	3.769751E-01
1.921470E-01	1.433224E-02
8.759500E-02	-6.671210E-03
3.770200E-02	1.766214E-03
S 20 1.00	
5.820021E+06	1.995818E-07
8.715234E+05	1.552973E-06
1.983350E+05	8.161259E-06
5.617631E+04	3.450747E-05
1.832582E+04	1.253275E-04
6.614955E+03	4.072990E-04
2.579199E+03	1.192734E-03
1.068849E+03	3.163140E-03
4.651045E+02	7.303942E-03
2.104130E+02	1.391279E-02
9.761629E+01	1.670620E-02
4.438020E+01	-4.035586E-03
2.142308E+01	-6.968861E-02
1.030891E+01	-1.030105E-01
4.553645E+00	4.471442E-02
2.132821E+00	2.150027E-01
9.296970E-01	2.220163E-01
1.921470E-01	-3.114776E-01
8.759500E-02	-5.693429E-01
3.770200E-02	-2.678440E-01
S 20 1.00	
5.820021E+06	-5.435910E-07
8.715234E+05	-4.336894E-06
1.983350E+05	-2.197572E-05
5.617631E+04	-9.747392E-05

1.832582E+04	-3.331615E-04
6.614955E+03	-1.166192E-03
2.579199E+03	-3.119308E-03
1.068849E+03	-9.239504E-03
4.651045E+02	-1.855471E-02
2.104130E+02	-4.281189E-02
9.761629E+01	-3.571095E-02
4.438020E+01	-1.638350E-02
2.142308E+01	2.644664E-01
1.030891E+01	2.086588E-01
4.553645E+00	-1.774382E-02
2.132821E+00	-1.353873E+00
9.296970E-01	8.182926E-01
1.921470E-01	1.695036E+00
8.759500E-02	-1.388656E+00
3.770200E-02	-2.188900E-01
S 20 1.00	
5.820021E+06	8.040791E-07
8.715234E+05	6.282936E-06
1.983350E+05	3.281868E-05
5.617631E+04	1.398858E-04
1.832582E+04	5.029836E-04
6.614955E+03	1.655419E-03
2.579199E+03	4.778677E-03
1.068849E+03	1.292479E-02
4.651045E+02	2.925831E-02
2.104130E+02	5.791816E-02
9.761629E+01	6.640681E-02
4.438020E+01	-7.388966E-03
2.142308E+01	-3.329989E-01
1.030891E+01	-5.917865E-01
4.553645E+00	9.011406E-01
2.132821E+00	1.585951E+00
9.296970E-01	-2.788008E+00
1.921470E-01	2.071884E+00
8.759500E-02	-6.012025E-01
3.770200E-02	-5.937184E-01
S 1 1.00	
3.770200E-02	1.000000E+00
P 15 1.00	
2.441198E+04	4.100000E-05
5.778518E+03	3.610000E-04
1.876862E+03	2.088000E-03
7.182361E+02	9.221000E-03
3.048327E+02	3.277300E-02
1.390453E+02	9.417900E-02

6.680417E+01	2.091320E-01
3.320699E+01	3.345690E-01
1.692816E+01	3.303590E-01
8.696229E+00	1.523470E-01
4.350510E+00	2.298400E-02
2.116523E+00	1.607000E-03
9.953870E-01	4.680000E-04
3.781120E-01	6.600000E-05
1.345790E-01	-2.000000E-06

P 16 1.00

2.441198E+04	-1.500000E-05
5.778518E+03	-1.350000E-04
1.876862E+03	-7.820000E-04
7.182361E+02	-3.478000E-03
3.048327E+02	-1.252000E-02
1.390453E+02	-3.701600E-02
6.680417E+01	-8.555900E-02
3.320699E+01	-1.447180E-01
1.692816E+01	-1.434420E-01
8.696229E+00	4.359500E-02
4.350510E+00	3.488880E-01
2.116523E+00	4.538650E-01
9.953870E-01	2.685940E-01
3.781120E-01	3.886800E-02
1.345790E-01	-2.492000E-03
4.628200E-02	1.014000E-03

P 16 1.00

2.441198E+04	3.000000E-06
5.778518E+03	2.500000E-05
1.876862E+03	1.440000E-04
7.182361E+02	6.450000E-04
3.048327E+02	2.311000E-03
1.390453E+02	6.898000E-03
6.680417E+01	1.588200E-02
3.320699E+01	2.735000E-02
1.692816E+01	2.662100E-02
8.696229E+00	-1.085800E-02
4.350510E+00	-7.985300E-02
2.116523E+00	-1.061270E-01
9.953870E-01	-6.888300E-02
3.781120E-01	1.843850E-01
1.345790E-01	5.617880E-01
4.628200E-02	4.144160E-01

P 16 1.00

2.441198E+04	5.000000E-06
5.778518E+03	4.200000E-05



1.876862E+03	2.380000E-04
7.182361E+02	1.088000E-03
3.048327E+02	3.821000E-03
1.390453E+02	1.164400E-02
6.680417E+01	2.616700E-02
3.320699E+01	4.675000E-02
1.692816E+01	4.330900E-02
8.696229E+00	-1.342900E-02
4.350510E+00	-1.538970E-01
2.116523E+00	-1.674130E-01
9.953870E-01	-8.499500E-02
3.781120E-01	4.508130E-01
1.345790E-01	6.408690E-01
4.628200E-02	5.417200E-02
P 16 1.00	
2.441198E+04	1.200000E-05
5.778518E+03	9.600000E-05
1.876862E+03	5.940000E-04
7.182361E+02	2.484000E-03
3.048327E+02	9.537000E-03
1.390453E+02	2.647900E-02
6.680417E+01	6.636600E-02
3.320699E+01	1.024580E-01
1.692816E+01	1.386830E-01
8.696229E+00	-8.014000E-02
4.350510E+00	-4.960690E-01
2.116523E+00	-4.635100E-01
9.953870E-01	8.745310E-01
3.781120E-01	6.297900E-01
1.345790E-01	-8.116860E-01
4.628200E-02	-1.089480E-01
P 1 1.00	
4.628200E-02	1.000000E+00
D 8 1.00	
2.056177E+02	2.342000E-03
6.144981E+01	1.860600E-02
2.305689E+01	7.710200E-02
9.577739E+00	2.020260E-01
4.133734E+00	3.294540E-01
1.747518E+00	3.609760E-01
6.995600E-01	2.716570E-01
2.516080E-01	1.049810E-01
D 8 1.00	
2.056177E+02	3.279000E-03
6.144981E+01	2.617600E-02
2.305689E+01	1.113670E-01

9.577739E+00	3.045810E-01
4.133734E+00	3.862990E-01
1.747518E+00	-5.837500E-02
6.995600E-01	-5.388760E-01
2.516080E-01	-3.454730E-01
D 8 1.00	
2.056177E+02	3.740000E-03
6.144981E+01	3.182500E-02
2.305689E+01	1.322290E-01
9.577739E+00	4.245500E-01
4.133734E+00	1.203700E-01
1.747518E+00	-7.626610E-01
6.995600E-01	-1.128230E-01
2.516080E-01	8.096230E-01
D 1 1.00	
2.516080E-01	1.000000E+00
F 1 1.00	
5.792200E+00	1.000000E+00
F 1 1.00	
1.485100E+00	1.000000E+00
G 1 1.00	
4.114400E+00	1.000000E+00
S 1 1.00	
1.623000E-02	1.000000E+00
P 1 1.00	
1.592000E-02	1.000000E+00
D 1 1.00	
9.049000E-02	1.000000E+00
F 1 1.00	
5.486100E-01	1.000000E+00
G 1 1.00	
1.829330E+00	1.000000E+00
****	

## The aug-CV(T+2d)Z Basis Set for calcium

-Ca

S 22 1.0

0.0254108441803 -0.00000238  
0.0630307004441 0.00000950  
0.1478138859055 -0.00002436  
0.3306287416437 0.00004424  
0.7116401635679 -0.00012829  
1.4869863512959 0.00011531  
3.0430732505456 -0.00021688  
6.1533119329301 0.00132105  
12.4030577392801 0.01054215  
25.1422485957806 0.11698026  
51.7091253452967 0.30641477  
108.8554557050285 0.33226934  
236.6384704702638 0.21552371  
535.9260256533751 0.10463039  
1275.6775212307653 0.04219866  
3219.7764745844952 0.01492711  
8693.4370914503652 0.00472921  
25332.0589264397786 0.00135120  
80370.1635951880162 0.00034488  
280089.4895136958221 0.00007922  
1081704.3511574361473 0.00001509  
4670489.0073897046968 0.00000334

S 22 1.0

0.0254108441803 0.00007752  
0.0630307004441 -0.00030441  
0.1478138859055 0.00076909  
0.3306287416437 -0.00103646  
0.7116401635679 0.00490140  
1.4869863512959 0.03080040  
3.0430732505456 0.31571028  
6.1533119329301 0.55947885  
12.4030577392801 0.26191142  
25.1422485957806 -0.07091442  
51.7091253452967 -0.18042054  
108.8554557050285 -0.13893101  
236.6384704702638 -0.07425808  
535.9260256533751 -0.03283320  
1275.6775212307653 -0.01265980  
3219.7764745844952 -0.00439118  
8693.4370914503652 -0.00137934  
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