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

Dissecting the cation-cation interaction between two uranyl units

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Supplementary Information

1 Computational Details

All geometries have been optimized in the TURBOMOLE v6.6 [1–3] software package employing the BP86 exchange–correlation (xc) functional [4, 5] and the def-TZVP (triple-ζ valence polarization) basis set for the uranium atom and the def2-TZVP basis set for the oxygen atom [6]. For the uranium atom a small-core effective potential [7, 8] (60 electrons in the core) was used to account for scalar relativistic effects. The same computational set up was used to numerically calculate vibrational spectra and ensure that the optimized structures are true (local) minima. In all calculations, C_{2h} point group symmetry was imposed for diamond shaped clusters, while C_{2v} point group symmetry was used for T-shaped dications. If convergence difficulties were encountered during geometry optimization (slow or no convergence), the cluster was allowed to relax freely within C_1 symmetry. For comparison, we also optimized the geometry using C_1 symmetry for all CCI clusters. However, we should note that the differences between the symmetry-constrained and symmetry-relaxed structures are negligible and hence, whenever available, only the symmetry-constrained structures have been used in subsequent calculations.

Analytical and numerical vibrational spectra as well as electronic spectra were calculated using the ADF2014 software package [9–11]. A Triple-ζ Polarization (TZP) and a Double-ζ Polarization (DZP) basis sets were used for the uranium centre and oxygen atoms, respectively [12]. We employed the PBE0 [13] xc functional for the calculation of excitation energies and the BP86 xc functional for a vibrational frequency analysis [4,5]. Scalar relativistic effects were accounted for using the Zero-th Order Regular Approximation (ZORA) Hamiltonian. [14] Moreover, we increased the convergence criteria by applying a Quadruple-ζ quality basis for the auxiliary fit set and by setting the integration grid to 10^{-10}.

All structure optimizations and single-point calculations were performed using the COSMO solvation model with a dielectric constant of water ($\epsilon = 80$) [15].

1.1 BP86 optimized geometries

All molecular geometries are given in xyz-format (Å). Singlet, doublet, triplet, etc., denotes the spin multiplicity M. The point group symmetry imposed in calculations in given in parenthesis.

1.1.1 Diamond singlet $[(UO_2)_2]^{4+}$ (C_{2h})

O −1.6780253 2.7625730 0.0000000
U −1.3578769 1.0766394 0.0000000
O −0.9944895 −0.6994527 0.0000000
O 0.9944895 0.6994527 0.0000000
U 1.3578769 −1.0766394 0.0000000
O 1.6780253 −2.7625730 0.0000000

1.1.2 Diamond triplet $[(\mathbf{UO_2})_2]^{4+}$ (C_{2h})

O −1.903748 2.9012495 0.00000000
U −1.376416 1.2315639 0.00000000
O −1.0821964 −0.5534559 0.00000000
O 1.0821964 0.5534559 0.00000000
U 1.376416 −1.2315639 0.00000000
O 1.903748 −2.9012495 0.00000000

1.1.3 Diamond quintet $[(\mathbf{UO_2})_2]^{4+}$ (C_{2h})

O −1.7402352 2.8445492 0.00000000
U −1.3606718 1.1036524 0.00000000
O −1.0158401 −0.7048892 0.00000000
O 1.0158401 0.7048892 0.00000000
U 1.3606718 −1.1036524 0.00000000
O 1.7402352 −2.8445492 0.00000000

1.1.4 Diamond doublet $[(\mathbf{UO_2})_2]^{3+}$ (C_{2h})

O −1.6745905 2.7747533 0.0000000
U −1.3207282 1.0679586 0.0000000
O −0.9904405 −0.7545899 0.0000000
O 0.9904405 0.7545899 0.0000000
U 1.3207282 −1.0679586 0.0000000
O 1.6745905 −2.7747533 0.0000000

1.1.5 Diamond quartet $[(\mathbf{UO_2})_2]^{3+}$ (C_{2h})

O −1.8490872 2.8959182 0.0000000
U −1.3405347 1.1827597 0.0000000
O −1.0420600 −0.6512770 0.0000000
O 1.0420600 0.6512770 0.0000000
U 1.3405347 −1.1827597 0.0000000
O 1.8490872 −2.8959182 0.0000000

1.1.6 Diamond singlet $[(UO_2)_2]^{2+}$ (C_1)

O −1.5980817 2.7702240 0.0003999
U −1.3178134 1.0113599 0.0001350
O −0.9419642 −0.8596874 −0.0005464
O 0.9436754 0.8599048 −0.0005270
U 1.3179384 −1.0112496 0.0001167
O 1.5962455 −2.7705517 0.0004217

1.1.7 Diamond triplet $[(UO_2)_2]^{2+}$ (C_{2h})

O −1.6564872 2.8125736 0.0000000
U −1.3173973 1.0576571 0.0000000
O −0.9496822 −0.8274218 0.0000000
O 0.9496822 0.8274218 0.0000000
U 1.3173973 −1.0576571 0.0000000
O 1.6564872 −2.8125736 0.0000000

1.1.8 Diamond quintet $[(UO_2)_2]^{2+}$ (C_1)

O −1.6007708 2.8172175 0.0009483
U −1.3294510 1.0168478 −0.0000708
O −0.9192598 −0.8984794 −0.0008759
O 0.9233475 0.8976229 −0.0009226
U 1.3277831 −1.0162083 0.0000202
O 1.5983510 −2.8170006 0.0009008

1.1.9 T-shape singlet $[(UO_2)_2]^{4+}$ (C_{2v})

U 0.00000000 0.00000000 −2.1383081
O 0.7288205 0.00000000 −2.0923716
O −0.7288205 0.00000000 −2.0923716
U 0.00000000 0.00000000 2.1274275
O 0.00000000 0.00000000 0.3561864
O 0.00000000 0.00000000 3.8394373

1.1.10 T-shape triplet $[(UO_2)_2]^{4+}$ (C_{2v})

U 0.00000000 0.00000000 −2.1336633
O 1.7300408 0.00000000 −2.0970638
O −1.7300408 0.00000000 −2.0970638
U 0.00000000 0.00000000 2.1185743
O 0.00000000 0.00000000 0.3112734
O 0.00000000 0.00000000 3.8979432

1.1.11 T-shape quintet $[(UO_2)_2]^{4+}$ (C_1)

U 0.0001610 0.0001210 −2.0966140
O 1.7743923 −0.0000366 −2.0842396
O −1.7740267 −0.0000366 −2.0845499
U −0.0011125 0.0002805 2.1022513
O −0.0004734 −0.0002182 0.2751869
O 0.0010594 −0.0001102 3.8879654

1.1.12 T-shape doublet $[(UO_2)_2]^{3+}$ (C_1)

U 0.0000000 0.0000000 −2.0469754
O 1.7489935 0.0000000 −2.0602186
O −1.7489935 0.0000000 −2.0602186
U 0.0000000 0.0000000 2.09235939
O 0.0000000 0.0000000 0.23342744
O 0.0000000 0.0000000 3.84162572

1.1.13 T-shape quartet $[(UO_2)_2]^{3+}$ (C_1)

U −0.001893 −0.0001831 −2.0139359
O 1.7908261 0.000204 −2.0623036
O −1.7937469 0.0002048 −2.0871531
U 0.0016184 −0.0008283 2.1038524
O −0.0045014 0.0000325 0.2017043
O 0.0076967 0.0005702 3.8578361

1.1.14 T-shape singlet $[(\mathbf{UO_2})_2]^{2+}$ (C_{2v})

U 0.00000000 0.00000000 −2.0599199
O 1.7872992 0.00000000 −2.0965754
O −1.7872992 0.00000000 −2.0965754
U 0.00000000 0.00000000 2.1173042
O 0.00000000 0.00000000 0.2367425
O 0.00000000 0.00000000 3.8990241

1.1.15 T-shape triplet $[(\mathbf{UO_2})_2]^{2+}$ (C_{2v})

U 0.00000000 0.00000000 −2.0721744
O 1.7907133 0.00000000 −2.1023997
O −1.7907133 0.00000000 −2.1023997
U 0.00000000 0.00000000 2.1230413
O 0.00000000 0.00000000 0.2507902
O 0.00000000 0.00000000 3.9031422

1.1.16 T-shape quintet $[(\mathbf{UO_2})_2]^{2+}$ (C_{2v})

U 0.0000000 0.0000000 −2.1034678
O 1.7993086 0.0000000 −2.1502356
O −1.7993086 0.0000000 −2.1502356
U 0.0000000 0.0000000 2.1488905
O 0.0000000 0.0000000 0.2425827
O 0.0000000 0.0000000 4.0124658

1.2 BP86 vibrational frequencies

All numeric vibrational frequencies calculated in TURBOMOLE were positive, indicating that the optimized cluster structures are true (local) minima. The only exception was the T-shape $[(UO_2)_2]^{3+}_{[M=2]}$ cluster for which the numerical frequencies could not be converged. The analytic vibrational frequencies were calculated in ADF using the geometries optimized in TURBOMOLE. These analytic vibrational frequencies were used to plot the graphs in the main article.

Table 1: $[(UO_2)_2]^{4+}_{[M=1]}$

Frequency [cm^{-1}]			
Diamond shape		T-shape	
Analytic (ADF)	Numeric (Turbomole)	Analytic (ADF)	Numeric (Turbomole)
750.0	749.4	888.3	879.43
826.8	820.6	966.1	954.1
1008.0	999.9	1027.2	1019.2
1021.8	1011.4	1027.8	1018.7

Table 2: $[(UO_2)_2]^{4+}_{[M=3]}$

Frequency [cm^{-1}]			
Diamond shape		T-shape	
Analytic (ADF)	Numeric (Turbomole)	Analytic (ADF)	Numeric (Turbomole)
554.6	736.1	656.7	765.7
754.7	756.2	860.0	799.8
781.2	854.1	952.8	941.7
905.8	901.3	969.0	1013.6

Table 3: $[(UO_2)_2]^{4+}_{[M=5]}$

Frequency [cm^{-1}]			
Diamond shape		T-shape	
Analytic (ADF)	Numeric (Turbomole)	Analytic (ADF)	Numeric (Turbomole)
618.2	666.6	720.8	710.5
697.5	681.2	809.2	806.8
806.8	790.9	852.2	830.4
815.6	797.5	857.9	852.0

Table 4: $[(UO_2)_2]^{3+}_{[M=2]}$

Frequency [cm^{-1}]			
Diamond shape		T-shape	
Analytic (ADF)	Numeric (Turbomole)	Analytic (ADF)	Numeric (Turbomole)
660.0	680.9	706.9	–
713.4	706.9	731.6	–
942.1	930.4	763.5	–
966.5	947.9	929.4	–

Table 5: $[(UO_2)_2]^{3+}_{[M=4]}$

Frequency [cm^{-1}]			
Diamond shape		T-shape	
Analytic (ADF)	Numeric (Turbomole)	Analytic (ADF)	Numeric (Turbomole)
621.7	690.9	591.5	688.6
697.6	707.1	798.5	806.0
756.2	761.6	819.9	825.6
842.4	829.3	920.4	913.0

Table 6: $[(UO_2)_2]^{2+}_{[M=1]}$

Frequency [cm^{-1}]			
Diamond shape		T-shape	
Analytic (ADF)	Numeric (Turbomole)	Analytic (ADF)	Numeric (Turbomole)
619.0	419.3	669.7	677.3
717.0	659.2	830.9	833.9
751.2	669.2	891.6	874.9
879.5	856.0	908.8	882.3
905.5	874.1		

Table 7: $[(UO_2)_2]^{2+}_{[M=3]}$

Frequency [cm^{-1}]			
Diamond shape		T-shape	
Analytic (ADF)	Numeric (Turbomole)	Analytic (ADF)	Numeric (Turbomole)
578.9	576.7	757.2	657.6
647.2	654.4	865.7	810.6
834.3	836.2	879.6	888.1
867.8	879.1	893.3	884.1

Table 8: $[(UO_2)_2]^{2+}_{[M=5]}$

Frequency [cm^{-1}]			
Diamond shape		T-shape	
Analytic (ADF)	Numeric (Turbomole)	Analytic (ADF)	Numeric (Turbomole)
471.0	553.3	672.5	628.2
604.8	622.0	732.2	669.1
683.4	748.0	814.9	793.7
791.3	787.6	838.6	837.6

Table 9: Stability of the diamond and T-shaped structures in kcal/mol. M denotes the spin multiplicity. The relative energies of the compounds with a total charge of 4+, 3+, and 2+ are adjusted to the most stable one within each charge group.

System	PBE0		B3LYP		BP86		M06		M06-L	
Compound	Diamond	T-shape	Diamond	T-shape	Diamond	T-shape	Diamond	T-shape	Diamond	T-shape
$[(UO_2)_2]^{4+}_{[M=1]}$	20.5	0.0	20.4	0.0	16.1	0.0	23.5	0.0	19.9	0.00
$[(UO_2)_2]^{4+}_{[M=3]}$	100.6	57.5	92.9	56.7	67.2	63.1	103.5	61.0	71.4	51.7
$[(UO_2)_2]^{4+}_{[M=5]}$	168.4	117.6	159.7	115.2	124.8	111.9	126.1	116.1	127.3	104.8
$[(UO_2)_2]^{3+}_{[M=2]}$	21.0	0.0	18.7	0.00	7.4	0.0	28.6	0.0	12.2	0.0
$[(UO_2)_2]^{3+}_{[M=4]}$	111.4	57.4	101.7	55.5	66.8	59.1	75.2	76.6	60.7	54.6
$[(UO_2)_2]^{2+}_{[M=1]}$	39.2	48.4	33.3	43.5	12.8	53.7	50.9	53.4	25.0	32.5
$[(UO_2)_2]^{2+}_{[M=3]}$	27.6	0.0	21.6	0.0	0.0	3.4	5.6	0.0	0.0	2.3
$[(UO_2)_2]^{2+}_{[M=5]}$	60.4	88.0	72.6	64.7	61.1	69.4	62.1	74.0	56.9	62.7

1.3 Low-lying vertical (spin–free) PBE0 excitation energies

Table 10: $[(UO_2)_2]^{4+}_{[M=1]}$

Diamond shape		T-shape	
singlet–singlet			
Excitation energy [eV]	Intensity	Excitation energy [eV]	Intensity
3.21	0.4445E-04	3.25	0.0
3.21	0.0	3.30	0.1283E-06
3.24	0.0	3.34	0.1826E-08
3.24	0.2534E-03	3.34	0.8481E-09
3.74	0.0	3.87	0.6702E-04
3.76	0.7313E-04	3.88	0.4351E-04
3.80	0.9104E-03	3.90	0.1184E-06
3.81	0.0	3.90	0.0
singlet–triplet			
2.64	0.0	2.69	0.0
2.64	0.0	2.71	0.0
2.67	0.0	2.71	0.0
2.67	0.0	2.74	0.0
2.67	0.0	2.78	0.0
2.72	0.0	2.78	0.0
2.72	0.0	2.79	0.0

Table 11: $[(UO_2)_2]^{4+}_{[M=3]}$

Diamond shape		T-shape	
spin-unrestricted			
Excitation energy [eV]	Intensity	Excitation energy [eV]	Intensity
1.06	2.16E-09	0.33	0.000
1.09	5.71E-07	0.46	0.3482E-06
1.10	0.0	0.46	0.3246E-06
1.11	0.0	1.36	0.2789E-03
1.12	7.53E-06	1.38	0.3856E-03
1.27	0.0	1.83	0.5932E-03
1.72	0.0	2.13	0.8366E-05
2.14	9.20E-05	2.18	0.4055E-05
2.28	0.0	2.32	0.3490E-03
2.33	5.63E-03	2.36	0.1264E-02
2.46	0.0	2.70	0.000
2.56	1.15E-03	2.71	0.1050E-02
2.66	0.0	2.71	0.2651E-08
2.76	2.75E-02	2.74	0.4832E-01
2.86	0.0	2.76	0.7596E-08
2.91	2.17E-06	2.89	0.3520E-05
2.93	0.0	2.99	0.1112E-01
3.10	0.0	3.26	0.000
3.10	7.12E-02	3.26	0.000
3.37	0.3074	3.32	0.2470E-05
3.53	1.18E-04	3.47	0.2252E-01
3.76	0.0	3.49	0.5287E-03
3.97	0.0	3.88	0.5112E-04
3.99	1.53E-04	3.88	0.2383E-04

Table 12: $[(UO_2)_2]^{4+}_{[M=5]}$

Diamond shape		T-shape	
spin-unrestricted			
Excitation energy [eV]	Intensity	Excitation energy [eV]	Intensity
0.05	4.48E-05	0.33	0.7654E-08
0.16	0.0	0.34	0.3005E-12
1.55	1.55E-07	0.45	0.5137E-06
1.55	0.0	0.45	0.3859E-06
1.56	0.0	0.46	0.1804E-06
1.56	8.11E-08	0.50	0.1207E-10
1.83	0.0	1.30	0.3314E-03
1.86	0.0	1.31	0.3725E-03
1.92	8.42E-04	1.76	0.2723E-09
1.94	1.40E-05	1.77	0.5660E-05
2.83	1.30E-03	2.00	0.7568E-03
2.83	0.0	2.07	0.8918E-05
2.87	0.0	2.08	0.2720E-01
2.88	7.68E-04	2.12	0.1460E-04
2.99	1.59E-02	2.24	0.1376E-01
3.02	0.0	2.26	0.1796E-03
3.03	3.50E-07	2.32	0.2505E-02
3.07	0.0	2.35	0.9836E-03
3.21	2.14E-02	2.36	0.2262E-04
3.21	5.30E-07	2.39	0.1301E-10
3.32	0.0	2.42	0.8301E-03
3.36	0.0	2.50	0.1608E-05
3.48	0.0	2.50	0.3642E-04
3.49	0.0	2.67	0.4844E-04

Table 13: $[(UO_2)_2]^{3+}_{[M=2]}$

Diamond shape		T-shape	
spin-unrestricted			
Excitation energy [eV]	Intensity	Excitation energy [eV]	Intensity
0.24	0.2384E-03	0.32	0.1018E-06
0.26	0.0	0.32	0.1324E-06
0.26	0.9316E-05	0.33	0.0
0.28	0.0	1.59	0.7770E-04
0.30	0.8910E-05	1.73	0.7071E-04
0.52	0.0	1.96	0.0
0.73	0.8900E-01	2.09	0.1116E-03
1.78	0.6348E-05	2.23	0.4024E-05
1.82	0.0	2.32	0.1855E-05
1.87	0.0	2.66	0.1304E-06
1.96	0.2348E-01	2.69	0.1991E-05
2.84	0.0	2.72	0.0
2.93	0.2377E-04	2.77	0.1099E-06
3.02	0.0	3.24	0.0
3.02	0.2252E-05	3.30	0.1226E-04
3.09	0.0	3.69	0.5271E-05
3.10	0.1074E-05	3.69	0.4018E-05
3.36	0.0	3.75	0.2493E-04
3.37	0.1144E-04	3.76	0.5611E-06
3.68	0.0	3.78	0.1008E-02
3.69	0.6930E-04	3.86	0.2275E-05
3.69	0.0	3.89	0.0
3.69	0.2532E-04	3.91	0.1765E-05
3.84	0.3996E-03	3.96	0.5257E-02

Table 14: $[(UO_2)_2]^{3+}_{[M=4]}$

Diamond shape		T-shape	
spin-unrestricted			
Excitation energy [eV]	Intensity	Excitation energy [eV]	Intensity
0.05	4.48E-05	0.27	0.3025E-06
0.17	0.0	0.27	0.2683E-06
0.78	1.55E-07	0.37	0.2857E-06
1.41	0.0	0.50	0.5815E-11
1.41	0.0	0.53	0.3490E-05
1.41	8.11E-08	0.57	0.2735E-09
1.41	0.0	1.32	0.5592E-10
1.70	0.0	1.40	0.6022E-06
1.71	8.42E-04	1.53	0.2701E-03
1.78	1.40E-05	1.79	0.5697E-09
1.79	1.30E-03	2.01	0.1872E-01
2.64	0.0	2.03	0.3463E-02
2.79	0.0	2.19	0.2862E-05
2.82	7.68E-04	2.23	0.1489E-10
2.93	1.59E-02	2.41	0.2268E-02
2.94	0.0	2.64	0.1466E-05
2.94	3.50E-07	2.65	0.4671E-06
2.95	0.0	2.79	0.1630E-10
2.95	2.14E-02	2.81	0.6035E-01
3.05	5.30E-07	2.92	0.7163E-09
3.11	0.0	3.14	0.1891E-01
3.15	0.0	3.60	0.7388E-10
3.16	0.0	3.67	0.5484E-02
3.23	0.0	3.69	0.1069E-09

Table 15: $[(UO_2)_2]^{2+}_{[M=1]}$

Diamond shape		T-shape	
singlet–singlet			
Excitation energy [eV]	Intensity	Excitation energy [eV]	Intensity
0.10	0.3170E-05	0.02	1.23E-06
0.18	0.1226E-08	0.03	0.0
0.18	0.5550E-09	0.05	0.0
0.22	0.4742E-04	0.17	7.26E-08
0.26	0.3362E-03	0.18	3.83E-08
0.31	0.1703E-09	1.34	9.48E-04
1.22	0.3878E-04	1.50	1.83E-04
1.38	0.1556E-08	1.68	0.0
1.52	0.1283E-02	1.70	5.89E-05
1.64	0.2081E-07	1.74	0.0
2.23	0.5117E-05	2.33	0.0
2.74	0.5959	2.45	0.7237
3.06	0.2477E-07	2.47	0.0
3.17	0.4897E-07	2.69	0.2434
3.46	0.4900E-03	3.19	1.09E-02
singlet–triplet			
1.35	0.0	1.21	0.0
1.39	0.0	1.21	0.0
1.44	0.0	1.49	0.0
1.46	0.0	1.50	0.0
1.59	0.0	1.56	0.0
1.80	0.0	1.69	0.0
2.60	0.0	2.59	0.0
2.62	0.0	2.73	0.0
2.91	0.0	3.27	0.0
2.92	0.0	3.29	0.0

Table 16: $[(UO_2)_2]^{2+}_{[M=3]}$

Diamond shape		T-shape	
spin-unrestricted			
Excitation energy [eV]	Intensity	Excitation energy [eV]	Intensity
0.17	5.98E-04	0.20	0.0
0.31	0.0	0.23	0.5375E-05
1.56	1.11E-08	0.28	0.3366E-07
1.59	0.0	0.28	0.3116E-07
1.60	0.0	0.33	0.0
1.66	1.56E-04	0.44	0.4185E-05
1.73	0.0	1.61	0.4787E-05
1.73	2.62E-06	1.63	0.1633E-03
1.98	0.0	1.76	0.3868E-04
2.03	9.24E-04	1.76	0.1449E-05
2.58	4.53E-04	1.86	0.4191E-04
2.61	0.0	1.92	0.2188E-04
2.64	3.15E-05	2.10	0.1021E-03
2.65	1.30E-02	2.75	0.6171E-02
2.71	0.0	2.90	0.9229E-02
2.75	0.0	3.14	0.7987E-04
2.87	1.82E-03	3.53	0.4007E-05
2.88	0.0	3.53	0.2128E-05

Table 17: $[(UO_2)_2]^{2+}_{[M=5]}$

Diamond shape		T-shape	
spin-unrestricted			
Excitation energy [eV]	Intensity	Excitation energy [eV]	Intensity
0.36	0.3440E-05	0.44	1.52E-06
0.38	0.7835E-06	0.47	0.0
0.40	0.1185E-07	0.49	1.35E-10
0.42	0.1288E-05	0.56	3.21E-04
0.65	0.6016E-05	0.73	0.0
0.66	0.1165E-04	0.78	3.91E-09
1.08	0.2726E-05	0.81	1.48E-10
1.11	0.4296E-04	0.81	5.60E-09
1.43	0.1103E-04	0.86	0.0
1.47	0.9867E-04	1.00	0.0
1.62	0.5292E-04	1.06	8.62E-06
1.65	0.3962E-04	1.07	0.0
1.79	0.1704E-02	1.48	0.0
1.90	0.4657E-03	1.65	4.54E-07
2.18	0.8608E-02	1.66	7.97E-06

References

[1] TURBOMOLE V5.10 2008, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from `http://www.turbomole.com`.

[2] O. Treutler and R. Ahlrichs. Efficient molecular numerical integration schemes. *J. Chem. Phys.*, 102:346, 1995.

[3] M. von Arnim and R. Ahlrichs. Performance of parallel TURBOMOLE for density functional calculations. *J. Comput. Chem.*, 19:1746, 1998.

[4] J. P. Perdew. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. *Phys. Rev. B*, 33:8822–8824, 1986.

[5] A.D Becke. Density-functional exchange-energy approximation with correct asymphotic-behavior. *Phys. Rev. A*, 38:3098, 1988.

[6] K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs. Auxiliary basis sets for main row atoms and transition metals and their use to approximate Coulomb potentials. *Theor. Chem. Acc.*, 97:119, 1997.

[7] X. Cao and Michael Dolg. Segmented contraction scheme for small-core actinide pseudopotential basis sets. *J. Mol. Struct. (Theochem)*, 673:203–209, 2004.

[8] A. Nicklass, M. Dolg, H. Stoll, and H. Preuss. An-initio energy-adjusted pseudopotentials for the noble-gases ne through Xe - calculation of atomic dipole and quadrupole polarizabilities. *J. Chem. Phys.*, 102:8942, 1995.

[9] G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, and T. Ziegler. Chemistry with ADF. *J. Comput. Chem.*, 22:931–967, 2001.

[10] C. F. Guerra, J. G. Snijders, G. te Velde, and E. J. Baerends. Towards an Order-N DFT Method. *Theor. Chem. Acc.*, 99:391, 1998.

[11] ADF2013.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, `http://www.scm.com`.

[12] E. van Lenthe and E. J. Baerends. Optimized Slater-type basis sets for the elements 1-118. *J. Comput. Chem.*, 24:1142, 2003.

[13] M. Ernzerhof and G. Scuseria. Assessment of the Perdew-Burke-Ernzerhof exchange–correlation functionals. *J. Chem. Phys.*, 110:5029, 1999.

[14] E. van Lenthe, E. J. Baerends, and J. G. Snijders. Relativistic regular two–component Hamiltonians. *J. Chem. Phys.*, 99:4597, 1993.

[15] A. Klamt and G. Schürmann. COSMO - a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. *J. Chem. Soc. Perkin Trans.*, 2:799–805, 1993.