Supplementary Material to: An ab Initio Investigation of Zinc Chloro Complexes

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Geometries

Monochloroaquazinc complexes

The C_{2v} monohydrate was not a minimum at either HF/STO-3G or HF/3-21G. For the dihydrate, two different C_{2v} structures were tried in which the water molecules were either embedded in or bisected by a symmetry plane. The first C_{2v} dihydrate structure was a minimum at HF/3-21G. The preferred dihydrate structure was C_s at HF/STO-3G. Neither of the C_{2v} structures were stable at the higher levels. The preferred trihydrate structure was C_3 at HF/STO-3G and was C_{3v} at HF/3-21G. For the tetrahydrate, SCF convergence difficulties were resolved by the SCF=QC keyword. For the pentahydrate, some of the waters decoordinate in the C_{2v} structure at HF/STO-3G. At HF/3-21G, the imaginary frequency suggests desymmetrization to a C_s structure. At HF/6-31G*, the imaginary frequency suggests desymmetrization to C_2.

Dichloroaquazinc complexes

The anhydrate had an imaginary Π_u mode at HF/STO-3G and HF/3-21G. The planar C_{2v} monohydrate structure was stable at HF/3-21G, but a C_s structure is preferred at HF/STO-3G. The *trans* trihydrate exists as a D_{3h} istructure at HF/3-21G. Four different C_{2v} *trans* structures were also tried, but possessed imaginary frequencies and were higher in energy. Four analogous C_{2v} *cis* structures were tried, some of which became *trans*. For the tetrahydrate, The *trans* isomer was not stable with D_{4h} symmetry. Four C_{2v} *cis* isomers were tried, and the highest frequency imaginary mode of the

lowest energy isomer suggested that a C_2 structure should be tried.

Trichloroaquazinc complexes

Attempts to locate a C_{2v} *cis* diaqua structure at the HF/STO-3G, HF/3-21G, and HF/6-31G* levels led either to distortion to the *trans* isomer, dissociation of a water, or formation of a structure with imaginary modes. Attempts to locate a C_{2v} *mer* triaqua structure resulted in dissociation of the axial water molecule at HF/STO-3G and of the axial chloride ion at HF/3-21G. At HF/6-31G*, three of the four structures possessed imaginary frequencies, whereas the fourth underwent simultaneous dissociation of water and chloride. The first C_{2v} structure has three imaginary frequencies, and the largest magnitude imaginary frequency suggested desymmetrization to a C_s structure. The imaginary frequency remaining suggested two possible structures with no symmetry, but both of these dissociate a chloride ion.

Tetrachloroaquazinc complexes

Attempts to coordinate water via two different C_{2v} structures either resulted in dissociation of a water molecule or of two chloride ions at all levels up to HF/6-31G*.

Table 1: Total energies of $Zn(H_2O)_n^{2+}$ and Cl^-

n	structure	Total energies (a.u.)		
		HF/STO-3G	HF/3-21G	HF/6-31G*
0	K_h	-1756.5114908	-1768.2750421	-1776.6120743
1	C_{2v}	-1831.6648083	-1844.0541414	-1852.7735461
2	D_{2d}	-1906.6834351	-1919.8150057	-1928.9177884
	D_{2h}	-1906.8513263	-1919.8141293	-1928.9173423
3	D_3	-1981.7506607	-1995.5412712	-2005.0302302
	D_{3h}	-1981.8042476	-1995.5389698	-2005.0268992
4	S_4	-2056.9786709	-2071.2363098	-2081.1209709
	C_{2v}	-2056.9689888	-2071.2321949	-2081.1172170
5	C_2	-2131.9819785		
	C_{2v}	-2131.9871054	-2146.8873508	-2157.1825386
6	T_h	-2206.8530788	-2222.5249511	-2233.2376942
Cl^-	K_h	-454.4804216	-457.3535854	-459.5259969

Table 1: Total energies of $Zn(H_2O)_n^{2+}$ and Cl^-

n	structure	Total energies (a.u.)		
		HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	K_h	-1776.6390043	-1776.8142736	-1776.8595402
1	C_{2v}	-1852.8006713	-1853.1788006	-1853.2290805
2	D_{2d}	-1928.9465699	-1929.5253587	-1929.5823039
3	D_3	-2005.0558880	-2005.8322902	-2005.8891119
4	S_4	-2081.1462159	-2082.1157498	-2082.1769782
	C_{2v}	-2081.1422239	-2082.1114145	-2082.1721250
5	C_{2v}	-2157.2111859	-2158.3685925	-2158.4391043
6	T_h	-2233.2732116	-2234.6138327	-2234.6987875
Cl^-	K_h	-459.5396601	-459.6521044	-459.6711454

Table 2: Total energies of $ZnCl(H_2O)_n^+$

n	structure	Total energies (a.u.)		
		HF/STO-3G	HF/3-21G	HF/6-31G*
0	$C_{\infty v}$	-2211.7336932	-2226.1812978	-2236.7063923
1	C_{2v}	-2286.7796849	-2301.9070702	-2312.8158438
2	C_{2v} # 1	-2361.7531654	-2377.6059248	-2388.8943936
	C_{2v} # 2	-2361.8079544	-2377.6016576	-2388.8902910
	C_s	-2361.8272178	C_{2v} # 1	C_{2v} # 1
	C_2	-2361.7698534	C_{2v} # 1	-2388.8943993
3	C_{3v}	-2436.7489071	-2453.2838610	-2464.9588331
	C_3	-2436.7566760	C_{3v}	-2464.9599433
		-2436.8289753		
4	C_{4v} # 1	-2511.7948253	-2528.8962635	-2540.9875938
	C_{4v} # 2	-2511.8417981	-2528.9075638	-2540.9940147
	C_{2v} # 1	-2511.8154028	-2528.9082447	-2540.9953364
	C_{2v} # 2	-2511.8615290	-2528.9160145	-2540.9964510
	C_{2v} # 3	-2511.8379158	-2528.9219678	-2541.0040305
	C_2	-2511.8617335	-2528.9220142	-2541.0040597
	C_2 5-pl	-2511.6091454		
5	C_{2v}		-2604.5540630	-2617.0411740
	C_2			-2617.0416244
	C_s		-2604.5543750	
	C_s [5+1]	-2586.8647728	-2604.5598458	-2617.0421895
	C_1 [5+1]		-2604.5571619	
	C_1 [5+1] # 2		-2604.5638810	-2617.0441092
	C_1 [4+2]	-2586.8833391	-2604.5578671	-2617.0421209

Table 2: Total energies of $ZnCl(H_2O)_n^+$ (continued)

n	structure	Total energies (a.u.)		
		HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	$C_{\infty v}$	-2236.7465615	-2237.0706881	-2237.1438579
1	C_{2v}	-2312.8550769	-2313.3776723	-2313.4535146
2	C_2	-2388.9302518	-2389.6472349	-2389.7237856
3	C_{3v}	-2464.9944739	-2465.9044678	-2465.9851393
4	C_{2v}	-2541.0409289	-2542.1389445	-2542.2278524
	C_2	-2541.0409289	-2542.1403154	-2542.2284102
5	C_2	-2617.0832500	-2618.3684234	-2618.4686348
	C_1		-2618.3685500	-2618.4687279
	C_s [5+1]	-2617.0831214	-2618.3698735	-2618.4674461
	C_1 [5+1] # 2	-2617.0846506	-2618.3729428	-2618.4707045
	C_1 [4+2]	-2617.0846731	-2618.3714897	-2618.4704102

Table 3: Total energies of $ZnCl_2(H_2O)_n$

n	structure	Total energies (a.u.)		
		HF/STO-3G	HF/3-21G	HF/6-31G*
0	$D_{\infty h}$	-2666.5653518	-2683.8828962	-2696.5780289
1	C_{2v} # 1	-2741.5818723	-2759.5529842	-2772.6263839
	C_{2v} # 2	-2741.5670129	-2759.5464029	-2772.6194014
		-2741.3851259		
	C_s	-2741.6038921		
2	C_{2v} # 1	-2816.6013573	-2835.2108566	-2848.6709461
	C_{2v} # 2	-2816.5809653	-2835.1940686	-2848.6548500
3	D_{3h} *trans*	-2891.5057160	-2910.8564952	-2924.6989752
	C_{3h} *trans*	-2891.5078548	D_{3h}	-2924.6996636
	C_{2v} *cis* # 1		-2910.8141208	-2924.6773350
	C_{2v} *cis* # 2		D_{3h}	-2924.6999663
	C_{2v} *cis* # 3		C_{2v} # 7	-2924.7029953
	C_{2v} *cis* # 4		-2910.8177703	-2924.6806359
	C_{2v} *trans* # 5		-2910.8066761	-2924.6628245
	C_{2v} *trans* # 6		D_{3h}	D_{3h}
	C_{2v} *trans* # 7		-2910.8455939	C_{2v} # 3
	C_{2v} *trans* # 8		-2910.8276043	-2924.6762505
	C_s *cis*	-2891.5695751		-2924.7035728
	C_1 [4+1]	-2891.5978137	-2910.8419305	-2924.7045763

Table 3: Total energies of $ZnCl_2(H_2O)_n$ (continued)

n	structure	Total energies (a.u.)		
		HF/STO-3G	HF/3-21G	HF/6-31G*
4	*trans* D_{4h}	-2966.4792161	-2986.4652893	-3000.7209103
	trans C_{4h}	-2966.4857195	-2986.4661600	-3000.7290621
	C_{2v} [4+2]	-2966.5450128	-2986.4554887	-3000.7335803
	C_{2v} *cis* # 1		-2986.4481244	-3000.7021111
	C_{2v} *cis* # 2		-2986.4630220	-3000.7172547
	C_{2v} *cis* # 3		-2986.4801376	-3000.7207202
	C_{2v} *cis* # 4		-2986.4379862	-3000.7041056
	C_2 *cis*			-3000.7268776

Table 3: Total energies of $ZnCl_2(H_2O)_n$ (continued)

n	structure	Total energies (a.u.)		
		HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	$D_{\infty h}$	-2696.6237404	-2697.0864071	-2697.1761579
1	C_{2v} # 1	-2772.6691509	-2773.3237878	-2773.4155634
	C_s # 1		-2773.3238090	-2773.4155900
2	C_{2v} # 1	-2848.7116561	-2849.5594322	-2849.6544956
3	C_{3h} *trans*	-2924.7405106	-2925.7779885	-2925.8787345
	C_s *cis*	-2924.7460232	-2925.7840989	-2925.8867235
	C_{2v} *trans*	-2924.7398729	-2925.7765820	-2925.8776640
	C_1 [4+1]	-2924.7488089	-2925.7860963	-2925.8895653
4	*trans* C_{4h}	-3000.7756569	-3001.9987666	-3002.1139338
	trans S_4		-3001.9992121	
	C_{2v} [4+2]	-3000.7834176	-3002.0107991	-3002.1264721
	cis C_2	-3000.7718950	-3002.0001232	-3002.1111970

Table 4: Total energies of $ZnCl_3(H_2O)_n^-$

n	structure	Total energies (a.u.)		
		HF/STO-3G	HF/3-21G	HF/6-31G*
0	D_{3h}	-3121.0890368	-3141.3715689	-3156.2099974
1	C_s # 1	-3196.1690442	-3217.0084666	-3232.2349418
	C_s # 2	-3196.1614515	-3217.0103041	-3232.2417999
2	*trans* C_{2v}	-3271.1228799	-3292.6425377	-3308.2666402
	trans C_2			-3308.2660112
	C_s [4+1]		-3292.6114206	-3308.2671460
	cis C_s # 1		-3292.6072277	
	cis C_s # 2		-3292.6181357	
	cis C_s # 3		-3292.6089043	
3	*mer* C_{2v} # 1			-3384.2728094
	mer C_{2v} # 2			-3384.2509254
	mer C_{2v} # 3			-3384.2607993
	mer C_s			-3384.2761932
	[5+1] C_1			-3384.3001303
	fac C_{3v} # 1		-3368.2520808	-3384.2821510
	fac C_{3v} # 2	-3346.1313714	-3368.1622340	-3384.2695435
	C_s [4+2]		-3368.2651063	-3384.3103068

Table 4: Total energies of $ZnCl_3(H_2O)_n^-$ (continued)

n	structure	Total energies (a.u.)		
		HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	D_{3h}	-3156.2551723	-3156.8468039	-3156.9462824
1	C_s # 2	-3232.2864891	-3233.0714648	-3233.1755813
2	*trans* C_{2v}	-3308.3128789	-3309.2896018	-3309.4002948
	trans C_2	-3308.3129088	-3309.2883224	3309.4002015
	C_s [4+1]	-3308.3188930	-3309.2868850	-3309.4055238
3	*fac* C_{3v}	-3384.3312327	-3385.4984385	-3385.6185821
	C_s [4+2]	-3384.3621722	-3385.5272833	-3385.6512176

Table 5: Total energies of $ZnCl_4(H_2O)_n^{2-}$

n	structure	Total energies (a.u.)		
		HF/STO-3G	HF/3-21G	HF/6-31G*
0	T_d	-3575.3582459	-3598.6881258	-3615.6772554
1	$ZnCl_2(H_2O)$ + $2Cl^-$ C_{2v} # 1		-3674.3087989	-3691.6968715
	$ZnCl_2(H_2O)$ + $2Cl^-$ C_{2v} # 2		-3674.2679244	-3691.6629302
	$ZnCl_4^{2-}$ + H_2O C_{2v}		-3674.3034887	-3691.7140924
2	*trans* D_{2h}	-3725.4129195	-3749.8855843	-3767.6610160
	$ZnCl_4^{2-}$ + $2H_2O$ C_{2v}		-3749.9156200	-3767.7467809
	$ZnCl_4^{2-}$ + $2H_2O$ D_{2d}	-3725.5105756	-3749.9175343	-3767.7497225
	$ZnCl_4^{2-}$ + $6H_2O$ T_d	-4025.2939102	-4052.3587188	-4071.8771921
		HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	T_d	-3615.7267246	-3616.4391991	-3616.5542692
1	$ZnCl_4^{2-}$ + H_2O C_{2v}	-3691.7696625	-3692.6676839	-3692.7958982
2	$ZnCl_4^{2-}$ + $2H_2O$ C_{2v}	-3767.8079409	-3768.8922334	-3769.0324237
	$ZnCl_4^{2-}$ + $2H_2O$ D_{2d}	-3767.8115370	-3768.8946474	-3769.0361352
	$ZnCl_4^{2-}$ + $6H_2O$ T_d	-4071.9648662	-4073.7840897	-4073.9784734

Table 6: Total CPCM-HF/A//HF/A energies $ZnCl_4(H_2O)_n^{2-}$

structure	Total energies (a.u.)	
	HF/6-31G*	HF/6-31+G*
Zn^{2+}	-1777.2332096	-1777.2608112
Cl^-	-459.6522868	-459.6619966
H_2O	-76.0208619	-76.0292323
$Zn(H_2O)_6^{2+}$	-2233.5382101	-2233.5750210
$ZnCl(H_2O)_5^+$	-2617.1514565	-2617.1921106
$ZnCl(H_2O)_4^+ + H_2O$	-2617.1441082	-2617.1844085
$ZnCl(H_2O)_3^+ + 2H_2O$	-2617.1381299	-2617.1812203
$ZnCl_2(H_2O)_4$ trans	-3000.7643067	-3000.8085557
$ZnCl_2(H_2O)_4$ cis	-3000.7625124	-3000.8020770
$ZnCl_2(H_2O)_2 + 2H_2O$	-3000.7535501	-3000.8009511
$ZnCl_3(H_2O)^-$	-3232.3206874	-3232.3636561
$ZnCl_3(H_2O)_3^-$ fac	-3384.3611549	-3384.4011621
$ZnCl_3(H_2O)^- + 2H_2O$	-3385.3706499	-3384.4215486
$ZnCl_4^{2-}$	-3615.9454646	-3615.9923829

Table 7: Zn-O Bond Length of $Zn(H_2O)_n^{2+}$

n	structure	Bond Length (Å)			
		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
1	C_{2v}	1.8843	1.8955	1.8573	1.8699
2	D_{2d}	1.8926	1.8996	1.8560	1.8619
3	D_3	1.9529	1.9639	1.9220	1.9344
4	S_4	2.0047	2.0177	1.9742	1.9884
5	C_{2v}	2.0420	2.0557	2.0090	2.0227
		2.0556	2.0663	2.0187	2.0328
		2.1180	2.1344	2.0877	2.1086
6	T_h	2.1249	2.1374	2.0891	2.1057

Table 8: Zn-O Bond Lengths of $ZnCl(H_2O)_n^+$

n	structure	Bond Lengths (Å)			
		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
1	C_{2v}	1.9305	1.9439	1.8903	1.9028
2	C_2	1.9983	2.0261	1.9688	2.0056
3	C_3	2.0514	2.0820	2.0219	2.0589
4	C_2	2.0743	2.0902	2.0998	2.0687
		2.1765	2.2174	2.1494	2.1993
5	$C_{2/1}$	2.1444	2.1724	2.0969	2.1483
		2.1704	2.1984	2.1360	2.1546
		2.1859	2.2091	2.1470	2.1667
				2.1531	2.1703
				2.1976	2.2055

Table 9: Zn-Cl Bond Lengths of $ZnCl(H_2O)_n^+$

n	structure	Bond Lengths (Å)			
		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	$C_{\infty v}$	2.0715	2.0757	2.0407	2.0441
1	C_{2v}	2.0726	2.0777	2.0310	2.0352
2	C_2	2.1148	2.1131	2.0733	2.0678
3	C_3	2.1552	2.1475	2.1127	2.0967
4	C_2	2.2006	2.1899	2.1494	2.1325
5	$C_{2/1}$	2.2737	2.2555	2.2264	2.1961

Table 10: Zn-O Bond Lengths of $ZnCl_2(H_2O)_n$

n	structure	Bond Lengths (Å)			
		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
1	$C_{2v/s}$ # 1	2.0773	2.1331	2.0465	2.1156
2	C_{2v} # 1	2.1025	2.1512	2.0696	2.1246
3	C_{3h} *trans*	2.1259	2.1833	2.0949	
	C_s *cis*	2.1069	2.1463	2.0701	2.1232
		2.2163	2.2810	2.1831	2.2572
4	C_{4h}/S_4 *trans*	2.1870	2.2339	2.1505	2.2072
	C_2 *cis*	2.2176	2.2798	2.1605	2.2505
		2.1960	2.2410	2.1608	2.2169

Table 11: Zn-Cl Bond Lengths of $ZnCl_2(H_2O)_n$

n	structure	Bond Lengths (Å)			
		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	$D_{\infty v}$	2.1143	2.1235	2.0668	2.0744
1	$C_{2v/s}$ # 1	2.1641	2.1665	2.1168	2.1133
2	C_{2v} # 1	2.2205	2.2139	2.1760	2.1564
3	C_{3h} *trans*	2.3241	2.3017	2.2750	
	C_s *cis*	2.2759	2.2593	2.2360	2.1959
		2.2597	2.2443	2.2082	2.1793
4	C_{4h}/S_4 *trans*	2.3677	2.3419	2.3426	2.2734
	C_2 *cis*	2.3794	2.3383	2.3609	2.2617

Table 12: Zn-O Bond Lengths of $ZnCl_3(H_2O)_n^-$

n	structure	Bond Lengths (Å)			
		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
1	C_s # 2	2.2044	2.2942	2.1751	2.2707
2	C_{2v} *trans*	2.2560	2.4139	2.2030	2.3966
	C_2 *trans*	2.2737	2.4208	2.2340	2.4020
3	C_3 *fac*	2.2840	2.4167	2.2204	2.3447

Table 13: Zn-Cl Bond Lengths of $ZnCl_3(H_2O)_n^-$

n	structure	Bond Lengths (Å)			
		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	D_{3h}	2.2466	2.2507	2.1996	2.1916
1	C_s # 2	2.2573	2.2560	2.2029	2.1891
		2.3195	2.3095	2.2788	2.2466
2	C_{2v} *trans*	2.2669	2.2552	2.2099	2.1843
		2.4360	2.3733	2.4224	2.3018
	C_2 *trans*	2.3270	2.3044	2.2750	2.2327
		2.4399	2.3733	2.4296	2.3019
3	C_{3v} *fac*	2.4644	2.4042	2.4410	2.3384

Table 14: Zn-Cl Bond Lengths of $ZnCl_4(H_2O)_n^-$

n	structure	Bond Lengths (Å)			
		HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
0	T_d	2.3890	2.3901	2.3366	2.3099

Table 15: Zn-O stretching vibrational modes of $Zn(H_2O)_n^{2+}$

n	structure	Irr.	Frequencies (cm^{-1})			
		Rep.	HF		MP2	
			6-31G*	6-31+G*	6-31G*	6-31+G*
1	C_{2v}	A_1	541.7	526.8	563.7	543.9
2	D_{2d}	A_1	453.4	446.3	478.0	466.2
		B_2	576.0	568.3	614.3	604.8
3	D_3	A_1	424.8	411.4	446.6	426.4
		E	463.7	449.6	492.0	471.2
4	S_4	A	396.5	383.3	416.1	397.8
		E	398.2	384.0	427.1	407.2
		B	404.9	390.4	442.1	420.0
5	C_{2v}	A_1	251.9	235.2	262.6	240.5
		B_2	334.1	321.3	338.4	324.7
					380.9	367.7
		A_1	359.7	341.1	369.5	341.5
					396.8	375.1
		B_1	369.1	360.8	363.5	347.4
		A_1	372.4	357.8	390.9	370.4
6	T_h	E_g	238.9	226.9	251.8	236.1
		T_u	312.2	305.2	314.0	304.4
		A_g	346.0	335.2	364.9	349.4

Table 16: Vibrational modes of $ZnCl(H_2O)_n^{2+}$

n	structure	Irr. Rep.	Mode	Frequencies (cm^{-1})			
				HF		MP2	
				6-31G*	6-31+G*	6-31G*	6-31+G*
0	$C_{\infty v}$	Σ	Zn-Cl	472.2	479.7	475.3	483.4
1	C_{2v}	A_1	Zn-O	396.6	389.8	415.3	405.3
		A_1	Zn-Cl	531.6	528.4	561.7	555.6
2	C_2	A	Zn-O	375.9	360.1	394.5	374.4
		B	Zn-O	399.0	364.2	413.5	363.9
		A	Zn-Cl	459.3	465.5	483.0	491.1
3	C_3	E	Zn-O	352.0	321.3	369.6	332.4
		A	Zn-O	354.0	335.7	373.6	355.5
		A	Zn-Cl	421.7	428.6	429.7	450.5
4	C_2	A	Zn-O	229.4	205.8	241.0	214.4
		B	Zn-O	301.9	274.1	347.0	289.4
		A	Zn-O	340.7	322.2	358.6	341.3
		B	Zn-O	345.8	331.5	348.6	345.3
		A	Zn-Cl	379.1	391.4	396.4	422.3
5	$C_{2/1}$	A	Zn-O	217.0	200.8	231.5	215.2
		A	Zn-O	222.9	202.9	239.4	218.0
		B	Zn-O	251.0	240.3	281.0	263.3
		B	Zn-O	290.8	266.7	324.0	299.1
		A	Zn-O	320.9	300.8	343.2	320.3
		A	Zn-Cl	337.7	348.9	362.4	373.2

Table 17: Vibrational modes of $ZnCl_2(H_2O)_n$

n	structure	Irr. Rep.	Mode	Frequencies (cm^{-1})			
				HF		MP2	
				6-31G*	6-31+G*	6-31G*	6-31+G*
0	$D_{\infty v}$	Σ_g	Zn-Cl	350.5	353.2	365.1	368.5
		Σ_u	Zn-Cl	501.1	502.5	526.3	529.4
1	$C_{2v/s}$ # 1	A_1	both	328.0	284.9	340.6	292.3
		A_1	both	337.5	337.7	352.6	355.3
		B_2	Zn-Cl	442.4	449.0	463.6	479.7
2	C_{2v} # 1	A_1	both	298.4	272.3	311.3	294.0
		A_1	both	326.2	321.1	342.5	340.5
		B_1	Zn-O	328.7	281.9	351.1	298.3
		B_2	Zn-Cl	388.8	402.1	404.4	434.8
3	C_{3h} *trans*	A'	both	199.2	181.4	206.3	
		E'	Zn-O	303.4	261.8	328.8	
		A''	Zn-Cl	312.9	316.2	311.0	
		A'	both	318.4	350.5	332.5	
	C_s *cis*	A'	both	214.0	186.7	228.4	202.8
		A''	Zn-O	276.1	232.8	297.1	251.0
		A'	both	308.2	292.4	318.8	311.2
		A'	Zn-O	323.1	309.9	347.3	329.9
		A'	both	344.1	362.4	361.0	400.6

Table 17: Vibrational modes of $ZnCl_2(H_2O)_n$ (continued)

n	structure	Irr. Rep.	Mode	Frequencies (cm^{-1})			
				HF		MP2	
				6-31G*	6-31+G*	6-31G*	6-31+G*
4	C_{4h} *trans*	A_g	both	190.1	178.7	193.5	196.3
	(S_4 MP2/6-31G*)	B_g	Zn-O	224.8	197.6	229.1	215.7
		E_u	Zn-O	281.7	246.3	305.5	264.6
		A_g	Zn-Cl	301.4	288.4	316.3	306.7
		A_u	Zn-O	302.5	315.5	320.9	347.7
	C_2 *cis*	B	Zn-O	172.6	162.8	190.6	175.5
		A	both	210.9	194.5	215.3	212.4
		A	Zn-O	270.7	243.3	298.5	277.6
		B	Zn-O	278.2	247.3	294.7	262.5
		B	both	293.6	293.8	315.0	343.6
		A	both	305.0	296.0	326.2	315.8

Table 18: Vibrational modes of $ZnCl_3(H_2O)_n^-$

n	structure	Irr. Rep.	Mode	Frequencies (cm^{-1})			
				HF		MP2	
				6-31G*	6-31+G*	6-31G*	6-31+G*
0	D_{3h}	A_1'	Zn-Cl	292.3	294.8	300.9	314.1
		E_1	Zn-Cl	343.4	344.1	356.4	373.1
1	C_s # 2 *trans*	A'	both	232.7	189.5	239.3	206.2
		A'	both	290.1	282.2	304.2	303.8
		A''	Zn-Cl	297.1	299.5	296.7	327.2
		A'	both	329.8	332.2	349.3	367.8
2	C_{2v} # 1 *trans*	A_1	both	132.7	131.8	123.1	151.7
		B_1	Zn-O	234.9	186.5	265.9	206.7
		B_2	Zn-Cl	236.7	242.6	247.5	286.8
		A_1	both	279.3	264.8	297.3	287.7
		A_1	both	314.6	328.0	335.6	367.3
	C_2 *trans*	A	both	159.1	113.0	142.5	151.9
		B	both	217.2	179.8	235.3	195.9
		A	both	251.9	267.9	262.4	287.9
		A	both	280.8	284.5	294.9	311.8
		B	Zn-Cl	299.3	309.9	309.6	348.1

Table 18: Vibrational modes of $ZnCl_3(H_2O)_n^-$ (continued)

n	structure	Irr. Rep.	Mode	Frequencies (cm^{-1})			
				HF		MP2	
				6-31G*	6-31+G*	6-31G*	6-31+G*
3	C_{3v} *fac*	A_1	both	185.4	130.5	120.8	167.7
		E	both	190.3	170.6	161.2	185.0
		E	both	254.5	249.2	276.3	277.7
		A_1	both	281.0	267.6	302.1	292.1

Table 19: Vibrational modes of $ZnCl_4(H_2O)_n^-$

n	structure	Irr. Rep.	Mode	Frequencies (cm^{-1})			
				HF		MP2	
				6-31G*	6-31+G*	6-31G*	6-31+G*
0	T_d	T_2	Zn-Cl	234.4	229.7	245.5	265.1
		A_1	Zn-Cl	236.0	236.3	242.6	258.5
1	C_{2v}	B_2	Zn-Cl	222.7	218.2	232.6	253.5
		A_1	Zn-Cl	232.1	229.3	240.3	255.9
		A_1	Zn-Cl	245.9	245.0	256.7	275.3
		B_2	Zn-Cl	248.9	245.9	262.2	282.4
2	C_{2v}	B_1	Zn-Cl	213.2	208.2	221.9	244.9
		A_1	Zn-Cl	229.7	227.1	236.7	254.3
		A_1	Zn-Cl	256.4	255.9	268.5	286.6
		B_2	Zn-Cl	262.7	261.4	277.9	300.1
	D_{2d}	E	Zn-Cl	239.9	234.2	248.9	270.6
		A_1	Zn-Cl	240.9	241.5	248.5	263.7
		B_2	Zn-Cl	244.9	241.5	257.7	275.2

Table 20: Solution compositions

Zn:Cl Ratios		Concentrations (mol/L)	
Zn:Cl	Cl:Zn	[Zn]	[Cl]
∞	0.00000	1.2339	0.0000
4.3290	0.23100	1.2347	0.2852
1.4040	0.71223	1.2421	0.8846
0.8169	1.2242	1.2394	1.5173
0.5791	1.7268	1.2391	2.1397
0.4658	2.1467	1.2419	2.6660
0.3712	2.6940	1.2398	3.3399
0.3169	3.1555	1.2402	3.9134
0.2722	3.6741	1.2430	4.5669
0.2431	4.1133	1.0060	4.1378
0.2193	4.5590	1.0088	4.5990
0.1951	5.1253	1.0080	5.1663
0.1769	5.6544	0.7345	4.1533
0.1624	6.1565	0.7521	4.6301
0.1486	6.7288	0.7607	5.1187
0.1329	7.5235	0.7469	5.6195
0.1276	7.8361	0.6862	5.377

Table 21: Relative energies (kJ/mol) of $ZnCl_m(H_2O)_n^{2-m} + lH_2O$

m	n	l	HF/6-31G*	HF/6-31+G*	MP2/6-31G*	MP2/6-31+G*
				Electronic Gas Phase		
1	5	0	0.00	0.00	0.00	0.00
1	4	1	-6.52	-3.67	-11.53	-5.18
1	3	2	-1.30	-3.74	-7.72	-4.42
2	4	0t	0.00	0.00	0.00	0.00
2	4	0c	5.73	9.88	-2.39	7.19
2	2	2	-11.86	-20.38	-30.42	-32.92
3	3	0f	73.92	81.23	75.73	85.68
3	1	2	0.00	0.00	0.00	0.00
				ZPE correction		
1	5	0	0.00	0.00	0.00	0.00
1	4	1	1.28	0.31	0.72	1.22
1	3	2	3.00	2.35	2.53	3.14
2	4	0t	0.00	0.00	0.00	0.00
2	4	0c	3.79	3.23	3.47	2.05
2	2	2	6.81	6.53	9.44	8.57
3	3	0f	-2.04	-3.86	-4.16	-6.24
3	1	2	0.00	0.00	0.00	0.00