Supporting Information for:

"Hydration Energies of Zinc (II): Threshold Collision-induced Dissociation Experiments and Theoretical Studies" by Theresa Cooper, D. R. Carl, and P. B. Armentrout

Theoretical geometries of zinc water clusters. As described the text, geometry optimizations and frequency calculations were performed at the B3LYP/6-311+G(d,p) level of theory for $Zn^{2+}(H_2O)_n(H_2O)_m$, where *n* and *m* are the number of waters in the inner and outer shells, respectively, and complexes considered included $n = 1 – 4$ and $m = 0$, $n = 4$ and $m = 1 – 6$, $n = 5$ and $m = 0 – 5$, and $n = 6$ and $m = 0 – 4$. Single point energies including zero point energy corrections are calculated at four different levels of theory with a 6-311+G(2d,2p) basis set and relative energies are given for the lowest energy isomers in Table 3. Figures S1 and S2 shows the low-lying isomers of $Zn^{2+}(H_2O)_9$ and $Zn^{2+}(H_2O)_{10}$. In addition, a number of high energy isomers were investigated for all inner solvent shell sizes and this section details the geometries and relative energies of all isomers calculated for the zinc water complexes that are not explicitly described in the text. Tables S1 and S2 provide relative energies and critical bond angles and lengths, respectively, of all complexes. Figure S3 shows their geometries. Table S3 provides the experimental and theoretical 0 K bond energies for all reactant and product isomers analyzed in Table 3. Finally, Table S4 is a conversion of the 0 K thresholds in Table S3 to 298 K enthalpies and free energies.

Figures S3a and S3b show the structures of $Zn^{2+}(H_2O)_5$, which are described in the text. Figures S3c and S3d exhibit the geometries of the $Zn^{2+}(H_2O)_6$ complexes. In contrast to the (4,2)_2AA GS, the (4,2)_AA,A isomer has one second solvent shell water forming only one H-bond, thereby raising its energy by 4 – 8 kJ/mol, Table S1. In the (5,1)_A_aA_b and (5,1)_$A_aA_b$sym structures, where A_aA_b denotes a second water binding to both apex and base inner shell waters. In both of these structures, the sixth water binds in a similar fashion, such that (5,1)_$A_aA_b$sym is only slightly higher in energy (3 - 4 kJ/mol), Table S1. The (5,1)_$A_aA_b$sym structure maintains the symmetry of the inner solvent water molecules in the base found in both the (5,0) complexes, requiring that the apex water rotates to accommodate binding the sixth water bonding in a bridging site. The (5,1)_A_a isomer has the sixth water singly hydrogen bound to the apex of the square pyramid inner shell, whereas in (5,1)_A_bA_b, this water forms two H-bonds to the downward angled waters of the square pyramid base of (5,0).

Figures S3e and S3f show the structures of the $Zn^{2+}(H_2O)_7$ complexes. The (4,3) complexes include three isomers higher in energy than the (4,3)_3D,DD_2AA,A GS. The (4,3)_4D_AA,2A structure has two of the three second shell waters forming single H-bonds with different inner shell waters. Slightly higher in energy, (4,3)_2D,2DD_AA,2A is favored by free energy at the Bx levels. As discussed in the text, the (4,3)_2D,2DD_3AA isomer is highest in energy because of distortions in the inner shell tetrahedron as detailed in Table S2. From the (5,2)_4D_2A_bA_b GS, four high energy isomers were located, 1 - 12 kJ/mol higher in energy. The (5,2)_2D,DD_2A_aA_b structure allows both second shell waters to form two H-bonds to the inner shell, but are now bound between inner shell waters at the apex and base of the square

pyramid. The (5,2)_2D,DD_2A_bA_b structure is similar to (5,2)_4D_2A_bA_b GS except the second shell waters both H-bond to one inner shell water on the same side of the square pyramid. The (5,2)_3D_A_bA_b,$A_{a,trans}$ takes the (5,2)_4D_2A_bA_b GS structure and moves one of the second shell waters so that it is singly bound to the apex of the square pyramid and oriented trans to the AA water. Similar to this structure is the (5,2)_ 3D_A_bA_b,$A_{a,cis}$ complex, where now the A_a water is on the same side of the square pyramidal inner shell as the A_bA_b formation. This is the highest energy (5,2) complex.

We located six different (4,4) isomers, Figure S3g, each of which is progressively 1 – 4 kJ/mol higher in energy, Table S1. The (4,4)_2D,2DD_2AA,2A GS structure adds two single acceptor water molecules to the (4,2) GS or one to (4,3) GS. In (4,4)_3D,DD_AA,3A, only one second shell water forms two H-bonds with the inner shell, and three second shell waters form only one H-bond to the inner shell, with one of these sharing one inner shell water with the doubly H-bonded second shell water. Similar to the (4,4)_2D,2DD_2AA,2A GS, the (4,4)_2D,2DD_2AA,2A_share structure, two second shell waters are double H-bonded but share one inner shell water, with the remaining two second shell waters both singly H-bonded. The (4,4)_3D,DD_AA,A,AD,AA_p complex is similar to (4,4)_3D,DD_AA,3A except that two of the outer shell waters (those across from the double H-bonded second shell water) H-bond to one another, thereby forming a "pseudo third shell" and a ring-like series of H-bonds. This pseudo formation is denoted AD,AA_p, where the AD is both a single acceptor and a donor water molecule, and the AA_p is a double acceptor water that H-bonds to both the first and second solvent shell. The (4,4)_3D,DD_AA,A,AD,AA_p_share is again similar to the previous structure except now the doubly bound second shell water shares the inner shell water with the pseudo shell. The highest energy (4,4) isomer, (4,4)_2D,2DD_2AA,AD,AA_p, has two second shell waters forming two H-bonds to the inner shell and the remaining two in the H-bonded pseudo third shell. The (5,3) complex can form three isomers, the (5,3)_3AA GS, (5,3)_2AA,A, and (5,3)_AA,AAD,AA_p structures, Figure S3h, where each are ~ 7 kJ/mol higher in energy than each other at the Bx levels and 10 - 16 kJ/mol higher in energy than the GS at the Mx level. The (5,3)_2AA,A adds a water by a single H-bond to the apex of the square pyramid inner solvent shell water of (5,2)_2D,DD_2A_bA_b. The (5,3)_AA,AAD,AA_p structure H-bonds the third second shell water to the apex site and to one of the other second shell waters of (5,2), again creating this "pseudo third shell". The (6,2)_2D,DD_2AA GS and (6,2)_4D_2AA structures of Figure S3i are discussed previously in the text.

For the $Zn^{2+}(H_2O)_9$ complex, there are five high energy isomers located with a 4-coordinate inner shell, Figure S3j. The (4,5)_2D,2DD_AA,2A,AD,$AA_{p,trans}$ again demonstrates the ability of two second shell waters to H-bond to one another, with the remaining three waters forming a single, double, single H-bond pattern on the opposite (trans) side of the tetrahedral inner shell. Similar in energy and geometry is the (4,5)_2D,2DD_AA,2A,AD,$AA_{p,cis}$ where now the H-bond pattern is single, single, double opposite of the pseudo water formation. The (4,5)_D,3DD_2AA,A,AD,AA_p complex now has a double, single, double pattern for the remaining three second shell waters, where two of these share inner shell waters with the pseudo

formation. The remaining isomers are very similar in energy and involve the formation of a true third solvent shell, (4,4,1). Both (4,4,1)_3D,DD_AA,A,2AD_AA and (4,4,1)_4D_2A,2AD_AA are 20 kJ/mol higher in energy than the (4,5)_D,3DD_2AA,3A GS at the Bx levels and 37 – 57 kJ/mol higher at the Mx levels. In (4,4,1) _3D,DD_AA,A,2AD_AA, one of the second shell waters is doubly hydrogen bound to the inner shell, whereas in (4,4,1)_ 4D_2A,2AD_AA , all second solvent shell waters are singly bound to the first shell. Close in energy to the (5,4)_4A_bA_b GS is the (5,4)_2A_bA_b,2A_aA_b structure, Figure S3k, where two waters H-bond between the apex and base of the square pyramid and two waters form two H-bonds at the base of the pyramid maximizing the distance between each other. The remaining isomers have a similar naming scheme as discussed above where two of the complexes form a single H-bond to the apex of the pyramid, (5,4)_3A_bA_b,A_a and (5,4)_2A_bA_b,A_aA_b,A_a. The highest energy isomers both form a pseudo third shell with one water bound to both the first and second shell, (5,4)_AA,A,AAD,AA_p and (5,4)_2AA,AD,AA_p. The only high energy six coordinate isomer, (6,3)_4D,DD_3AA, is ~3 kJ/mol higher in energy than the (6,3)_6D_3AA GS because one inner shell water is shared between two second shell waters, Figure S3l.

Figures S3m, S3n, and S3o show the 4-, 5-, and 6-coordinate structures of $Zn^{2+}(H_2O)_{10}$, respectively. The (4,6)_2AA,4A GS forms a highly symmetric structure and is 10 and 20 kJ/mol lower in energy than the (4,5,1)_2AA,A,2AD_AA and (4,5,1)_AA,2A,AAD,AD_AA structures, where the tenth water forms a third solvent shell. The highest energy isomer is a (4,4,2)_4AD_2AA structure where two waters are both doubly H-bonded to pairs of waters in the second solvent shell. The (5,5)_4A_bA_b,A_a GS structure forms two higher energy isomers, similar in energy to each other. The (5,4,1)_3A_bA_b,A_bA_bD_A structure is similar to the (5,5) GS except the tenth water is now singly bound in the third shell at the base of the square pyramid. The (5,5)_3A_bA_b,A_bA_bD,AA_p allows the water hydrogen bound to the apex site in (5,5) GS to hydrogen bind to one of the other second shell waters. Slightly higher in energy than the (6,4)_4D,2DD_4AA GS, the (6,4)_4D,2DD_4AA_share structure has two inner solvent shell waters sharing with different second shell waters. Similar in energy is the (6,4)_5D,DD_3AA,A complex which takes (6,3) GS and singly H-bonds the tenth water molecule to the inner shell. The (6,4)_5D,DD_2AA,AD,AA_p complex is the highest energy isomer and H-bonds the singly bound second shell water of (6,4)_5D,DD_3AA,A with another second shell water.

Table S1. Relative calculated enthalpy (ΔH_0) and free energies (ΔG_{298})[a] (kJ/mol) of $Zn^{2+}(H_2O)_x(H_2O)_y$ where *x* is the number of waters in the inner solvent shell and *y* is the number of waters in the second shell.[b]

Complex (*x*,*y*)		B3LYP	B3P86	M06	MP2(full)
$Zn^{2+}(H_2O)_5$	(4,1)_AA	0.0 (2.6)	0.0 (2.9)	6.5 (8.2)	3.3 (4.3)
	(4,1)_A	1.1 (0.0)	0.8 (0.0)	14.9 (12.9)	8.4 (5.7)
	(5,0)	4.2 (5.8)	4.6 (6.4)	0.0 (0.6)	0.0 (0.0)
	(5,0)_switch	5.8 (5.4)	6.0 (5.8)	1.4 (0.0)	2.4 (0.3)
$Zn^{2+}(H_2O)_6$	(4,2)_2AA	0.0 (0.0)	0.0 (0.0)	13.1 (12.8)	3.8 (7.5)
	(4,2)_AA,A	4.5 (0.5)	4.4 (0.4)	26.1 (21.8)	11.7 (11.4)
	(5,1)_A_aA_b	8.2 (0.3)	8.6 (0.6)	12.2 (4.1)	4.2 (0.0)
	(5,1)_A_aA_b_sym	11.7 (8.0)	12.3 (8.6)	16.6 (12.8)	7.7 (7.8)
	(5,1)_A_a	17.1 (3.1)	17.4 (3.3)	26.6 (12.4)	16.9 (6.6)
	(5,1)_A_bA_b	18.9 (14.8)	19.2 (15.1)	21.9 (17.5)	15.3 (14.9)
	(6,0)	13.7 (14.0)	14.6 (14.8)	0.0 (0.0)	0.0 (3.9)
$Zn^{2+}(H_2O)_7$	(4,3)_3D,DD_2AA,A	0.0 (6.5)	0.0 (6.5)	14.9 (9.6)	10.8 (5.5)
	(4,3)_4D_AA,2A	1.9 (5.4)	1.6 (5.0)	21.6 (13.2)	16.1 (7.7)
	(4,3)_2D,DD_AA,2A	4.1 (0.0)	4.1 (0.0)	23.6 (7.7)	18.0 (2.1)
	(4,3)_2D,2DD_3AA	10.1 (23.0)	10.2 (23.0)	17.9 (18.9)	18.1 (19.1)
	(5,2)_4D_2A_bA_b	0.2 (12.0)	0.1 (12.0)	0.0 (0.0)	0.0 (0.0)
	(5,2)_2D,2DD_2A_aA_b	4.6 (14.6)	5.0 (15.0)	5.4 (3.6)	4.2 (2.4)
	(5,2)_2D,DD_2A_bA_b	7.3 (16.9)	7.4 (17.0)	8.8 (6.6)	7.0 (4.8)
	(5,2)_3D_A_bA_b,$A_{a,trans}$	7.5 (11.8)	7.4 (11.7)	11.5 (4.0)	10.4 (2.9)
	(5,2)_3D_A_bA_b,$A_{a,cis}$	8.4 (13.2)	8.4 (13.1)	15.7 (8.6)	11.5 (4.4)
	(6,1)_AA	18.4 (31.3)	18.7 (31.6)	3.2 (4.3)	8.7 (9.7)
$Zn^{2+}(H_2O)_8$	(4,4)_2D,2DD_2AA,2A	1.8 (0.0)	2.4 (0.1)	21.4 (12.5)	14.9 (6.1)

	(4,4)_3D,DD_AA,3A	4.2 (0.0)	4.8 (0.0)	28.2 (16.9)	20.7 (9.4)
	(4,4)_2D,2DD_2AA,2A_share	7.2 (3.0)	7.7 (2.9)	27.3 (15.9)	20.8 (9.4)
	(4,4)_3D,DD_AA,A,AD,AA_p	8.9 (6.6)	9.6 (6.6)	31.5 (21.0)	23.0 (13.5)
	(4,4)_3D,DD_AA,A,AD,AA_p	12.7 (8.1)	13.5 (8.4)	35.0 (23.3)	26.7 (15.0)
	(4,4)_2D,2DD_2AA,AD,AA_p	16.5 (19.2)	17.1 (19.4)	32.6 (28.3)	27.5 (23.1)
	(5,3)_3AA	0.0 (7.1)	0.0 (6.6)	0.0 (0.0)	0.0 (0.0)
	(5,3)_2AA,A	7.6 (7.9)	7.9 (7.6)	15.5 (8.6)	10.6 (3.7)
	(5,3)_AA,AAD,AA_p	14.0 (21.4)	14.3 (21.2)	12.4 (12.7)	13.2 (13.5)
	(6,2)_2D,DD_2AA	16.8 (23.5)	17.7 (23.9)	2.1 (1.7)	6.7 (6.3)
	(6,2)_4D_2AA	17.7 (25.0)	17.8 (24.6)	2.0 (2.2)	7.3 (7.5)
$Zn^{2+}(H_2O)_9$	(4,5)_D,3DD_2AA,3A	5.8 (0.0)	6.3 (0.0)	30.7 (14.6)	22.1 (6.0)
	(4,5)_2D,2DD_AA,2A,AD,$AA_{p,trans}$	11.9 (6.5)	12.5 (6.6)	40.0 (24.3)	28.8 (13.1)
	(4,5)_2D,2DD_AA,2A,AD,$AA_{p,cis}$	13.9 (9.8)	14.4 (9.7)	41.8 (27.4)	30.6 (16.2)
	(4,5)_D,3DD_2AA,A,AD,AA_p	15.0 (16.9)	15.5 (16.9)	37.5 (29.1)	28.9 (20.5)
	(4,4,1)_3D,DD_AA,A,2AD_AA	18.7 (23.0)	18.8 (22.6)	49.1 (43.1)	37.0 (30.9)
	(4,4,1)_4D_2A,2AD_AA	19.9 (10.4)	19.7 (9.6)	57.1 (37.2)	42.1 (22.2)
	(5,4)_$4A_bA_b$	0.0 (10.3)	0.0 (9.8)	0.0 (0.0)	0.0 (0.0)
	(5,4)_$2A_bA_b$,$2A_aA_b$	1.25 (12.8)	0.8 (11.8)	3.8 (5.0)	1.9 (3.1)
	(5,4)_$3A_bA_b$,A_a	7.0 (9.5)	7.1 (9.0)	12.7 (4.9)	10.2 (2.5)
	(5,4)_$2A_bA_b$,A_aA_b,A_a	9.2 (12.9)	9.1 (12.4)	16.7 (10.2)	12.5 (6.0)
	(5,4)_AA,A,AAD,AA_p	11.4 (19.6)	11.4 (19.1)	12.1 (10.0)	11.1 (9.0)
	(5,4)_2AA,AD,AA_p	14.9 (19.3)	14.8 (18.7)	23.6 (17.7)	19.1 (13.2)
	(6,3)_6D_3AA	13.5 (27.9)	13.1 (26.9)	2.8 (7.0)	3.9 (8.0)
	(6,3)_4D,DD_3AA	16.9 (26.0)	16.7 (25.3)	4.5 (3.4)	7.2 (6.0)
$Zn^{2+}(H_2O)_{10}$	(4,6)_2AA,4A	3.5 (0.0)	4.4 (0.0)	26.9 (16.3)	18.6 (8.0)
	(4,5,1)_2AA,A,2AD_AA	13.7 (18.7)	14.1 (18.2)	38.4 (36.2)	27.7 (25.6)

(4,5,1)_AA,A,AAD,AD_AA	22.1 (24.7)	21.9 (23.7)	44.6 (40.2)	35.8 (31.5)
(4,4,2)_4AD_2AA	22.9 (24.6)	22.5 (23.3)	58.1 (52.6)	41.7 (36.3)
(5,5)_4A_bA_b,A_a	0.0 (7.1)	0.0 (6.2)	0.0 (0.0)	0.0 (0.0)
(5,4,1)_3A_bA_b,AAD_A	5.6 (15.8)	4.4 (13.7)	5.4 (8.5)	6.7 (9.8)
(5,5)_3A_bA_b,A_bA_bD,AA_p	6.0 (21.7)	6.0 (20.9)	0.6 (9.2)	2.2 (10.9)
(6,4)_4D,2DD_4AA	18.1 (35.5)	16.9 (33.5)	0.0 (10.4)	5.5 (15.9)
(6,4)_4D,2DD_4AA_share	19.6 (34.2)	19.0 (32.8)	3.2 (10.7)	6.8 (14.3)
(6,4)_5D,DD_3AA,A	19.8 (29.3)	19.7 (28.4)	4.0 (6.5)	8.7 (11.2)
(6,4)_5D,DD_2AA,AAD,AA_p	20.3 (37.1)	19.6 (35.6)	0.1 (9.9)	6.6 (16.4)

[a] ΔG_{298} values given in parentheses.

[b] Values are single point energies calculated at the level shown using a 6-311+G(2d,2p) basis set with geometries calculated at the B3LYP/6-311+G(d,p) level. Zero point energy corrections are included.

Table S2. B3LYP/6-311+G(d,p) geometry optimized structures for the ground state of all inner shell sizes of $Zn^{2+}(H_2O)_{5\text{-}10}$ [a]

Complex	Sym	r(ZnO) (Å)	∠OZnO (°)[b]	∠ZnOH (°)	r(OH) (Å)[c]	r(O•••H) (Å)[d]	∠HOH (°)
(4,1)_AA	C_2	1.984 (2)	95.0, 104.5, 111.3 (2), 117.6 (2)	117.8 (2),130.8 (2)	0.988 (2), 0.970 (2)		110.4 (2)
		2.008 (2)		125.0 (2),126.8 (2)	0.970 (4)		107.6 (2)
		3.642		127.0	0.974 (2)	1.812 (2)	106.0
(4,1)_A	C_1	1.943	103.9, 104.6, 110.6 (2), 111.4, 115,8	127.0, 124.3	1.034, 0.969		108.6
		2.014		126.1, 125.8	0.969 (2)		107.8
		2.020		124.7, 127.7	0.970 (2)		107.5
		2.022		124.6, 127.7	0.970 (2)		107.5
		3.993		126.7, 126.4	0.967 (2)	1.486	106.9
(5,0)	C_{2v}	2.038 (2)	88.0 (4), 95.9 (2), 109.8 (2), 140.4, 168.1	126.0 (4)	0.968 (4)		108.0 (2)
		2.055		126.6 (2)	0.965 (2)		106.8
		2.127 (2)		124.6 (2),128.4 (2)	0.969 (4)		106.9 (2)
(5,0)_switch	C_{2v}	2.042	87.6 (4), 98.9 (2), 105.9 (2), 148.3, 162.3	127.5 (2)	0.953 (2)		104.9
		2.065 (2)		126.4 (4)	0.967 (4)		107.1 (2)
		2.107 (2)		126.9 (4)	0.969 (4)		107.1 (2)
(4,2)_2AA	D_{2d}	1.992 (4)	93.0 (2), 118.3 (4)	119.1 (4),130.3 (4)	0.986(4), 0.967 (4)		110.6 (4)
		3.688 (2)		127.4 (4)	0.970 (4)	1.816 (4)	105.2 (2)
(4,2)_AA,A	C_1	1.950	93.4, 104.9, 107.4, 112.9, 116.7, 121.4	126.8, 124.0	1.026, 0.966		108.6
		1.996		118.9, 130.6	0.985, 0.967		110.5
		2.002		118.6, 130.5	0.985, 0.967		110.3
		2.028		126.4, 125.7	0.969 (2)		107.9
		3.689		126.6, 128.3	0.970 (2)	1.823 (2)	105.2
		4.011		125.1, 128.1	0.966 (2)	1.513	106.8
(5,1)_A_aA_b	C_1	2.020	86.2, 86.6, 89.2, 90.9, 93.3, 93.7, 114.0, 121.8, 124.2, 179.9	122.1,127.9	0.986, 0.966		110.0
		2.051		124.3,127.7	0.968 (2)		108.0
		2.084		124.7,126.5	0.968 (2)		107.2
		2.087		121.0,129.1	0.982, 0.966		109.2
		2.123		123.2,128.7	0.968 (2)		107.2

		3.847		129.0,125.7	0.969 (2)	1.786,1.850	105.3
(5,1)_A_aA_b_sym	C_1	2.021	86.8, 87.2, 88.1, 90.1, 90.8, 97.3,	119.6, 131.2	0.969 (2)		107.9
		2.048	117.4, 118.3, 124.3, 174.6	125.9, 125.2	0.967 (2)		107.9
		2.051		125.7, 125.2	0.967 (2)		107.7
		2.102		119.3, 131.9	0.982, 0.966		108.8
		2.148		125.3, 128.2	0.968 (2)		106.5
		3.819		127.2, 127.4	0.969 (2)	1.847, 1.774	105.3
(5,1)_A_a	C_s	2.002	88.6 (2), 89.1 (2), 92.0 (2), 111.1,	128.9, 124.7	1.016, 0.966		108.4
		2.044	119.2, 129.7, 175.9	125.4 (2)	0.970 (2)		108.9
		2.086		126.7, 126.1	0.968 (2)		107.3
		2.123 (2)		123.8 (2), 127.8 (2)	0.967 (4)		107.2 (2)
		4.073		126.8 (2)	0.965 (2)	1.556	106.3
(5,1)_A_bA_b	C_2	2.034	85.5 (2), 88.9 (2), 96.2, 98.4 (2),	125.6 (2)	0.968 (2)		108.7
		2.041 (2)	131.9 (2), 169.0	116.0 (2), 130.5 (2)	0.984 (2), 0.967 (2)		109.5 (2)
		2.134 (2)		122.0 (2), 129.1 (2)	0.968 (4)		107.1 (2)
		3.673		127.6 (2)	0.970 (2)	1.851 (2)	104.9
(6,0)	T_h	2.128 (6)	90 (12), 180 (3)	126.0 (12)	0.971 (12)		108.1 (6)
(4,3)_3D,DD	C_s	1.948	91.9, 96.0, 114.6 (2), 120.7 (2)	118.3,130.6	0.976,1.011		111.1
_2AA,A		2.000		118.0,131.2	0.988,0.966		110.8
		2.004 (2)		119.7 (2),129.8 (2)	0.984 (2), 0.966 (2)		110.5 (2)
		3.678		127.4 (2)	0.969 (2)	1.766,1.968	105.2
		3.726		127.2,127.5	0.969 (2)	1.826 (2)	107.0
		4.107		126.3 (2)	0.966 (2)	1.563	105.2
(4,3)_4D_AA,2A	C_2	1.959 (2)	91.3, 109.4 (2), 112.7, 116.3 (2)	128.9 (2), 122.4 (2)	1.017 (2), 0.966 (2)		108.6 (2)
		2.022 (2)		119.6 (2), 129.6 (2)	0.984 (2), 0.966 (2)		110.1 (2)
		3.348		127.3 (2)	0.966 (4)	1.547 (2)	106.7 (2)
		4.095 (2)		125.4 (2), 127.9 (2)	0.970 (2)	1.828 (2)	105.4
(4,3)_2D,DD	C_1	1.955	96.6 (2), 101.4, 107.8, 113.3, 117.8,	118.2, 130.7	0.976, 1.010		
_AA,A		1.965	120.0	126.6, 123.2	1.018, 0.966		

		2.001		117.5, 131.6	0.988, 0.966		110.8
		2.039		124.9, 126.9	0.968 (2)		108.0
		3.670		126.1, 128.7	0.969 (2)	1.765, 1.982	105.2
		4.033		128.5, 124.8	0.966 (2)	1.542	106.6
		4.108		124.7, 128.3	0.966 (2)	1.568	106.6
(4,3)_2D,2DD _3AA	C_2	1.992 (2)	95.0 (2), 98.7, 107.8, 132.8 (2)	119.9 (2), 117.6 (2)	0.978 (2), 0.981 (2)		111.4 (2)
		1.993 (2)		118.0 (2), 132.2 (2)	0.988 (2), 0.966 (2)		110.8 (2)
		3.644		127.7 (2)	0.967 (2)	1.896	104.6
		3.688 (2)		123.9 (2), 131.0 (2)	0.969 (4)	1.785 (2), 1.947 (2)	105.1 (2)
(5,2)_4D_2A_bA_b	C_2	2.031 (2)	86.2 (2), 89.3 (2), 94.5 (2), 118.9 (2), 122.3, 178.6	122.2 (2),127.4 (2)	0.984 (2), 0.965 (2)		110.0 (2)
		2.061		126.0 (2)	0.966 (2)		108.0
		2.105 (2)		120.7 (2),130.2 (2)	0.981 (2), 0.466 (2)		109.0 (2)
		3.874 (2)		127.2 (2),127.4 (2)	0.968 (4)	1.804,1.849	105.3 (2)
(5,2)_2D,2DD _2A_aA_b	C_{2v}	2.011	88.1 (2), 91.0 (4), 117.1, 121.5, 176.2	123.8 (2)	0.978 (2)		112.3
		2.060 (2)		125.7 (4)	0.978 (4)		108.0 (2)
		2.101 (2)		118.3 (2), 132.9 (2)	0.984 (2), 0.965 (2)		108.9 (2)
		3.845 (2)		127.3 (4)	0.969 (4)	1.819 (2), 1.871 (2)	105.4 (2)
(5,2)_2D,DD _2A_bA_b	C_s	2.023 (2)	86.5, 89.3, 91.0 (4), 117.5 (2), 125.0, 175.8	118.5 (2), 130.1 (2)	0.987 (2), 0.965 (2),		109.4
		2.056		122.6, 128.8	0.967 (2)		109.4
		2.093		121.0 (2)	0.959 (2)		106.2
		2.133		121.8 (2)	1.033 (2)		115.5
		3.802 (2)		132.1 (2), 122.7 (2)	0.969 (2)	1.774 (2), 2.007 (2)	105.1 (2)
(5,2)_3D_A_bA_b,A_a ,trans	C_1	2.004	85.4, 86.8, 87.6, 89.4, 91.2, 100.9,	128.2, 123.0	1.011, 0.965		108.1

		2.034	116.0, 117.8, 126.2, 167.9	123.1, 126.9	0.984, 0.965		109.9
		2.054		123.6, 127.8	0.967 (2)		108.5
		2.111		120.2, 126.2	0.982, 0.966		108.4
		2.147		129.7, 122.9	0.967 (2)		107.4
		2.893		128.9, 125.8	0.969 (2)	1.801, 1.849	105.3
		4.135		123.5, 130.0	0.969 (2)	1.576	106.4
(5,2)_3D_A_bA_b,A_a ,cis	C_1	2.002	86.0, 86.4, 89.3, 90.6, 100.6, 111.8,	123.6, 127.6	0.965, 1.011		108.2
		2.026	123.6, 124.5, 168.6, 87.8	122.6, 127.3	0.985, 0.965		110.0
		2.060		127.9, 123.6	0.967 (2)		108.4
		2.113		120.2, 126.2	0.981, 0.966		108.4
		2.154		130.1, 122.6	0.967 (2)		107.3
		3.881		125.1, 129.6	0.969 (2)	1.866, 1.793	105.3
		4.123		127.2, 126.3	0.966 (2)	1.573	108.2
(6,1)_AA	C_1	2.102	84.0 (2), 85.7, 86.6, 88.5, 89.0, 90.1,	119.7/129.5	0.981, 0.965		108.1
		2.107	92.7, 93.0, 94.7, 96.0 (2), 167.9, 178.3,	122.0,128.7	0.981, 0.965		109.2
		2.135	179.6	124.9,125.8	0.967 (2)		108.2
		2.147		123.7,124.2	0.966,0.967		107.0
		2.149		124.4,124.7	0.966,0.967		107.1
		2.150		120.6,131.8	0.967 (2)		107.2
		3.92		126.2,128.7	0.969 (2)	1.844, 1.845	105.1
(4,4)_2D,2DD _2AA,2A	C_2	1.958 (2)	94.7 (2), 111.0, 116.6 (2), 124.4	118.5 (2),130.5 (2)	0.975 (2), 1.005 (2)		111.0 (2)
		2.009 (2)		118.7 (2),130.7 (2)	0.986 (2), 0.965 (2)		110.6 (2)
		3.724 (2)		127.3 (2),127.4 (2)	0.968 (2), 0.969(2)	1.816 (2), 1.943 (2)	105.2 (2)
		4.141 (2)		126.2 (2),126.5 (2)	0.965 (4)	1.587 (2)	106.8 (2)
(4,4)_3D,DD _AA,2A	C_1	1.971	94.7, 107.1, 110.6, 111.5, 113.1, 119.7	118.8, 129.7	0.974, 1.004		110.8
		1.972		127.1, 124.2	1.010, 0.965		108.7
		1.979		128.3, 123.1	1.009, 0.965		108.6
		2.016		118.4, 131.0	0.986, 0.965		110.5
		3.723		128.1, 126.7	0.968 (2)	1.787, 1.971	105.2

		4.078		128.9, 124.6	0.966 (2)	1.571	106.5
		4.118		128.3, 125.2	0.966 (2)	1.578	106.5
		4.126		118.8, 129.7	0.965 (2)	1.595	106.5
(4,4)_2D,2DD	C_1	1.964	95.1, 98.9, 108.0, 109.0, 121.3, 125.0	116.7, 131.9	0.976, 1.005		111.1
_2AA,2A_share		1.967		128.2, 122.4	1.012, 0.965		108.7
		2.010		118.1, 131.0	0.985, 0.965		110.7
		2.011		116.6, 119.3	0.981, 0.976		110.9
		3.649		132.6, 122.5	0.968 (2)	1.865, 1.953	105.0
		3.715		130.4, 124.5	0.968 (2)	1.971, 1.798	105.1
		4.098		124.2, 129.1	0.966 (2)	1.567	106.6
		4.154		129.4, 123.4	0.965 (2)	1.586	106.7
(4,4)_3D,DD	C_1	1.958	94.4, 102.7, 111.5, 112.7, 113.2, 122.7	124.0, 125.9	1.077, 0.965		110.2
_AA,A,AD,AA_p		1.963		118.6, 129.7	0.975, 1.007		110.8
		2.004		128.0, 123.4	0.994, 0.965		108.6
		2.020		118.5, 130.8	0.986, 0.965		110.6
		3.716		126.6, 128.1	0.969 (2)	1.777, 1.954	105.2
		3.898		98.2, 152.9	0.969, 0.965	1.532	108.9
		4.127		129.9, 122.6	0.965 (2)	1.580	106.8
		4.241		119.9, 129.6	0.968, 0.969	1.715, 2.056	105.4
(4,4)_3D,DD	C_1	1.961	95.4, 108.4, 109.6, 110.3, 115.3, 117.4	119.7, 128.3	1.013, 0.964		110.8
_AA,A,AD,AA_p		1.969		127.0, 124.2	1.013, 0.965		108.8
		2.001		117.7, 126.0	0.977, 0.989		110.5
		2.014		118.1, 130.4	0.985, 0.966		110.4
		3.705		128.0, 126.8	0.969 (2)	1.798, 1.949	105.1
		3.780		94.8, 156.1	0.970, 0.964	1.553	108.7
		4.076		125.7, 127.2	0.965 (2)	1.558	106.8
		4.166		132.0, 119.1	0.968 (2)	1.761, 2.040	105.1
(4,4)_2D,2DD	C_1	1.957	94.7, 98.9, 106.0, 109.0, 123.3, 126.4	120.8, 128.1	1.015, 0.965		111.0
_2AA,AD,AA_p		1.990		116.0, 128.0	0.978, 0.989		110.8
		2.000		116.8, 118.6	0.981, 0.978		110.8
		2.013		118.1, 129.6	0.984, 0.966		110.4
		3.649		124.5, 130.5	0.969 (2)	1.877, 1.926	105.0
		3.709		131.5, 123.5	0.969 (2)	1.821, 1.926	105.1

		3.796		96.3, 154.5	0.970, 0.965	1.541	108.8
		4.207		129.8, 128.9	0.968 (2)	1.756, 2.026	105.2
(5,3)_3AA	C_s	2.04	86.6, 87.7 (2), 91.9 (2), 94.3, 116.2 (2),	123.4,126.3	0.981, 0.965		110.3
		2.089	127.6, 179.0	119.2 (2)	0.977 (2)		109.3
		2.144		120.0,131.0	0.965, 0.981		109
		2.039 (2)		121.2 (2),127.3 (2)	0.984 (2), 0.965 (2)		209.8 (2)
		3.875 (2)		124.8 (2),129.9 (2)	0.968 (4)	1.799 (2), 1.926 (2)	105.2 (2)
		3.884		127.4 (2)	0.968 (2)	1.836,1.856	105.3
(5,3)_2AA,A	C_1	2.012	86.2, 87.2, 87.3, 87.4, 95.9, 96.7,	128.3, 123.3	1.006, 0.965		108.2
		2.020	108.9, 124.3, 126.8, 167.1	122.8, 122.7	0.978 (2)		111.3
		2.067		124.4, 125.1	0.966 (2)		108.7
		2.118		119.1, 125.7	0.980, 0.965		108.4
		2.126		118.6, 124.9	0.980, 0.966		108.0
		3.896 (2)		128.4 (2), 126.3 (2)	0.968 (4)	1.870 (2), 1.851 (2)	105.3
		4.162		128.9, 124.7	0.966 (2)	1.597	106.2
(6,2)_2D,DD	C_{2v}	2.080	82.5 (2), 86.3 (2), 90.5 (4), 93.7 (2),	123.9 (2)	0.980 (2)		112.2
_2AA		2.109 (2)	97.5 (2), 165.0, 172.0, 180.0	121.3 (2),129.2 (2)	0.981 (2), 0.965 (2)		109.5 (2)
		2.125		125.7 (2)	0.966 (2)		108.6
		2.171 (2)		123.6 (4)	0.967 (4)		107.0 (2)
		3.935 (2)		127.5 (4)	0.968 (4)	1.928 (2), 1.838 (2)	105.1 (2)
(6,2)_4D_2AA	C_2	2.105 (2)	84.5 (2), 84.8 (2), 87.3 (2), 89.3 (2), 89.7, 99.4 (2) 102.6, 169.3 (2), 170.6	122.4 (2), 124.5 (2)	0.980 (2), 0.965 (2)		109.1 (2)
		2.128 (2)		121.8 (2), 124.2 (2)	0.980 (2), 0.965 (2)		108.9 (2)
		2.157 (2)		116.7 (2), 131.9 (2)	0.967 (2), 0.966 (2)		107.0 (2)
		3.960 (2)		127.3 (2), 127.5 (2)	0.968 (4)	1.860 (2), 1.869 (2)	105.1 (2)

(4,5)_D,3DD _2AA,3A	C_s	1.969	93.3, 94.4, 113.7 (2), 121.5 (2)	119.3,130.0	0.973, 1.001		110.8
		1.972 (2)		117.7 (2),131.1 (2)	0.977 (2), 1.000 (2)		111.1 (2)
		2.027		119.2,130.1	0.983,0.963		110.7
		3.695		126.3,127.9	0.968 (2)	1.851 (2)	105.2
		3.752		123.9 (2)	1.030 (2)	1.794, 1.960	112.2
		4.155		126.2 (2)	0.974 (2)	1.606	106.5
		4.178 (2)		127.8 (2),125.2 (2)	0.965 (4)	1.675 (2)	106.6 (2)
(4,5)_2D,2DD _AA,2A,AD,$AA_{p,trans}$	C_1	1.970	91.1, 101.3, 109.8, 113.8, 115.7, 123.0	124.2, 125.4	1.012, 0.964		110.1
		1.973		117.3, 130.4	0.977, 1.000		110.8
		1.974		117.5, 131.5	0.977, 1.000		110.9
		2.018		128.3, 123.0	0.990, 0.965		108.5
		3.689		126.4, 128.4	0.968 (2)	1.898 (2)	105.2
		3.927		98.6, 152.4	0.969, 0.964	1.551	108.9
		4.169		131.1, 121.7	0.965 (2)	1.612	106.6
		4.191		125.8, 127.4	0.965 (2)	1.614	106.4
		4.285		118.8, 130.5	0.968 (2)	1.744, 2.048	105.3
(4,5)_2D,2DD _AA,2A,AD,$AA_{p,cis}$	C_1	1.964	97.9, 100.8, 107.9, 115.1, 115.8, 120.0	117.7, 131.0	0.976, 1.002		111.3
		1.978		129.7, 121.3	1.006, 0.965		109.0
		1.987		118.3, 126.8	1.009, 0.964		110.1
		2.006		116.8, 127.4	0.978, 0.985		111.0
		3.678		125.4, 129.4	0.968 (2)	1.921, 1.889	105.1
		3.775		95.2, 155.4	0.971, 0.964	1.568	108.7
		4.151		125.9, 127.4	0.965 (2)	1.589	106.6
		4.158		126.4, 126.0	0.965 (2)	1.603	106.6
		4.218		129.4, 121.7	0.968 (2)	1.791, 2.011	105.2
(4,5)_D,3DD _2AA,A,AD,AA_p	C_1	1.962	95.0, 97.3, 110.2, 109.7, 119.0, 127.6	118.0, 130.2	0.976, 1.003		110.8
		1.964		118.0, 120.2	0.975, 1.005		110.7
		1.997		116.8, 127.2	0.979, 0.986		111.2
		2.024		118.2, 130.5	0.984, 0.965		110.5
		3.686		124.8, 130.0	0.968 (2)	1.875, 1.925	105.2

		3.720		130.6, 124.2	0.968 (2)	1.800, 1.968	105.2
		3.841		95.2, 154.1	0.969, 0.964	1.583	108.8
		4.138		130.3, 122.4	0.965 (2)	1.598	106.7
		4.211		116.5, 133.8	0.968 (2)	1.783, 2.055	105.0
(4,4,1)_3D,DD _AA,A,2AD_AA	C_1	1.964	96.5, 102.8, 108.8, 110.0, 118.2, 120.5	119.0, 126.0	0.973, 1.009		111.4
		1.965		124.3, 125.5	1.017, 0.964		109.9
		1.981		128.8, 121.9	1.009, 0.965		108.6
		2.031		116.8, 130.0	0.986, 0.965		110.3
		3.702		130.1, 124.7	0.968 (2)	1.785, 2.013	105.2
		3.966		114.4, 136.9	0.977, 0.964	1.535	108.1
		4.011		113.3, 136.9	0.975, 0.964	1.563	108.1
		4.127		131.2, 122.2	0.965 (2)	1.577	106.6
		5.557		123.0, 131.7	0.968 (2)	1.875, 1.895	105.3
(4,4,1)_4D _2A,2AD_AA	C_1	1.975	107.2, 108.0, 108.7, 108.9, 110.1, 112.9	126.3, 124.5	1.016, 0.964		109.2
		1.981		126.3, 123.1	1.017, 0.964		108.8
		1.993		127.5, 124.2	1.008, 0.965		108.3
		1.979		128.0, 127.8	1.007, 0.965		108.9
		4.044		112.7, 138.4	0.967, 0.964	1.536	108.2
		4.045		114.5, 140.1	0.976, 0.964	1.544	107.9
		4.114		124.6, 128.7	0.965 (2)	1.585	106.6
		4.135		124.4, 128.9	0.965 (2)	1.582	106.6
		5.563		115.9, 138.9	0.968 (2)	1.881, 1.885	105.2
(5,4)_4A_bA_b	C_{2v}	2.030 (2)	89.5 (4), 91.3 (2), 112.7 (2), 134.6, **177.5**	123.1 (4)	0.980 (4)		112.9 (2)
		2.076		125.7 (2)	0.965 (2)		108.6
		2.083 (2)		119.3 (4)	0.974 (4)		109.7 (2)
		3.860 (4)		125.2 (4),129.7 (4)	0.968 (8)	1.912 (4), 1.880 (4)	105.2 (4)
(5,4)_3A_b	C_2	2.028	89.0 (2), 89.2 (2), 91.8 (2), 113.6, 123.2 (2), 178.6	123.6 (2)	0.979 (2)		112.8
		2.045 (2)		122.3 (2), 126.9 (2)	0.981 (2), 0.964 (2)		110.6 (2)
		2.093 (2)		118.8 (2), 118.1 (2)	0.976 (2), 0.977 (2)		109.1 (2)
		3.865 (2)		131.7 (2), 123.1 (2)	0.968 (4)	1.830 (2),	105.2 (2)

		3.870 (2)		130.7 (2), 124.1 (2)	0.968 (4)	1.945 (2) 1.869 (2), 1.918 (2)	105.2 (2)
(5,4)_3A_bA_b,A_a	C_1	2.010	82.3, 85.2, 88.5, 91.0, 92.9, 96.5,	128.3, 123.2	1.00, 0.964		108.4
		2.034	113.7, 118.1, 128.2, 170.4	122.6, 125.4	0.978, 0.976		112.0
		2.051		121.5, 128.1	0.982, 0.964		110.0
		2.092		119.4, 121.1	0.976, 0.975		109.7
		2.132		120.5, 130.4	0.980, 0.964		108.9
		3.878		131.5, 123.3	0.968 (2)	1.859, 1.921	105.2
		3.897		131.5, 123.2	0.968 (2)	1.808, 1.949	105.3
		3.937		126.2, 128.4	0.968 (2)	1.886, 1.846	105.4
		4.207		129.7, 123.9	0.965 (2)	1.626	106.4
(5,4)	C_s	1.995	86.5 (2), 88.5, 89.2 (2), 101.2,	120.9, 129.4	0.974, 0.996		109.7
_2A_bA_b,A_aA_b,A_a		2.056 (2)	116.2 (2), 127.4, 170.3	121.9 (2), 126.3 (2)	0.981 (2), 0.964 (2)		109.2 (2)
		2.088		120.8 (2)	0.975 (2)		109.4
		2.133		119.6, 131.1	0.981, 0.964		109.2
		3.881		127.3 (2)	0.968 (2)	1.826, 1.929	105.3
		3.911 (2)		129.5 (2), 125.1 (2)	0.968 (4)	1.811 (2), 1.931 (2)	105.3 (2)
		4.240		126.8 (2)	0.962 (2)	1.647	106.0
(5,4)	C_1	2.030	82.2, 85.4, 88.9, 93.1, 93.6, 94.2,	122.5, 124.8	0.979, 0.977		111.9
_AA,A,AAD,AA_p		2.050	100.1, 125.5, 134.4, 171.4	118.0, 130.8	0.983, 0.964		110.7
		2.059		122.1, 126.5	0.984, 0.964		108.9
		2.081		122.2, 119.6	0.975 (2)		111.3
		2.097		121.8, 128.1	0.980, 0.964		109.4
		3.660		96.1, 156.7	0.975, 0.966	1.811, 1.913	107.2
		3.894		126.8, 127.9	0.968 (2)	1.844, 1.917	105.3
		3.922		128.2, 126.4	0.938 (2)	1.886, 1.841	105.4
		4.150		126.3, 126.9	0.938 (2)	2.006	105.0
(5,4)	C_1	1.993	85.6, 86.7, 88.5, 88.9, 95.8, 96.3,	126.7, 122.7	1.007, 0.964		109.7
_2AA,AD,AA_p		2.055	114.8, 115.8, 129.3, 167.9	120.8, 125.4	0.983, 0.964		109.5
		2.057		121.9, 125.8	0.982, 0.964		109.6

		2.105		120.5, 121.4	0.976 (2)		109.4
		2.122		130.0, 122.5	0.986, 0.965		107.5
		3.901		123.8, 130.8	0.968 (2)	1.929, 1.808	105.3
		3.928		125.3, 129.3	0.968 (2)	1.923, 1.805	105.4
		4.021		99.7, 151.7	0.970, 0.964	1.577	108.5
		4.466		120.1, 129.5	0.968 (2)	1.796, 2.876	105.3
(6,3)_6D_3AA	D_3	2.127 (6)	53.2, 83.2 (2), 88.0 (6), 102.5 (3), 166.0 (3)	123.8 (6),123.3 (6)	0.964 (6), 0.978 (6)		109.2 (6)
		4.000 (3)		127.4 (6)	0.966 (6)	1.870 (6)	105.1 (3)
(6,3)_4D,DD _3AA	C_s	2.099	82.6, 83.3 (2), 85.1, 85.9 (2), 90.2, 95.0 (2), 97.7 (2), 102.1, 162.6, 167.7, 172.8	125.9, 122.9	0.975 (2)		110.4
		2.110		125.3, 124.8	0.978, 0.964		109.9
		2.121		124.5, 126.0	0.977, 0.963		109.5
		2.137 (2)		119.8 (2), 124.6 (2)	0.979 (2), 0.964 (2)		108.4 (2)
		2.161		124.3 (2)	0.965 (2)		107.9
		3.958 (2)		127.7 (2), 127.1 (2)	0.968 (4)	1.862 (2), 1.910 (2)	105.2 (2)
		4.012		127.5 (2)	0.965 (2)	1.867, 1.885	105.0
(4,6)_2AA,4A	D_{2d}	1.979 (4)	95.8 (2), 116.7 (4)	118.3 (4),130.8 (4)	0.975 (4), 0.995 (4)		110.9 (4)
		3.733 (2)		126.6 (4)	0.979 (4)	1.913 (2)	106.8 (2)
		4.202 (4)		125.6 (8)	0.988 (8)	1.648 (4)	108.4 (4)
(4,5,1)_2AA,A, 2AD_AA	C_1	1.968	94.5, 97.9, 110.4, 113.4, 118.0, 124.3	119.0, 124.4	0.973, 1.006		111.1
		1.968		118.1, 125.8	0.975, 1.004		111.8
		1.969		117.4, 131.1	0.976, 0.999		111.3
		2.025		118.8, 130.5	0.983, 0.964		110.7
		3.686		129.3, 125.5	0.967 (2)	1.900 (2)	105.2
		3.741		129.4, 125.2	0.968 (2)	1.988, 1.798	105.3
		3.993		112.5, 137.4	0.975, 0.964	1.577	108.0
		4.015		112.5, 138.1	0.975, 0.964	1.588	108.0
		4.178		124.4, 128.4	0.965 (2)	1.618	106.6
		5.541		126.0, 128.8	0.967 (2)	1.906, 1.898	105.2
(4,5,1)_AA,A,	C_1	1.971	94.0, 97.2, 114.7, 115.1, 118.2, 119.2	119.1, 128.1	0.974, 1.001		110.7

AAD,AD_AA		1.975		116.7, 131.5	0.978, 0.998		111.4
		1.977		111.1, 120.7	0.981, 1.001		104.8
		2.023		118.9, 130.4	0.984, 0.964		110.7
		3.660		118.2, 134.8	0.980, 0.966	1.893, 1.860	106.4
		3.740		127.7, 127.0	0.968 (2)	1.794, 1.970	105.4
		3.996		115.3, 136.7	0.973, 0.964	1.630	107.6
		4.119		131.0, 120.6	0.965 (2)	1.609	106.7
		4.193		124.7, 128.1	0.965 (2)	1.627	106.7
		5.355		115.2, 139.8	0.967 (2)	1.907, 2.003	104.9
(4,4,2)_4AD_2AA	C_1	1.976	104.5, 108.2 (2), 109.1, 111.8, 115.0	124.8, 124.6	1.012, 0.964		109.9
		1.978		126.2, 124.2	1.014, 0.964		108.9
		1.980		127.5, 122.3	1.015, 0.964		108.7
		1.985		124.6, 126.0	1.014, 0.964		109.4
		3.978		116.8, 134.4	0.976, 0.964	1.553	108.0
		4.009		114.8, 136.2	0.976, 0.964	1.550	108.0
		4.052		113.8, 136.7	0.976, 0.964	1.548	108.0
		4.083		113.0, 137.9	0.976, 0.964	1.544	108.1
		5.608		130.0, 124.7	0.968 (2)	1.885, 1.883	105.3
		5.620		113.8, 141.0	0.967 (2)	1.885, 1.886	105.2
(5,5)_4A_bA_b,A_a	C_s	2.018	87.2 (2), 89.0 (2), 90.9 98.6, 114.0 (2),	131.5,120.0	0.996,0.964		108.5
		2.045 (2)	132.1, 170.5	123.5 (2),123.8 (2)	0.976 (4)		112.3 (2)
		2.082		122.7 (2)	0.939 (2)		104.6
		2.111		121.6 (2)	0.944 (2)		105.4
		3.894 (2)		130.3 (2),124.4 (2)	0.967 (4)	1.888 (2),1.920 (2)	105.3 (2)
		3.909 (2)		130.4 (2),124.4 (2)	0.967 (4)	1.979 (2),1.921 (2)	105.2 (2)
		4.305		127.9 (2)	0.941 (2)	1.648	104.1
(5,4,1)	C_1	2.020	89.6 (2), 89.9, 90.0, 90.3, 90.6, 113.2,	124.0, 120.9	0.974, 0.985		113.3
_3A_bA_b,AAD_A		2.030	113.7, 133.0, 179.9	122.8, 123.5	0.977, 0.976		112.7
		2.076		116.4, 119.0	0.984, 0.975		110.2
		2.080		125.0, 126.1	0.965 (2)		108.9
		2.089		118.2, 118.9	0.977, 0.976		109.9

		3.757		132.2, 122.3	0.993, 0.966	1.783, 1.812	105.5
		3.854		129.1, 126.7	0.967 (2)	1.954, 1.869	105.2
		3.857		130.0, 124.8	0.967 (2)	1.903, 1.924	105.2
		3.868		129.4, 125.4	0.967 (2)	1.886, 1.922	105.2
		5.911		120.9, 131.7	0.964 (2)	1.692	106.1
(5,5)_3A_bA_b, A_bA_bD_AA_p	C_1	2.036	87.4, 87.6, 88.8, 89.3, 92.9, 97.4, 103.5, 116.0, 140.4, 169.8	123.1, 124.0	0.977, 0.976		112.2
		2.047		118.3, 125.6	0.977, 0.975		112.0
		2.059		126.6, 125.6	0.982, 0.964		109.4
		2.076		123.0, 119.9	0.975 (2)		112.0
		2.083		119.4, 120.6	0.977, 0.976		110.2
		3.660		95.6, 157.3	0.974, 0.966	1.905	107.1
		3.880		126.9, 128.0	0.967 (2)	1.905, 1.910	105.2
		3.902		127.6, 127.0	0.967 (2)	1.869, 1.924	105.4
		3.906		129.8, 125.0	0.967 (2)	1.881, 1.908	105.3
		4.157		119.7, 131.6	0.968 (2)	1.834, 2.033	104.9
(6,4)_4D,2DD_4AA	C_2	2.106 (2)	84.2, 84.4 (2), 87.2 (2), 89.5 (2), 92.5 (2), 96.3 (2), 98.1, 168.9 (2), 175.5	123.3 (2),118.9 (2)	0.975 (2), 0.976 (2)		110.3 (2)
		2.142 (2)		115.6 (4),119 (4)	0.978 (2), 0.965 (2)		107.3 (2)
		2.143 (2)		122.4 (2),125.5 (2)	0.975 (2), 0.964 (2)		108.9 (2)
		3.885 (2)		118.6 (2),136.2 (2)	0.967 (4)	1.897 (2), 1.907 (2)	105.3 (2)
		4.000 (2)		129.1 (2),125.8 (2)	0.967 (2)	1.925 (2), 1.876 (2)	105.2 (2)
(6,4)_4D,2DD_4AA_share	C_1	2.111	82.6, 84.1, 84.9, 85.0, 85.4, 87.4, 88.4, 89.6, 91.6, 100.1, 100.2, 105.7, 165.7, 166.4, 167.1	118.8, 115.9	0.975 (2)		107.7
		2.114		122.3, 125.9	0.974, 0.973		111.4
		2.126		122.5, 122.3	0.978, 0.964		109.2
		2.136		121.9, 123.3	0.978, 0.964		109.1
		2.139		122.4, 125.2	0.977, 0.963		109.0
		2.150		123.3, 123.9	0.977, 0.964		109.5
		3.920		120.4, 134.6	0.967 (2)	1.950, 1.917	105.0
		3.999		132.9, 121.6	0.967 (2)	1.882, 1.868	105.4

		4.002		124.1, 130.8	0.967 (2)	1.940, 1.872	105.1
		4.009		126.8, 129.1	0.967 (2)	1.936, 1.872	105.1
(6,4)_5D,DD _3AA,A	C_1	2.079	83.1 (2), 84.6, 84.9, 85.6, 87.3, 87.4, 89.4, 94.1, 98.0, 102.8, 103.9, 164.1, 165.5, 169.7	128.6, 121.5	0.988, 0.973		109.1
		2.121		124.1, 124.8	0.976, 0.963		109.4
		2.132		123.5, 127.3	0.978, 0.964		110.0
		2.143		122.7, 122.4	0.977, 0.964		109.0
		2.143		122.9, 123.3	0.977, 0.964		109.1
		2.146		122.3, 120.4	0.977, 0.964		108.8
		4.001		127.4 (2)	0.967 (2)	1.957, 1.847	105.2
		4.014		127.4, 127.3	0.968, 0.967	1.891, 1.884	105.2
		4.019		129.2, 125.5	0.967 (2)	1.884, 1.878	105.3
		4.310		126.3, 128.0	0.965 (2)	1.713	105.7
(6,4)_5D,DD _2AA,AAD,AA_p	C_1	2.117	83.7, 84.1, 85.3, 86.2, 87.5, 88.7, 89.0, 89.8, 92.2, 97.6, 99.3, 99.4, 167.6, 170.1, 170.7	120.1, 122.0	0.977, 0.975		108.8
		2.118		121.6, 128.1	0.979, 0.963		110.1
		2.126		126.1, 123.3	0.977, 0.964		109.5
		2.128		117.9, 122.0	0.980, 0.964		108.9
		2.134		122.5, 120.6	0.977, 0.965		108.9
		2.134		122.7, 123.0	0.977, 0.964		109.4
		3.792		97.4, 155.0	0.976, 0.966	1.832, 1.848	107.7
		3.987		127.3, 127.5	0.967 (2)	1.938, 1.867	105.2
		3.997		130.6, 124.2	0.967 (2)	1.879, 1.893	105.2
		4.329		119.7, 131.0	0.968 (2)	1.936, 1.959	104.8

[a] Values in parentheses indicate degeneracies. [b] Inner shell water molecules only. [c] Covalent bond length. [d] Hydrogen bond length between the first and second shell.

Table S3. Comparison of experimental 0 K bond energies (kJ/mol) to theoretical values. The reactant and product complex is the GS of each inner shell size, unless otherwise noted.

n	Reactant	Product	Experiment	B3LYP[a]	B3P86[a]	MP2(full)[a]
6	(4,2)	(4,1)	98.4[b,c] (3.9)	97.0	100.6	95.7
			109.0[c] (4.8)			
	(6,0)	(5,0)	94.6[b,c] (3.9)	87.1	90.1	93.6
			105.8[c] (4.8)			
	(5,1)	(5,0)	90.7[b,c](3.9)	93.0	96.5	92.0
			99.3[c] (4.8)			
7	(4,3)	(4,2)	78.2[b] (4.8)	79.8	82.5	76.5
			92.6[c] (5.8)			
	(4,3)_2D,DD _AA,2A	(4,2)	71.4[b] (4.8)	75.7	78.4	69.3
	(5,2)	(6,0)	79.2[b] (4.8)	93.5	97.0	83.3
	(5,2)	(5,1)	82.0[b] (4.8)	87.9	91.0	87.5
8	(5,3)	(4,3)	70.4[b] (5.8)	75.8	78.6	86.3
			71.4[c] (8.7)			
	(5,3)	(5,2)	67.5[b] (5.8)	76.0	78.8	75.4
	(4,4)	(5,2)	59.8[b] (5.8)	74.9	77.1	61.8
	(4,4)	(4,3)	63.7[b] (5.8)	74.8	77.0	72.7
9	(5,4)	(5,3)	53.1[d] (7.7)	70.8	72.5	71.6
			70.4[c] (2.9)			
	(4,5)	(5,3)	45.3[d] (7.7)	65.6	66.8	50.9
	(4,5)	(4,4)	47.3[d] (7.7)	67.4	69.1	65.8
			63.7[c] (2.9)			
10	(5,5)	(5,4)	42.5[d] (2.9)	60.6	62.4	59.0
	(4,6)	(5,4)	36.7[d] (2.9)	57.2	58.1	40.2

[a] Geometry optimizations calculated using a B3LYP/6-311+G(d,p) level and SPE values calculated with a 6-311+G(2d,2p) basis set for each level. ZPE and cp corrected. [b] Values including competitive shift reported in following publication.[20] [c] Sequential dissociation modeled using eqs 4 and 6. [d] Single channel model using eq 4.

Table S4. Conversion of 0 K thresholds to 298 K enthalpies and free energies for water loss from $Zn^{2+}(H_2O)_n$. The reactant and product complex is the GS of each inner shell size, unless otherwise noted. All values in kJ/mol with uncertainties in parentheses.

n	Dissociation	ΔH_0[a]	$\Delta H_{298} - \Delta H_0$[b]	ΔH_{298}	$T\Delta S_{298}$[b]	ΔG_{298}
6	(4,2) → (4,1)	98.4 (3.9)	4.7 (0.4)	103.1 (3.9)	46.6 (1.0)	56.5 (4.1)
	(6,0) → (5,0)	94.6 (3.9)	2.1 (0.5)	96.7 (3.9)	45.5 (1.4)	51.2 (4.1)
	(5,1) → (5,0)	90.7 (3.9)	4.0 (0.4)	94.7 (3.9)	42.7 (1.1)	52.0 (4.1)
7	(4,3) → (4,2)	78.2 (4.8)	1.6 (0.3)	79.8 (4.8)	31.1 (1.2)	48.7 (4.9)
	(4,3)_2D,DD_AA,2A → (4,2)	71.4 (4.8)	-1.0 (0.3)	70.4 (4.8)	17.9 (1.4)	52.5 (5.0)
	(5,2) → (6,0)	79.2 (4.8)	6.2 (0.3)	85.4 (4.8)	39.1 (1.2)	46.3 (4.9)
	(5,2) → (5,1)	82.0 (4.8)	4.3 (0.4)	86.3 (4.8)	47.1 (1.0)	39.2 (4.9)
8	(5,3) → (4,3)	70.4 (5.8)	3.6 (0.6)	74.0 (5.8)	46.0 (1.2)	28.0 (5.9)
	(5,3) → (5,2)	67.5 (5.8)	4.2 (0.4)	71.7 (5.8)	41.2 (1.1)	30.5 (5.9)
	(4,4) → (5,2)	59.8 (5.8)	1.6 (0.2)	59.8 (5.8)	29.8 (1.1)	30.0 (5.9)
	(4,4) → (4,3)	63.7 (5.8)	1.1 (0.3)	64.8 (5.8)	34.6 (1.6)	30.2 (6.0)
9	(5,4) → (5,3)	53.1 (7.7)	2.6 (0.4)	55.7 (6.8)	40.6 (1.1)	15.1 (7.8)
	(4,5) → (5,3)	45.3 (7.7)	-1.4 (0.1)	43.9 (7.7)	20.7 (1.6)	23.2 (7.9)
	(4,5) → (4,4)	47.3 (7.7)	1.2 (0.3)	48.4 (7.7)	32.1 (1.6)	16.3 (7.9)
10	(5,5) → (5,4)	42.5 (2.9)	1.1 (0.3)	43.6 (2.9)	29.2 (1.0)	14.4 (3.1)
	(4,6) → (5,4)	36.7 (2.9)	-3.2 (0.04)	33.8 (2.9)	10.9 (1.4)	22.9 (3.2)

[a] Experimental values from Table 3.

[b] Values calculated from the vibrations and rotations calculated at the B3LYP/6-311+G(d,p) level. Uncertainties found by scaling the frequencies up and down by 10%.

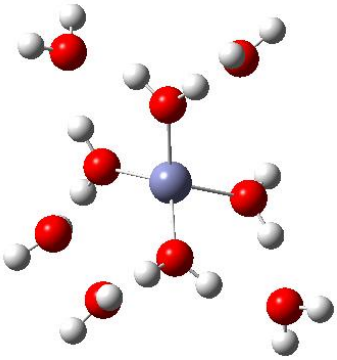
Figure Captions

Figure S1. Low energy isomers of $Zn^{2+}(H_2O)_9$ calculated at B3LYP/6-311+G(d,p).

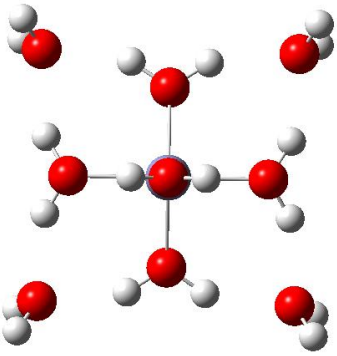
Figure S2. Low energy isomers of $Zn^{2+}(H_2O)_{10}$ calculated at B3LYP/6-311+G(d,p).

Figure S3a-o. Geometries for all low and high energy isomers of the $Zn^{2+}(H_2O)_x(H_2O)_y$ complexes, where *x* and *y* are the number of waters in the inner shell and outer shell and complexes considered include $x = 4$ and $y = 1 – 6$, $x = 5$ and $y = 0 – 5$, and $x = 6$ and $y = 0 – 4$.

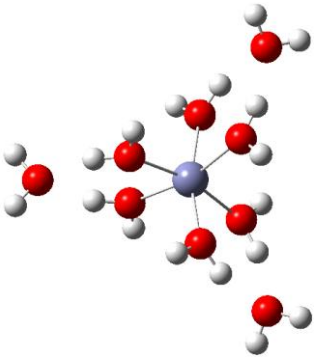
Figures



(4,5)_D,3D_2AA,3A

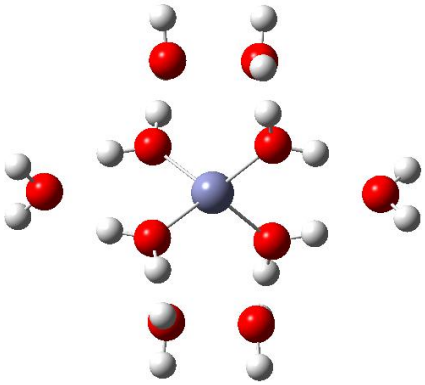


(5,4)_4A_bA_b

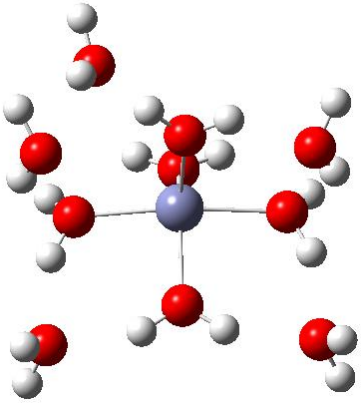


(6,3)_6D_3AA

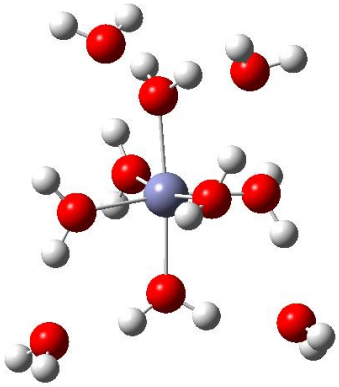
Figure S1



(4,6)_2AA,4A



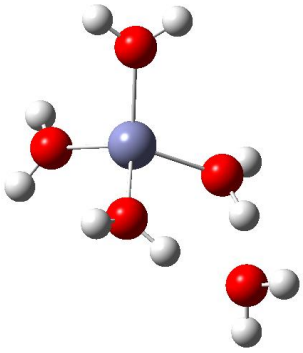
(5,5)_4A_bA_b,A_a



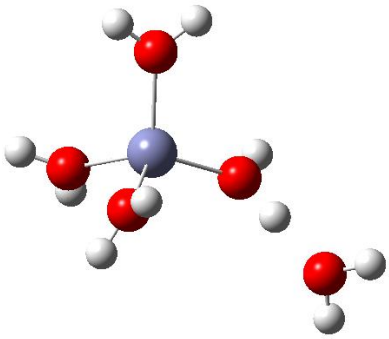
(6,4)_4D,2DD_4AA

Figure S2

a)

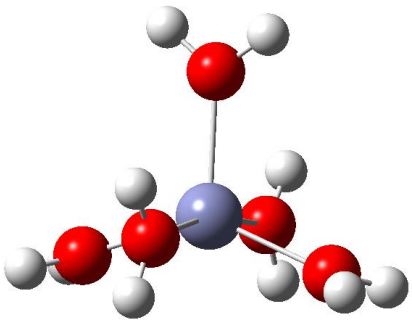


(4,1)_AA

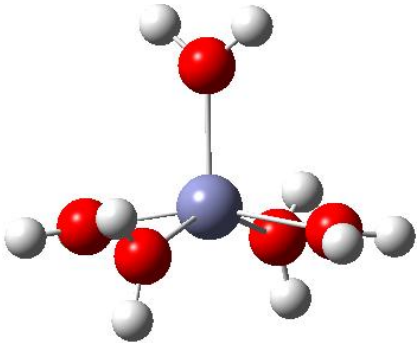


(4,1)_A

b)

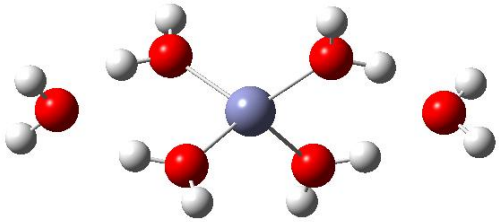


(5,0)

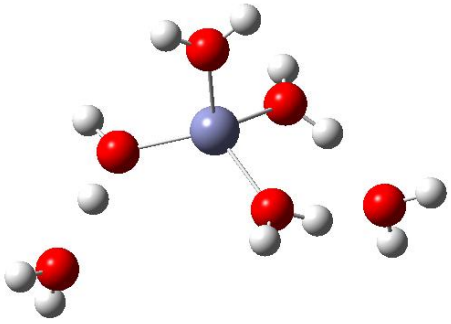


(5,0)_switch

c)

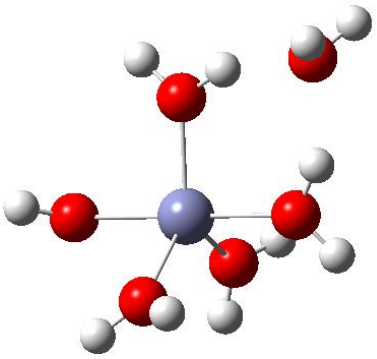


(4,2)_2AA

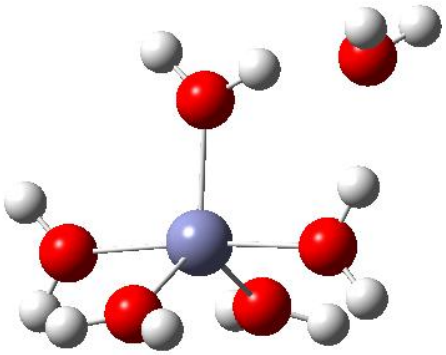


(4,2)_AA,A

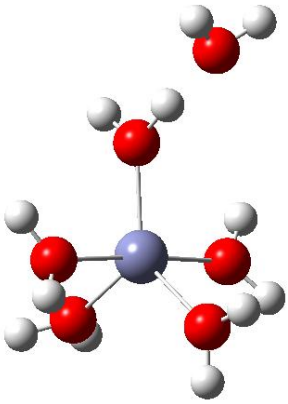
d)



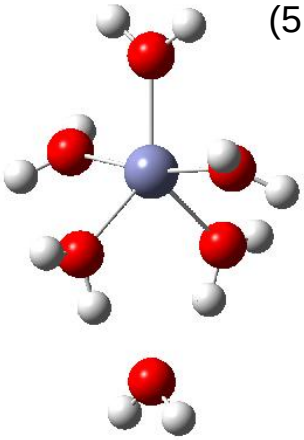
(5,1)_A_aA_b



(5,1)_A_aA_b_sym

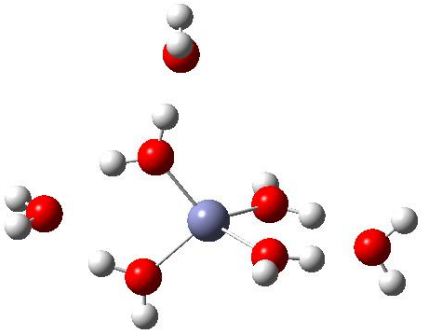


(5,1)_A_a

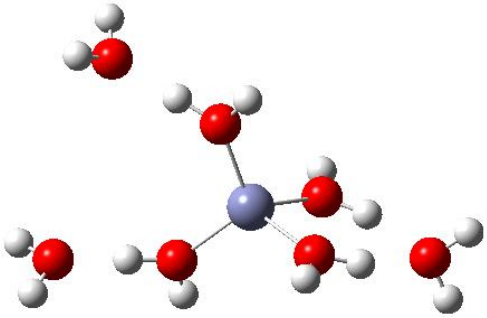


(5,1)_A_bA_b

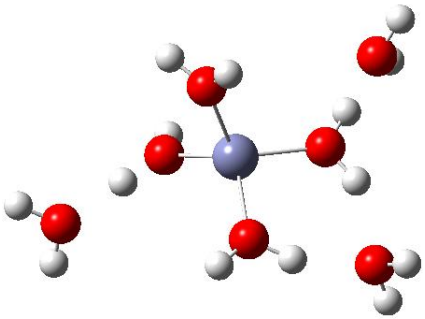
e)



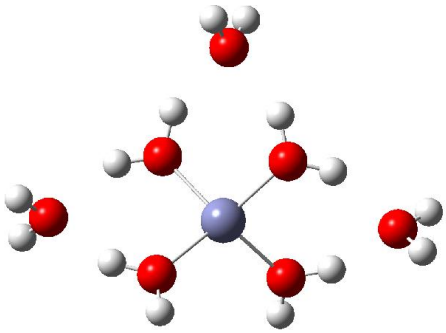
(4,3)_3D,DD_2AA,A



(4,3)_4D_AA,2A

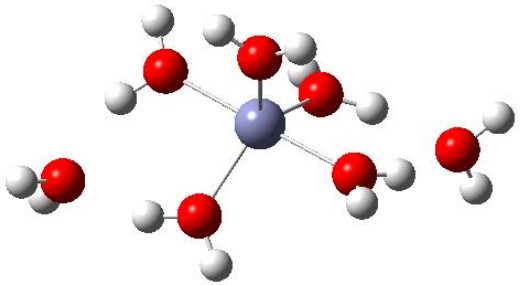


(4,3)_2D,DD_AA,2A

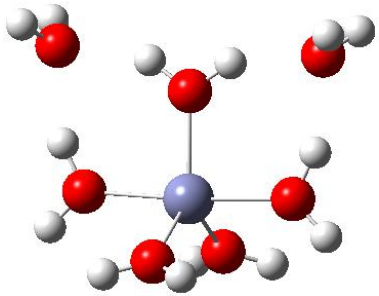


(4,3)_3D,2DD_3AA

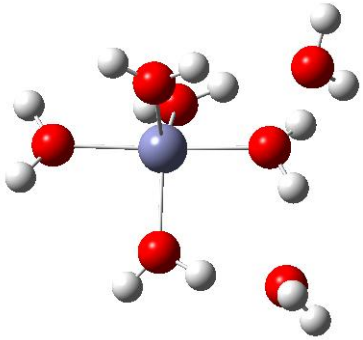
f)



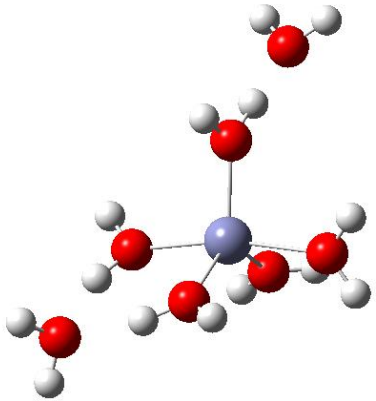
(5,2)_4D_2A_bA_b



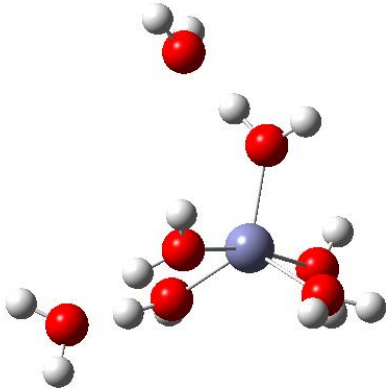
(5,2)_2D,2DD_2A_a



(5,2)_2D,DD_2A_bA_b

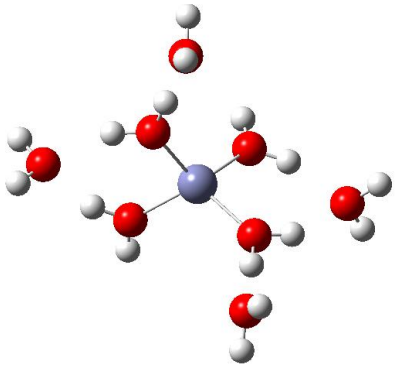


(5,2)_3D_A_bA_b,$A_{a,trans}$

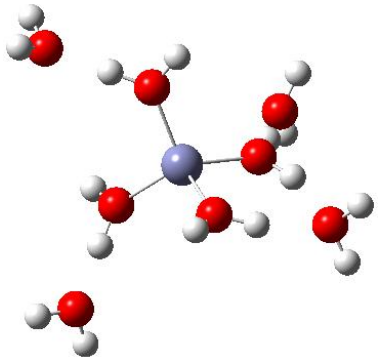


(5,2)_3D_A_bA_b,$A_{a,cis}$

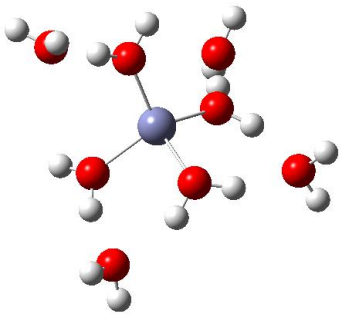
g)



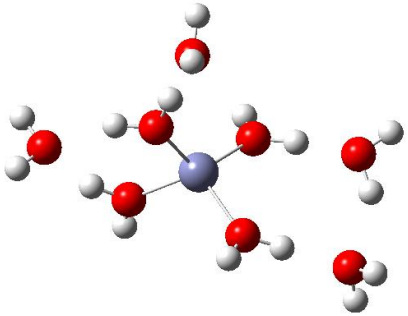
(4,4)_2D,2DD_2AA,2A



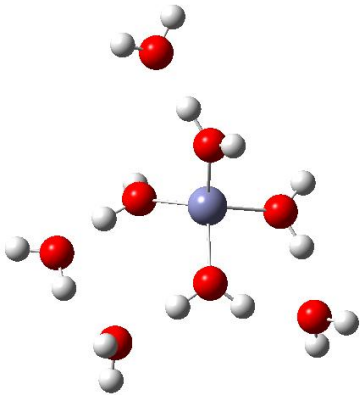
(4,4)_3D,DD_AA,3A



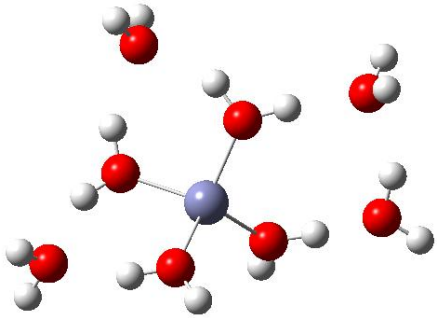
(4,4)_2D,2DD_2AA,2A



(4,4)_3D,DD_AA,A,AD,AA_p

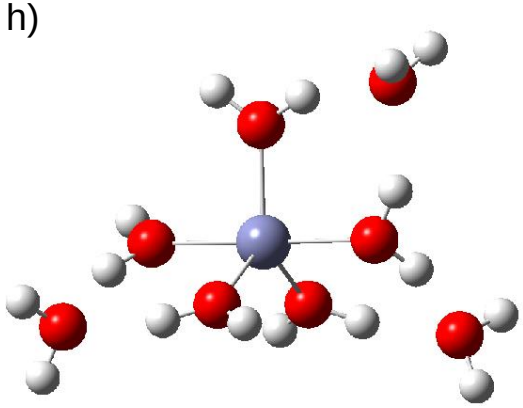


(4,4)_3D,DD_AA,A,AD,AA_p

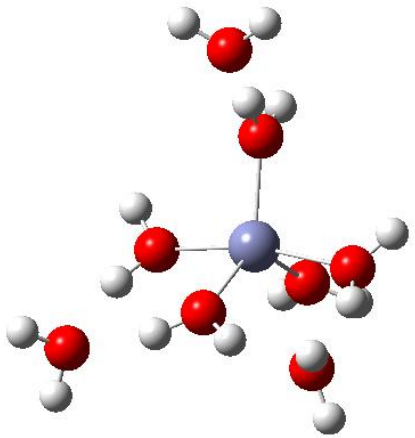


(4,4)_2D,2DD_2AA,AD,AA_p

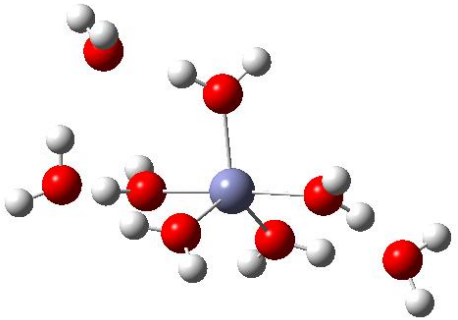
h)



(5,3)_3AA

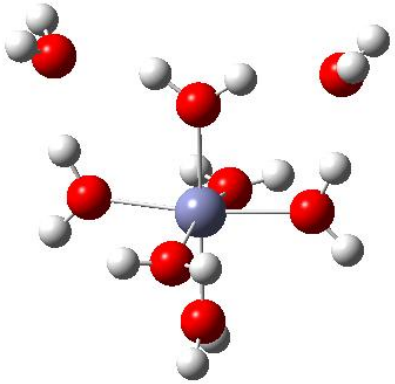


(5,3)_2AA,A

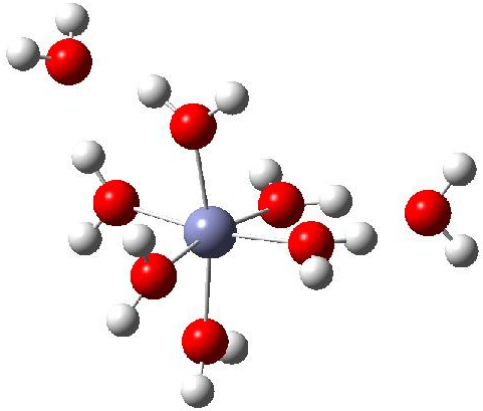


(5,3)_AA,AAD,AA_p

i)

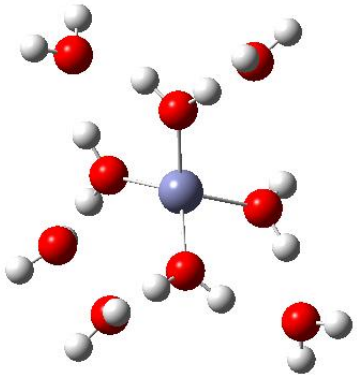


(6,2)_2D,DD_2AA

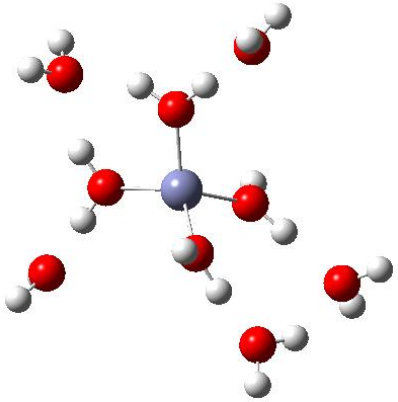


(6,2)_4D_2AA

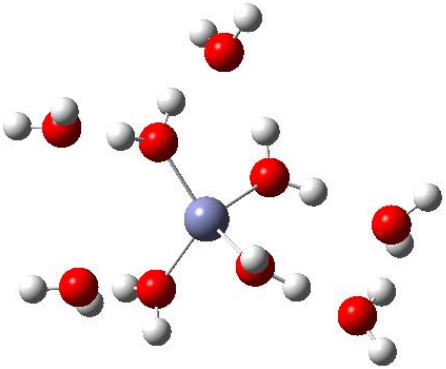
j)



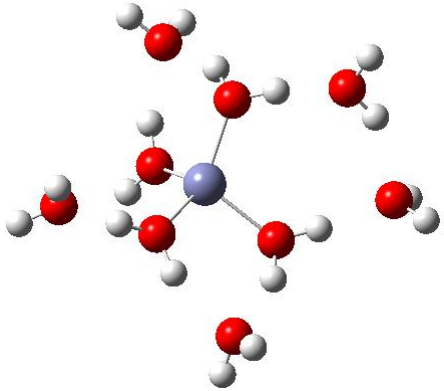
(4,5)_D,3DD_2AA,3A



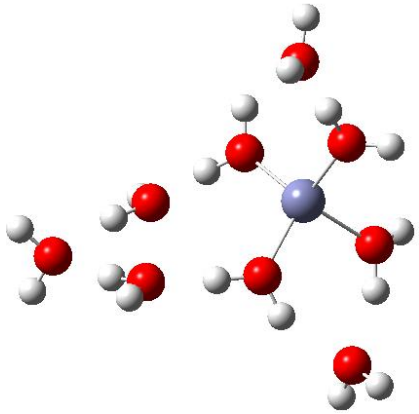
(4,5)_2D,2DD_AA,2A,AD,$AA_{p,trans}$



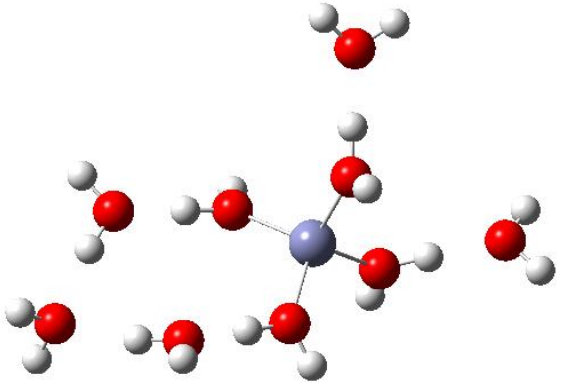
(4,5)_2D,2DD_AA,2A,AD,$AA_{p,cis}$



(4,5)_D,3DD_2AA,A,AD,AA_{p}

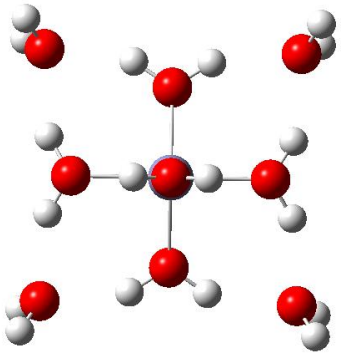


(4,4,1)_3D,DD_AA,A2AD_AA

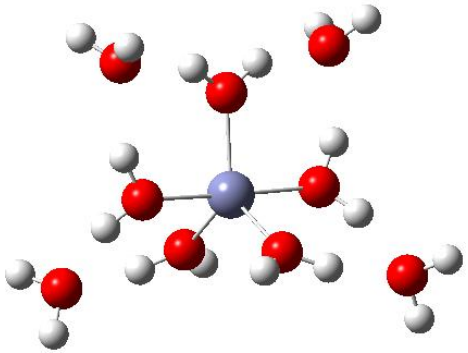


(4,4,1)_4D_2A,2AD_AA

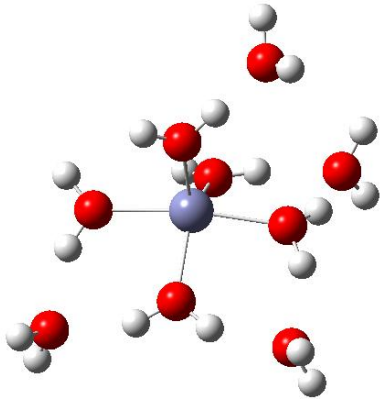
k)



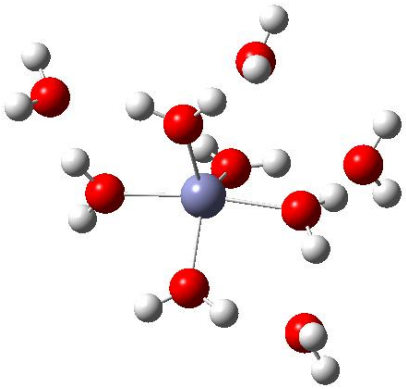
(5,4)_4A_bA_b



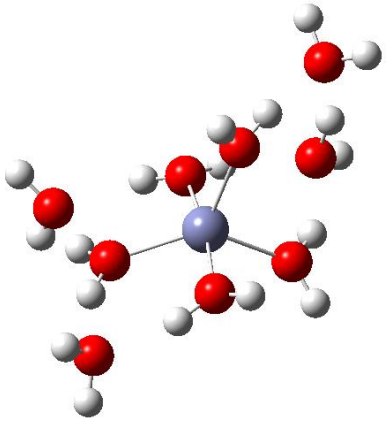
(5,4)_2A_bA_b,2A_aA_b



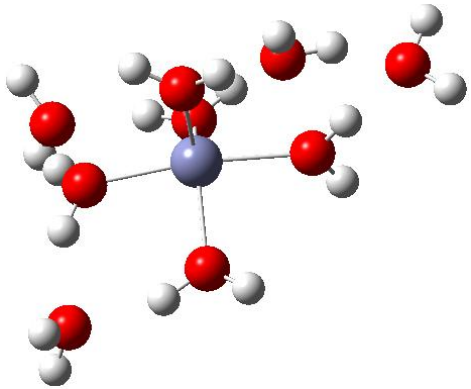
(5,4)_3A_bA_b,A_a



(5,4)_2A_bA_b,A_aA_b,A_a

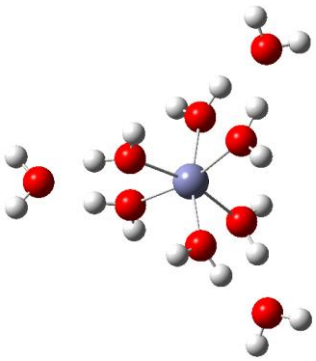


(5,4)_AA,A,AAD,AA_p

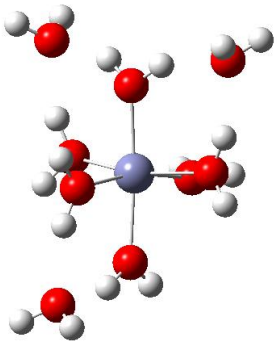


(5,4)_2AA,AD,AA_p

l)

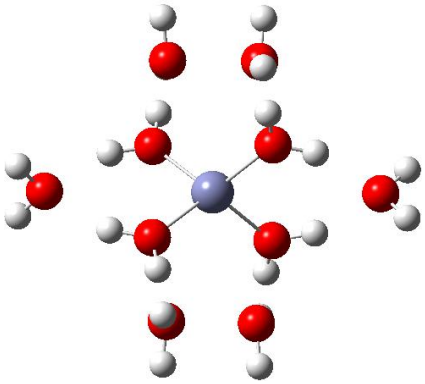


(6,3)_6D_3AA

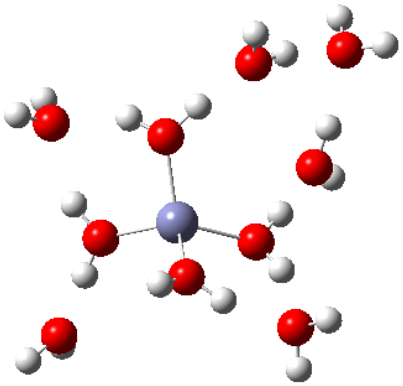


(6,3)_4D,DD_3AA

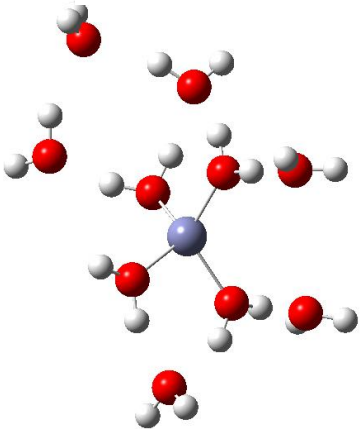
m)



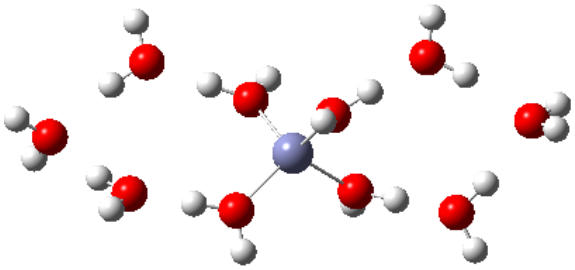
(4,6)_2AA,4A



(4,5,1)_2AA,A,2AD_AA

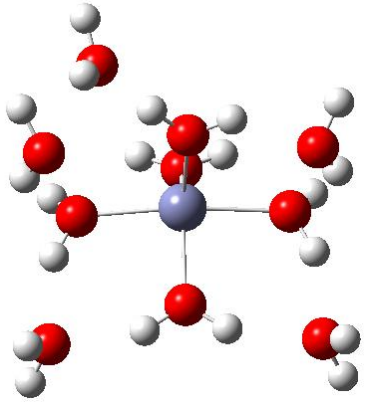


(4,5,1)_AA,A,AAD,AD_AA

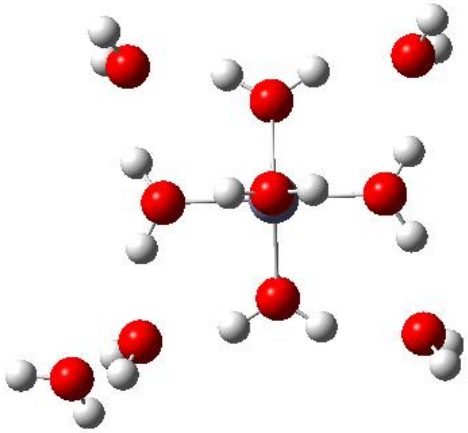


(4,4,2)_4AD_2AA

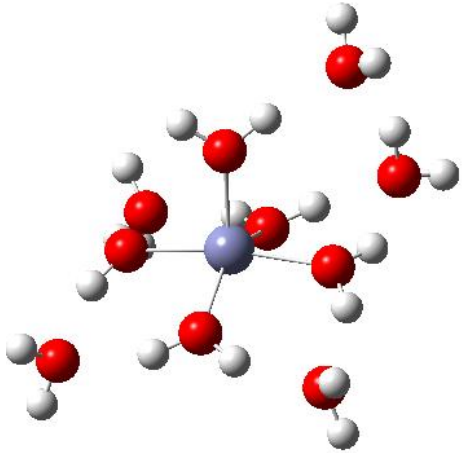
n)



(5,5)_4A_bA_b,A_a

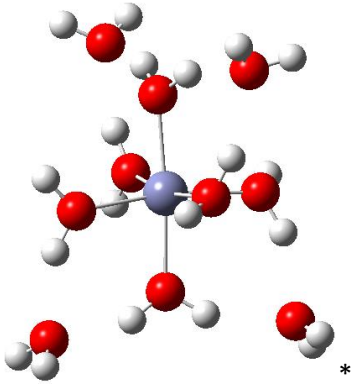


(5,4,1)_3A_bA_b,AAD_A

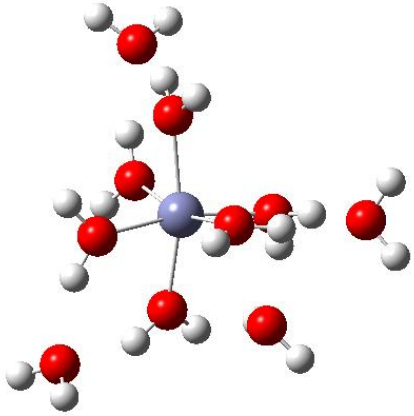


(5,5)_3A_bA_b,A_bA_bD,AA_p

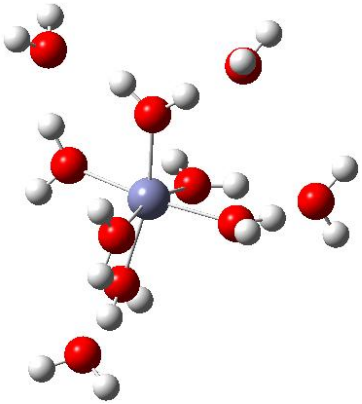
o)



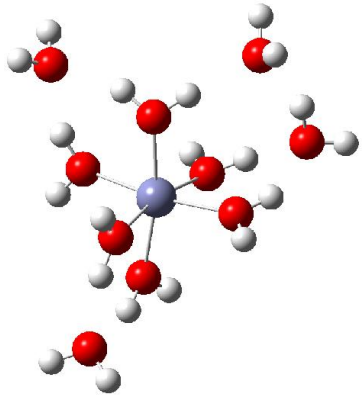
(6,4)_4D,2DD_4AA



(6,4)_4D,2DD_4AA_share



(6,4)_4D,2DD_4A



(6,4)_5D,DD_2AA,AAD,AA_p

Figure S3