CHAPTER 3 - APPENDIX A

SUPPLEMENTARY MATERIALS

Table 3A.1: Total energies for the optimized geometries of water, chloride, hydroxide and ammonia.

		Total Energy (Hartrees)			
Ligand	**Point Group**	**HF**	**MP2**	**B3LYP**	**C-PCM†**
H_2O	C_{2v}	-76.0177432	-76.2097764	-76.4225724	-76.433884
Cl^-	O_h	-459.5396609	-459.6711454	-460.2747259	-460.387014
OH^-	$C_{\infty v}$	-75.3764241	-75.5883641	-75.7966809	-75.931078
NH_3	C_{3v}	-56.1894994	-56.3631970	-56.5569857	-56.561088

†Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.2: Total energies for the stable geometries of $[Ni(H_2O)_n]^{2+}$, where n=0 – 6.

		Total Energy (Hartrees)			
n	**Point Group**	**HF**	**MP2**	**B3LYP**	**C-PCM†**
0	O_h	-1505.7832337	-1505.9225289	-1507.1343557	-1507.891672
1	C_s#1	1581.9313885	-1582.2188866	-1583.7441270	--
	C_s#2	-1581.8705465	-1582.2188866	-1583.7441129	-1584.308604
	C_{2v}	-1581.9537553	-1582.2989264	-1583.7441129	--
2	D_{2h}	-1658.0668942	-1658.6205866	-1660.2834407	-1660.747780
	D_{2d}	-1658.0748061	-1658.6263636	-1660.2876884	--
	C_s	-1658.0000750	-1658.5554510	-1660.2953768	--
	C_{2v}	-1658.0693425	-1658.6206930	-1660.2834410	-1660.747780
	C_2	-1658.0000751	-1658.5554510	-1660.2116357	-1660.743887
3	D_{3h}#1	-1734.1550982	-1734.8983665	-1736.7583650	--
	C_3	-1734.2037103	-1734.9538443	-1736.8247506	-1737.211909
	D_3	-1734.1666671	-1734.9157047	-1736.7868449	-1737.154660
	D_{3h}#2	-1734.1589583	-1734.9226233	-1736.8085537	-1737.184957
4	D_{4h}	-1810.2310590	-1811.1905298	-1813.2831239	--
	C_s#1	-1810.2967183	-1811.2457977	-1813.3218407	--
	C_2#1	-1810.2821941	-1811.2336714	-1813.3121517	-1813.658191
	C_2#2	-1810.2962889	-1811.2452445	-1813.3212448	-1813.671785
	C_s#2	-1810.2976555	-1811.2467159	-1813.3226296	-1813.672828
	C_4	-1810.2866201	-1811.2357411	-1813.3122940	--
	S_4	-1810.2926944	-1811.2404337	-1813.3164877	--
5	C_{2v}	-1886.3739823	-1887.5222347	-1889.8041655	-1890.140211
	C_2	-1886.3004572	-1887.4548028	-1889.8041655	-1890.140211
6	T_h#1	-1962.3816073	-1963.7180048	-1966.2013289	-1966.583284
	T_h#2	-1962.4418358	-1963.7896800	-1966.2764639	-1966.598582
	D_{2h}	-1962.4202853	-1963.7613287	-1966.2469053	-1966.589797

NOT Stable

†Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.3: Ni-O bond lengths for stable geometries of $[Ni(H_2O)_n]^{2+}$, where n=1 – 6.

		Optimized Ni-O Bond Lengths (Å)		
n	**Point Group Symmetry**	**HF/6-31+G***	**MP2/6-31+G***	**B3LYP/6-31+G***
1	C_s#1	1.946	1.941	--
	C_s#2	1.975	1.941	1.861
	C_{2v}	1.924	1.882	--
2	D_{2h}	--	1.893	1.876
	D_{2d}	--	1.903	--
	C_{2v}	--	1.904	1.877
	C_2	1.970	1.921	1.922
	C_s	1.971	1.921	--
3	D_{3h}	1.944	1.891	1.886
	D_3	2.024	1.981	1.970
	C_3	1.985	1.942	1.928
4	C_2#1	2.029 2.029	1.988 1.988	1.984 1.984
	C_2#2	2.029 2.034	1.989 1.993	1.984 1.996
	C_s	2.042 2.020 2.029	2.005 1.976 1.987	2.004 1.968 1.987
5	C_2	2.275 2.048 2.062	2.255 1.992 2.020	2.026 2.065 2.016
	C_{2v}	2.067 2.102 2.058	2.022 2.061 2.014	2.026 2.065 2.016
6	D_{2h}	2.183 2.080 2.231	2.135 2.034 2.212	2.119 2.035 2.257
	T_h#1	2.207	2.175	2.186
	T_h#2	2.117	2.071	2.079

Table 3A.4: Vibrational stretching frequencies of stable geometries of $[Ni(H_2O)_n]^{2+}$, where n=1 – 6, calculated at HF/6-31+G*.

n	Point Group	Freq. (cm^{-1})	Irr. Rep. Symm.	Mixing
1	C_s#1	491.5	a'	
	C_s#2	474.9	a'	
	C_{2v}	507.7	a_1	
2	C_s	400.3	a'	
		527.6	a'	
	C_2	401.0	a	
		528.5	b	
3	D_{3h}	423.0	a_1'	
		487.0	e'	H_2O wag
		487.0	e'	H_2O wag
	D_3	376.9	a_1	
		415.6	e	
		415.6	e	
	C_3	415.0	a	
		436.2	e	H_2O wag
		436.2	e	H_2O wag
4	C_2#1	366.9	b	
		372.7	a	
		375.5	a	
		421.1	b	H_2O wag
	C_2#2	355.8	a	H_2O wag
		379.7	b	H_2O wag
		387.9	a	H_2O wag
		394.6	b	H_2O wag
	C_s	351.9	a'	
		379.9	a'	
		391.9	a'	H_2O wag
		403.2	a"	H_2O wag
5	C_2	245.3	a	H_2O wag
		308.7	a	
		361.2	a	
		374.3	b	H_2O wag
		377.7	b	H_2O wag
	C_{2v}	265.2	a_1	
		333.1	a_1	H_2O wag
		344.4	b_2	H_2O wag
		361.6	a_1	
		371.4	b_1	H_2O wag

6	D_{2h}	191.2	a_g	
		249.9	a_g	
		281.8	b_{3u}	H_2O wag
		291.9	b_{2u}	H_2O wag
		331.1	a_g	
		355.7	b_{1u}	H_2O wag
	T_h#1	211.8	e_g	
		221.3	e_g	
		288.4	t_u	H_2O wag
		290.3	t_u	H_2O wag
		307.8	t_u	H_2O wag
		315.3	a_g	
	T_h#2	246.9	e_g	
		246.9	e_g	
		322.5	t_u	H_2O wag
		322.5	t_u	H_2O wag
		322.5	t_u	H_2O wag
		335.3	a_g	

Table 3A.5: Vibrational stretching frequencies of stable geometries of $[Ni(H_2O)_n]^{2+}$, where n=1 – 6, calculated at MP2/6-31+G*.

n	Point Group	Freq. (cm^{-1})	Irr. Rep. Symm.	Mixing
1	C_{2v}	531.7	a_1	
	C_s#1	495.5	a'	
	C_s#2	495.4	a'	
2	D_{2h}	439.0	a_g	
		585.5	b_{1u}	
	D_{2d}	438.4	a_1	
		580.5	b_2	
	C_{2v}	450.7	a_1	
		617.8	b_2	
	C_2	427.4	a	
		574.3	b	
	C_s	427.1	a'	
		574.0	a'	
3	D_{3h}	448.0	a_1'	
		533.2	e'	
		533.2	e'	
	D_3	391.7	a_1	
		433.1	e	
		433.1	e	
	C_3	431.5	a	
		473.5	e	
		473.5	e	
4	C_2#1	381.1	b	H_2O wag
		393.0	a	
		406.9	a	H_2O wag
		449.4	b	
	C_2#2	370.3	a	H_2O wag
		408.6	a	H_2O wag
		414.8	b	H_2O wag
		433.3	b	H_2O wag
	C_s	363.1	a'	H_2O wag
		383.3	a'	H_2O wag
		386.4	a'	H_2O wag
		404.8	a'	H_2O wag
		429.3	a'	H_2O wag
		439.9	a"	H_2O wag

5	C_{2v}	282.1	a_1	
		351.0	a_1	H_2O wag
		374.9	b_2	H_2O wag
		385.2	a_1	H_2O wag
		427.4	b_1	H_2O wag
	C_2	251.9	a	H_2O wag
		353.0	a	H_2O wag
		364.8	b	H_2O wag
		384.8	a	
		401.0	b	H_2O wag
		439.8	a	H_2O twist
		439.8	a	H_2O wag
6	T_h#1	214.3	e_g	
		227.5	e_g	
		286.9	t_u	H_2O wag
		294.6	t_u	H_2O wag
		314.2	t_u	H_2O wag
		328.0	a_g	
	T_h#2	268.3	e_g	
		268.3	e_g	
		322.0	t_u	H_2O wag
		322.0	t_u	H_2O wag
		322.0	t_u	H_2O wag
		355.0	a_g	
	D_{2h}	185.2	a_g	
		267.1	a_g	
		282.2	b_{3u}	H_2O wag
		282.2	b_{2u}	H_2O wag
		345.4	b_{2u}	H_2O wag
		349.8	a_g	

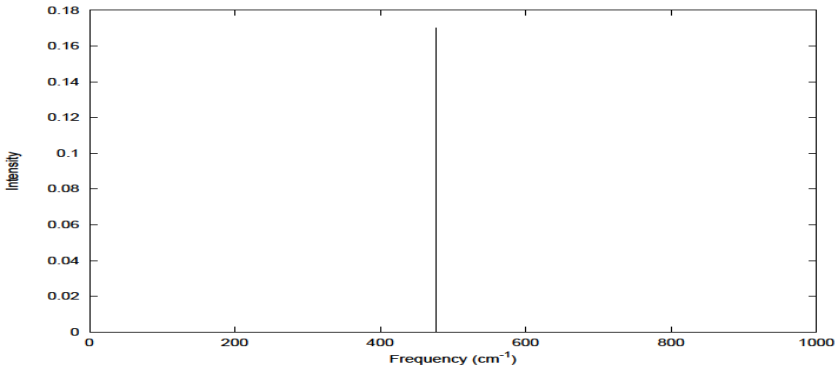
Table 3A.6: Vibrational stretching frequencies of stable geometries of $[Ni(H_2O)_n]^{2+}$, where n=1 – 6, calculated at B3LYP/6-31+G*.

n	Point Group	Freq. (cm^{-1})	Irr. Rep. Symm.	Mixing
1	C_s	524.4	a'	H_2O wag
2	D_{2h}	444.2	a_g	
		587.2	b_{1u}	
	C_{2v}	443.1	a_1	
		585.8	b_2	
	C_2	425.8	a	
		565.6	b	
3	D_{3h}	456.5	a_1'	
		549.8	e'	
		550.0	e'	
	D_3	394.3	a_1	
		427.8	e	
		427.8	e	
	C_3	432.4	a	H_2O wag
		478.2	e	H_2O wag
		478.3	e	H_2O wag
4	C_2#1	367.6	b	H_2O wag
		389.7	a	H_2O wag
		395.4	a	
		445.8	b	
	C_2#2	358.0	a	H_2O wag
		406.9	a	H_2O wag
		411.0	b	H_2O wag
		424.4	b	H_2O wag
	C_s	368.7	a'	H_2O wag
		401.5	a'	H_2O wag
		425.8	a''	H_2O wag
		430.3	a'	H_2O wag
5	C_2	275.2	a	
		356.5	b	H_2O wag
		359.1	a	H_2O wag
		378.8	a	
		413.3	b	H_2O wag
	C_{2v}	275.1	a_1	
		356.5	b_2	H_2O wag
		359.0	a_1	H_2O wag
		378.7	a_1	
		413.2	b_1	H_2O wag

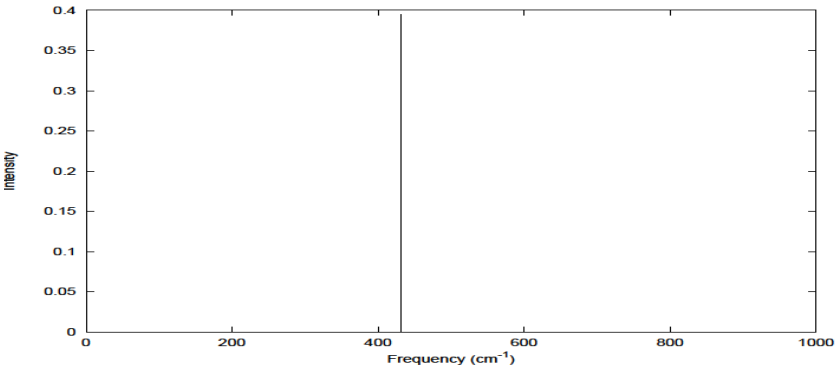
6	T_h#1	191.4 209.6 265.0 272.4 303.6 318.4	e_g e_g a_g t_u t_u t_u	 H_2O wag H_2O wag H_2O wag
	T_h#2	258.9 258.9 350.3 351.2 351.2 351.2	e_g e_g a_g t_u t_u t_u	 H_2O wag H_2O wag H_2O wag
	D_{2h}	154.8 248.0 256.6 265.4 328.4 346.5 362.6 401.0	a_g b_{3u} a_g b_{2u} b_{2u} a_g b_{1u} b_{1u}	H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag

Figure 3A-1: Simulated polarized Raman spectra for $[Ni(H_2O)_n]^{2+}$, where n=1 – 6

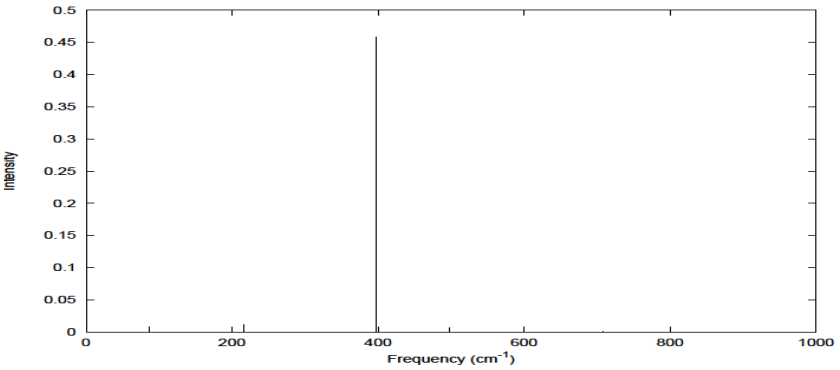
(H_2O)



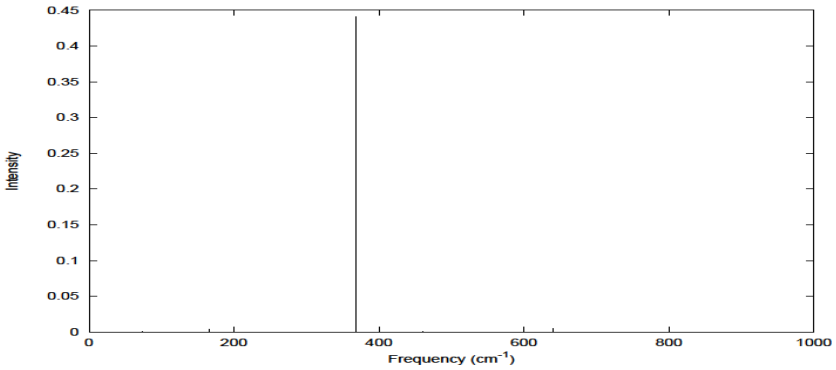
$(H_2O)_2$



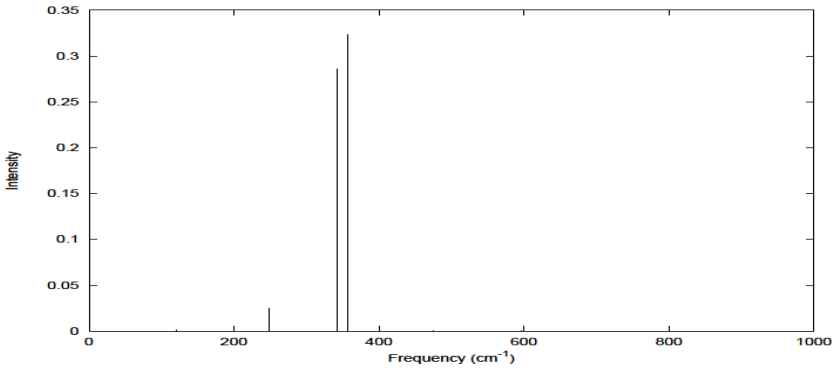
$(H_2O)_3$



$(H_2O)_4$



$(H_2O)_5$



$(H_2O)_6$

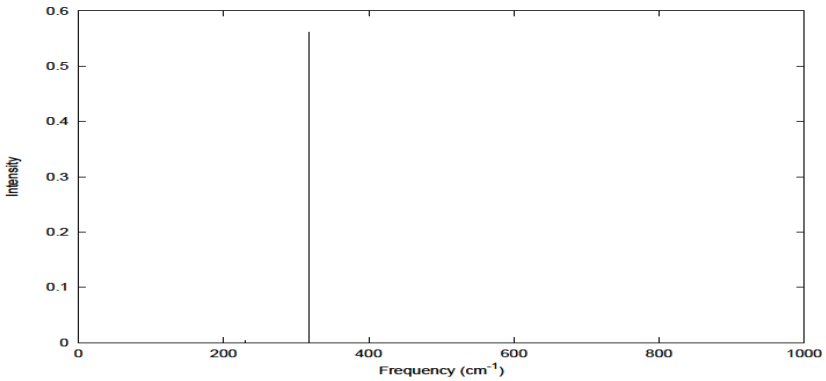


Table 3A.7: Total energies for all stable geometries of $[NiCl_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

			Total Energy (Hartrees)			
n	**m**	**Point Group**	**HF**	**MP2**	**B3LYP**	**C-PCM†**
1	0	$C_{\infty v}$ #1	-1965.884361	-1966.19764	-1968.057802	-1968.285348
		$C_{\infty v}$ #2	-1965.884361	-1966.19764	-1968.057144	-1968.283182
1	1	C_{2v}	-2041.9665359	-2042.4833722	-2044.5510704	--
		C_s #1	-2041.9922628	-2042.5021509	-2044.5512728	-2044.720267
		C_s #2	-2041.9901332	-2042.4194259	-2044.5684609	--
		C_1	-2041.9019069	-2042.4194259	-2044.5685071	-2044.737069
1	2	C_{2v}	-2118.0354508	-2118.743896	-2121.0130535	-2121.169272
		C_s	-2118.0354504	-2118.743896	-2121.0474062	--
		C_1	-2118.0719511	-2118.7819982	-2121.0501868	-2121.186794
1	3	C_3	-2194.1408265	-2195.0510299	-2197.5192907	--
		C_1	-2194.1408523	-2195.05103	-2197.5193688	-2197.638896
1	4	C_4	-2270.1810505	-2271.2850097	-2273.9571295	-2274.092667
		C_2	-2270.1936202	-2271.3032993	-2273.9774761	-2274.101670
		C_1	-2270.1936199	-2271.3032993	-2273.977544	-2274.102898
1	5	C_2	-2346.2473016	-2347.5558748	-2350.4328404	--
		C_1	-2346.2473016	-2347.5559681	-2350.4327465	-2350.554839
2	0	$D_{\infty h}$ #1	-2425.666213	-2426.136892	-2428.646861	-2428.699499
		$D_{\infty h}$ #2	-2425.743116	-2426.214835	-2428.667267	-2428.695876
2	1	C_{2v}	-2501.8039684	-2502.4640566	-2505.1072273	--
		C_1	-2501.8064892	-2502.4704149	-2505.1210337	-2505.157899
2	2	C_{2v}	-2577.8573807	-2578.7182479	-2578.7182479	-2581.609313
2	3	C_{3h}	-2653.851715	-2654.9020493	-2657.9646699	--
		C_1	-2653.8984113	-2654.9592091	-2658.017955	-2658.048699
2	4	cis-C_2	-2729.9326862	-2731.195399	-2734.4610234	-2734.497656
		cis-C_1	-2729.9229515	-2731.1869407	-2734.4542947	-2734.497876
		trans-C_{4h}	-2729.939175	-2731.2016	-2734.463343	-2734.506911
		trans-C_2	-2729.934947	-2731.19616	-2734.458202	-2734.50354
		trans-C_1	-2729.939175	-2731.2016	-2734.463151	-2734.507602
3	0	D_{3h}	-2885.35664	-2885.960392	-2888.994213	-2889.089456
		C_{2v}	-2885.38723	-2885.9933925	-2889.029186	-2889.089058
		C_s	-2885.3748156	-2885.9955507	-2889.0340637	-2889.112569
		C_1	-2885.3441753	-2885.9687215	-2889.0213546	-2889.091440
3	1	C_s	-2961.4276848	-2962.2336031	-2965.4744365	--
		C_1	-2961.4276847	-2962.23361	-2965.4744329	-2965.548567

3	2	C_{2v}	-3037.4482676	-3038.4506277	-3041.8998775	--
		C_1	-3037.4609235	-3038.4674474	-3041.9150537	-3041.992615
3	3	fac-C_{3v}	-3113.4890229	-3114.6994586	-3118.3546164	-3118.434093
		fac-C_1	-3113.4890229	-3114.6994558	-3118.3546002	-3118.435810
		mer-C_1	-3113.488086	-3114.697826	-3118.3508	-3118.437062
4	0	T_d #1	-3344.854000	-3345.589235	-3349.211157	-3349.491459
		T_d #2	-3344.861014	-3345.599857	-3349.224403	-3349.502449
4	1	C_{2v} [3+2]	-3420.846244	-3421.797304	-3425.669942	-3425.908713
4	2	C_{2v} [4+2]	-3496.946267	-3498.087819	-3502.136855	-3502.37884

NOT Stable †Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.8: Ni-Cl and Ni-O bond lengths for stable geometries of $[NiCl_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

			Optimized Ni-O and Ni-Cl Bond Lengths (Å)					
			HF/6-31+G*		**MP2/6-31+G***		**B3LYP/6-31+G***	
n	**m**	**Point Group Symmetry**	**Ni-Cl**	**Ni-O**	**Ni-Cl**	**Ni-O**	**Ni-Cl**	**Ni-O**
1	0	$C_{\infty v}$ #1	2.106	N/A	2.045	N/A	2.055	N/A
		$C_{\infty v}$ #2	2.106	N/A	2.045	N/A	2.024	N/A
1	1	C_{2v}	2.111	1.992	--	--	--	--
		C_s #1	2.122	1.977	2.072	1.944	2.076	1.966
		C_s #2	2.114	1.977	2.069	1.964	--	--
		C_1	2.117	2.017	2.069	1.964	2.034	1.926
1	2	C_{2v}	2.153	2.093	2.091	2.056	2.106	2.063
		C_s	2.153	2.092 2.092	2.092	2.056 2.056	--	--
		C_1	2.151	2.031 2.031	2.079	2.006 1.973	2.071	2.028 1.965
1	3	C_3	--	--	2.109	2.037	--	--
		C_1	2.184	2.072 2.068 2.077	2.109	2.037 2.037 2.037	2.105	2.056 2.057 2.052
1	4	C_4	--	--	--	--	2.141	2.181
		C_2	2.263	2.115 2.115	2.204	2.063 2.063	2.243	2.072 2.071
		C_1	2.262	2.115 2.115 2.115 2.115	2.204	2.063 2.063 2.063 2.063	2.240	2.071 2.072 2.072 2.072
1	5	C_2	2.321	2.152 2.145 2.145	--	--	--	--
		C_1	2.321	2.152 2.145 2.152 2.145 2.145	2.251	2.096 2.103 2.109 2.089 2.095	2.290	2.107 2.137 2.116 2.101 2.107
2	0	$D_{\infty h}$ #1	2.165	N/A	2.111	N/A	2.136	N/A
		$D_{\infty h}$ #2	2.157	N/A	2.080	N/A	2.074	N/A
2	1	C_{2v}	2.212	2.110	2.153	2.038	--	--
		C_1	2.209 2.209	2.072	2.139 2.139	2.139	2.143 2.143	2.042
2	2	C_{2v}	2.259	2.096	2.191	2.044	2.213	2.047

2	3	C_{3h}	2.312	2.311	--	--	--	--
		C_1	2.321 2.327	2.172 2.131 2.107	2.241 2.258	2.122 2.082 2.061	2.253 2.310	2.132 2.096 2.091
2	4	cis-C_2	2.400	2.162 2.194	2.314	2.113 2.134	2.363	2.126 2.152
		cis-C_1	2.417 2.417	2.169 2.169 2.142 2.142	2.338 2.338	2.113 2.115 2.093 2.094	2.374 2.374	2.134 2.134 2.122 2.122
		trans-C_{4h}	2.387	2.159	2.307	2.104	2.343	2.122
		trans-C_2	2.386 2.387	2.159 2.159	2.307 2.307	2.104 2.104	2.343 2.343	2.122 2.122
		trans-C_1	2.386 2.387	2.159 2.159 2.159 2.159	2.307 2.307	2.104 2.104 2.104 2.104	2.340 2.340	2.120 2.120 2.121 2.121
3	0	D_{3h}	2.304	N/A	2.234	N/A	2.250	N/A
		C_{2v}	2.282 2.291	N/A	--	N/A	2.242 2.211	N/A
		C_s	2.302 2.274	N/A	2.202 2.203	N/A	2.209 2.208	N/A
		C_1	2.255 2.255 2.255	N/A	2.159 2.159 2.159	N/A	2.181 2.181 2.181	N/A
3	1	C_s	2.309 2.346	2.177	--	--	--	--
		C_1	2.309 2.346 2.346	2.176	2.221 2.274 2.272	2.123	2.232 2.306 2.306	2.144
3	2	C_{2v}	2.311 2.476	2.284	--	--	--	--
		C_1	2.377 2.426 2.377	2.219 2.219	2.289 2.340 2.288	2.161 2.160	2.330 2.368 2.330	2.175 2.174
3	3	fac-C_{3v}	2.486	2.233	2.390	2.172	2.439	2.191
		fac-C_1	2.485 2.486 2.486	2.219 2.219	2.388 2.390 2.394	2.161 2.160	2.440 2.440 2.440	2.175 2.174
		C_1 [5+1]	2.426 2.426	2.129 2.207 2.208	2.336 2.336	2.051 2.122 2.123	2.378 2.378	2.061 2.134 2.134

4	0	T_d #1	2.449	N/A	2.365	N/A	2.400	N/A
		T_d #1	2.434	N/A	2.344	N/A	2.376	N/A
4	1	C_{2v} [3+2]	2.256	1.920	2.166	1.858	2.242	1.882
4	2	C_{2v} [4+2]	2.332	2.075	2.251	2.029	2.281	2.037

Table 3A.9: Ni-O and Ni-Cl vibrational stretching frequencies of $[NiCl_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n) calculated at HF/6-31+G*.

n	m	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	Cl/H_2O	Mixing
1	0	$C_{\infty v}$ #1	474.5	σ_g	Cl	
1	1	C_s #1	385.5	a'	Cl/H_2O	
			519.4	a'	Cl/H_2O	
1	2	C_1	358.6	a	Cl/H_2O	
			370.9	a	H_2O	
			468.8	a	Cl/H_2O	H_2O rock
1	3	C_1	327.7	a	H_2O	H_2O wag
			336.9	a	H_2O	H_2O wag
			342.5	a	H_2O	H_2O wag
			429.1	a	Cl	H_2O wag
1	4	C_2	254.1	a	H_2O	H_2O twist
			306.0	a	H_2O	H_2O twist
			316.9	a	H_2O	H_2O twist
			334.2	b	H_2O	H_2O twist
			334.2	b	H_2O	H_2O twist
			363.5	a	Cl	H_2O rock
1	5	C_2	225.9	a	Cl/H_2O	H_2O twist
			234.7	a	Cl/H_2O	H_2O twist
			286.6	b	H_2O	H_2O wag
			308.1	b	H_2O	H_2O wag
			308.6	a	H_2O	H_2O twist
			333.9	a	Cl/H_2O	H_2O twist
2	0	$D_{\infty h}$ #2	340.0	σ_g	Cl	
			497.9	σ_u	Cl	
2	1	C_1	322.3	a	Cl/H_2O	
			334.1	a	H_2O	
			443.6	a	Cl	H_2O rock
2	2	C_{2v}	301.8	a_1	Cl/H_2O	
			318.7	b_1	H_2O	
			320.3	a_1	H_2O	
			397.5	b_2	Cl	H_2O twist
2	3	C_1	220.3	a	Cl/H_2O	
			292.5	a	Cl/H_2O	
			305.4	a	H_2O	H_2O rock
			306.9	a	Cl/H_2O	H_2O rock
			317.2	a	Cl/H_2O	H_2O wag
			354.8	a	Cl	H_2O rock

2	4	trans-C_{4h}	211.2 229.8 248.7 297.0 299.8 299.8 312.7	a_g b_g a_u a_g e_u e_u a_u	Cl/H_2O H_2O Cl Cl/H_2O H_2O H_2O Cl	 H_2O rock H_2O wag H_2O wag H_2O rock
3	0	C_{2v}	284.1 344.6 345.4	a_1 a_1 b_2	Cl Cl Cl	
3	1	C_s	249.7 283.0 298.9 330.4	a' a' a" a'	Cl/H_2O Cl/H_2O Cl Cl/H_2O	 H_2O rock
3	2	C_1	178.4 247.6 251.8 274.6 295.8	a a a a a	Cl/H_2O Cl/H_2O Cl Cl/H_2O Cl	 H_2O rock H_2O rock
3	3	fac-C_{3v}	198.4 198.4 211.7 260.8 260.8 278.9	e e a_1 e e a_1	Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O	
4	0	T_d #2	228.6 230.8 230.8 232.8	t_2 e e a_1	Cl Cl Cl Cl	
4	1	C_{2v} [4+1]	313.0 365.8 524.8	a_1 b_1 a_1	Cl Cl H_2O	 H_2O wag
4	2	C_{2v} [4+2]	284.7 309.0 334.1 386.3	a_1 b_2 b_1 a_1	Cl Cl H_2O H_2O	 H_2O rock

Table 3A.10: Ni-O and Ni-Cl vibrational stretching frequencies of $[NiCl_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n) calculated at MP2/6-31+G*.

n	m	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	Cl/H_2O	Mixing
1	0	$C_{\infty v}$ #1	487.5	σ_g	Cl	
1	1	C_s #1	398.5	a'	Cl/H_2O	
			537.9	a'	Cl/H_2O	
1	2	C_1	382.0	a	Cl/H_2O	
			389.5	a	H_2O	
			459.2	a	Cl	
1	3	C_3	354.4	e	H_2O	
			354.4	e	H_2O	
			359.4	a	Cl/H_2O	
			461.7	a	Cl/H_2O	H_2O wag
1	4	C_2	280.6	a	H_2O	H_2O twist
			341.9	a	Cl/H_2O	H_2O twist
			369.4	b	H_2O	H_2O rock
			369.5	b	H_2O	H_2O rock
			382.2	a	Cl/H_2O	H_2O rock
1	5	C_1	248.7	a	Cl/H_2O	H_2O rock
			251.3	a	H_2O	H_2O twist
			277.6	a	Cl/H_2O	H_2O wag
			284.3	a	H_2O	H_2O twist
			315.6	a	H_2O	H_2O wag
			333.3	a	H_2O	
			341.9	a	H_2O	H_2O rock
			353.6	a	Cl/H_2O	H_2O rock
			373.0	a	Cl/H_2O	H_2O rock
2	0	$D_{\infty h}$ #2	353.7	σ_g	Cl	
			526.8	σ_u	Cl	
2	1	C_1	340.6	a	Cl	
			365.5	a	H_2O	
			471.3	a	Cl	H_2O rock
2	2	C_{2v}	323.5	a_1	Cl	
			353.8	b_1	H_2O	
			356.6	a_1	H_2O	
			423.4	b_2	Cl	H_2O twist
2	3	C_1	248.2	a	Cl/H_2O	
			315.6	a	Cl/H_2O	
			338.6	a	H_2O	H_2O rock
			349.3	a	H_2O	H_2O rock
			381.1	a	Cl/H_2O	H_2O rock

2	4	trans-C_{4h}	239.6 260.0 320.8 335.3 335.3 341.4	a_g b_g a_g e_u e_u a_u	Cl/H_2O H_2O Cl/H_2O H_2O H_2O Cl	 H_2O rock
3	0	C_s	304.4 381.3 381.5	a' a" a'	Cl Cl Cl	
3	1	C_1	276.3 305.1 323.9 366.0	a a a a	Cl/H_2O Cl/H_2O Cl Cl/H_2O	 H_2O rock H_2O wag
3	2	C_1	208.7 282.2 285.9 298.6 335.8	a a a a a	Cl/H_2O H_2O Cl Cl/H_2O Cl/H_2O	 H_2O rock H_2O rock
3	3	C_{3v}	224.3 224.4 247.0 294.6 294.6 306.6	e e a_1 e e a_1	Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O	 H_2O rock H_2O rock
4	0	T_d #2	247.4 258.2 258.3 266.0	t_2 e e a_1	Cl Cl Cl Cl	
4	1	C_{2v} [4+1]	336.2 398.9 587.3	a_1 b_1 a_1	Cl Cl H_2O	
4	2	C_{2v} [4+2]	272.7 305.1 343.5 369.8 415.9	a_1 a_1 b_2 b_1 a_1	Cl Cl Cl H_2O H_2O	 H_2O rock

Table 3A.11: Ni-O and Ni-Cl vibrational stretching frequencies of $[NiCl_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n) calculated at B3LYP/6-31+G*.

n	m	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	Cl/H_2O	Mixing
1	0	$C_{\infty v}$ #1	452.2	σ_g	Cl	
1	1	C_1	391.8	a	Cl/H_2O	
			526.6	a	Cl/H_2O	
1	2	C_1	363.8	a	Cl/H_2O	H_2O wag
			367.9	a	H_2O	H_2O wag
			376.0	a	Cl/H_2O	H_2O wag
			485.2	a	Cl/H_2O	H_2O wag
1	3	C_1	325.5	a	H_2O	
			332.3	a	H_2O	
			346.9	a	Cl/H_2O	
			400.6	a	Cl/H_2O	
1	4	C_1	267.7	a	H_2O	
			320.7	a	Cl/H_2O	H_2O rock
			353.3	a	Cl/H_2O	
			354.3	a	H_2O	
			354.5	a	H_2O	
1	5	C_1	234.6	a	Cl/H_2O	H_2O twist
			239.3	a	Cl/H_2O	H_2O rock
			252.3	a	H_2O	H_2O wag
			269.2	a	H_2O	H_2O twist
			299.9	a	H_2O	H_2O wag
			307.4	a	Cl/H_2O	H_2O rock
			324.4	a	Cl/H_2O	H_2O rock
			332.7	a	Cl/H_2O	H_2O rock
			343.7	a	Cl/H_2O	H_2O rock
2	0	$D_{\infty h}$ #2	352.3	σ_g	Cl	
			514.1	σ_u	Cl	
2	1	C_1	327.7	a	Cl/H_2O	
			351.0	a	H_2O	
			446.6	a	Cl	H_2O rock
2	2	C_{2v}	301.9	a_1	Cl	
			345.8	b_1	H_2O	
			349.0	a_1	H_2O	
			389.4	b_2	Cl	H_2O twist
2	3	C_1	234.5	a	Cl/H_2O	
			289.1	a	Cl/H_2O	H_2O rock
			313.8	a	Cl/H_2O	
			324.6	a	H_2O	H_2O rock
			340.8	a	Cl/H_2O	H_2O rock
			356.3	a	Cl/H_2O	H_2O rock

2	4	trans-C_{4h}	217.3 244.8 308.7 313.1 313.1 313.6	a_g b_g a_g e_u e_u a_u	Cl/H_2O H_2O Cl/H_2O H_2O H_2O Cl	 H_2O rock
3	0	C_s	290.9 353.4 354.9	a' a' a''	Cl Cl Cl	
3	1	C_1	249.0 287.6 290.3 337.9	a a a a	Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O	
3	2	C_1	187.7 257.5 258.6 285.8 288.1	a a a a a	Cl/H_2O Cl Cl/H_2O Cl/H_2O Cl	 H_2O rock H_2O rock H_2O rock
3	3	fac-C_{3v}	207.7 207.7 219.6 269.5 269.5 289.5	e e a_1 e e a_1	Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O	H_2O twist H_2O twist
4	0	T_d #2	215.4 215.4 225.6 229.1	t_2 e e a_1	Cl Cl Cl Cl	
4	1	C_{2v} [4+1]	283.0 318.1 484.2	a_1 b_1 a_1	Cl Cl H_2O	
4	2	C_{2v} [4+2]	256.6 288.2 301.8 350.9 400.2	a_1 a_1 b_2 b_1 a_1	Cl Cl Cl H_2O H_2O	 H_2O rock

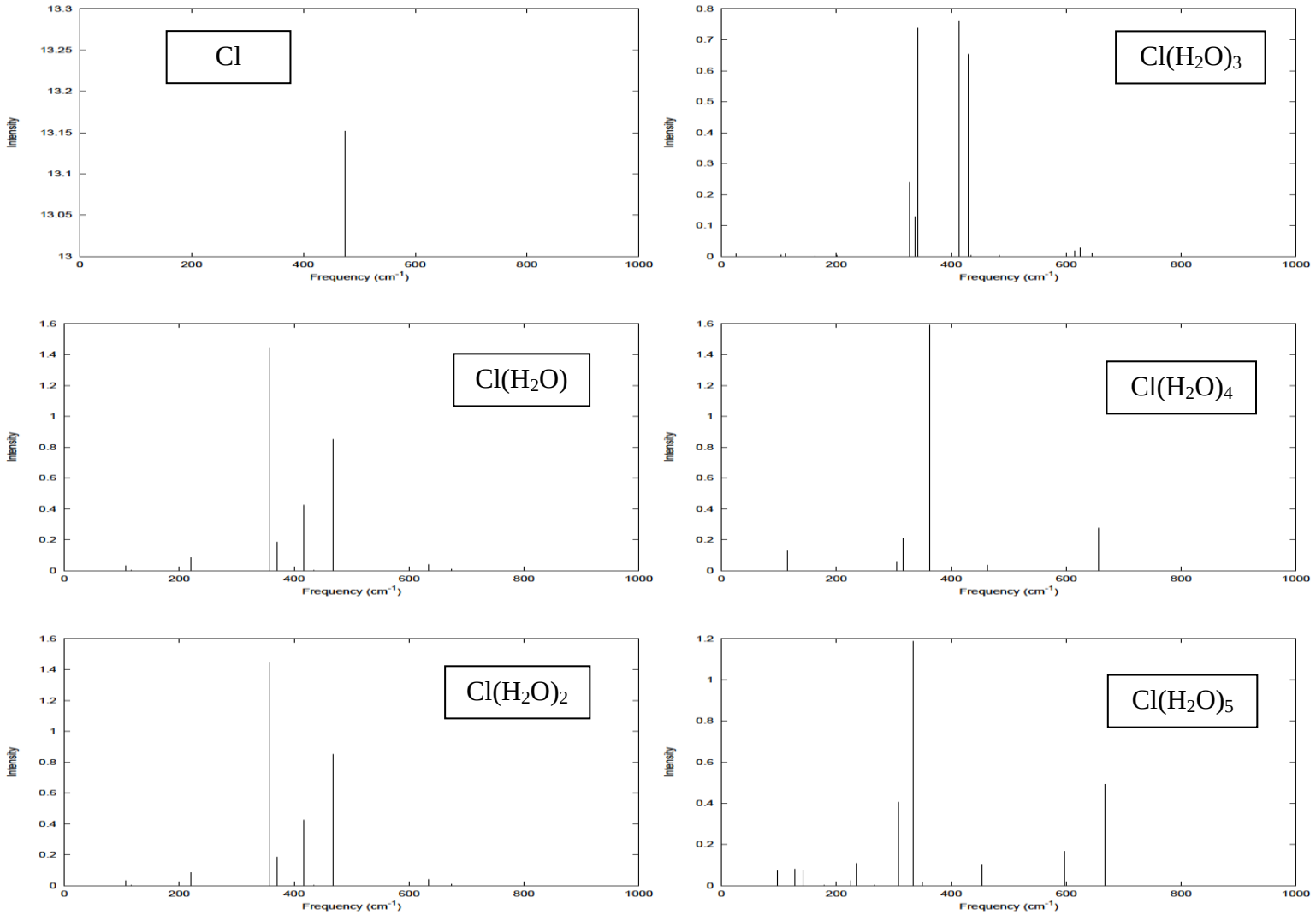


Figure 3A-2: Simulated polarized Raman spectra for $[NiCl_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

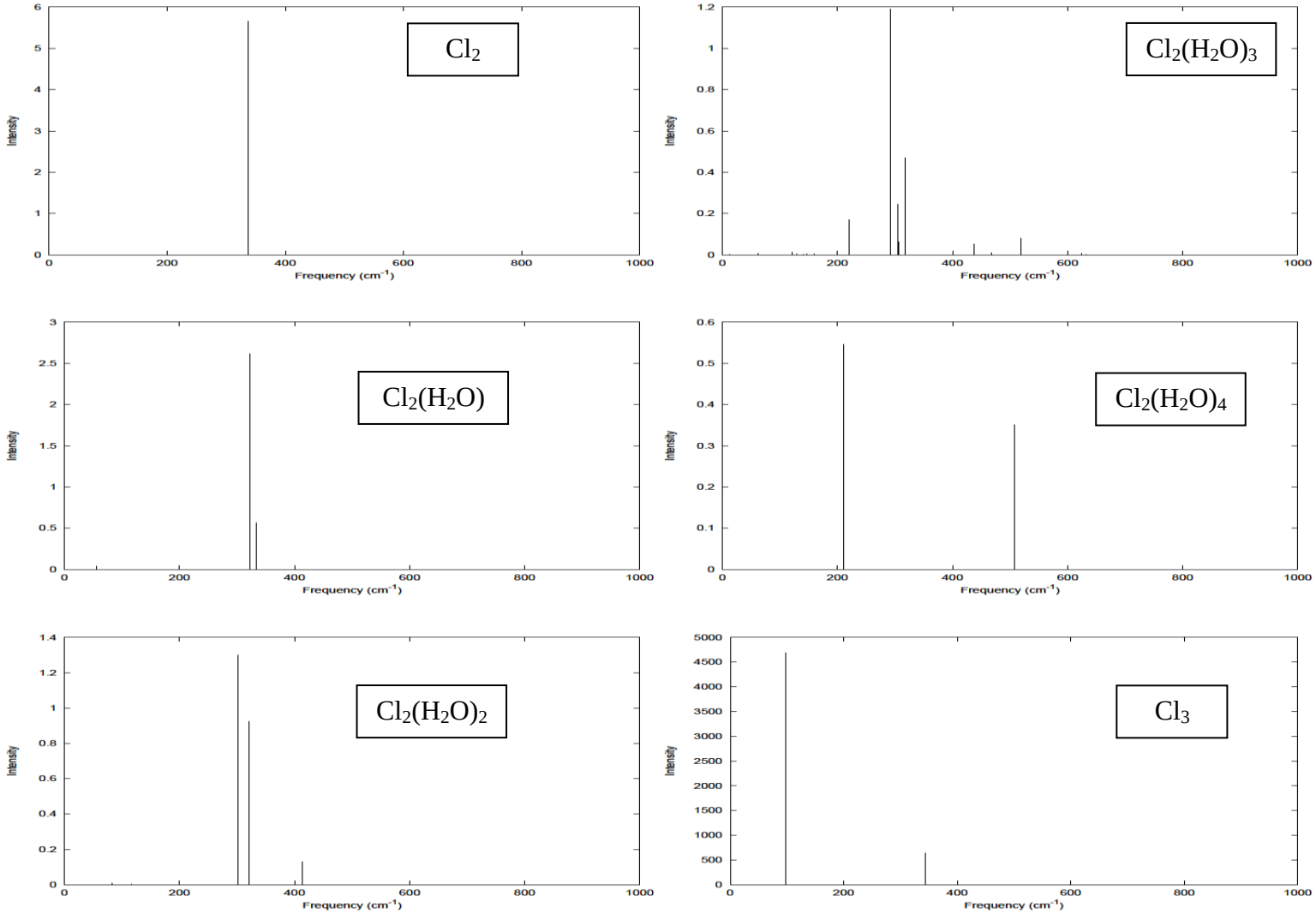


Figure 3A-2: *(continued)*

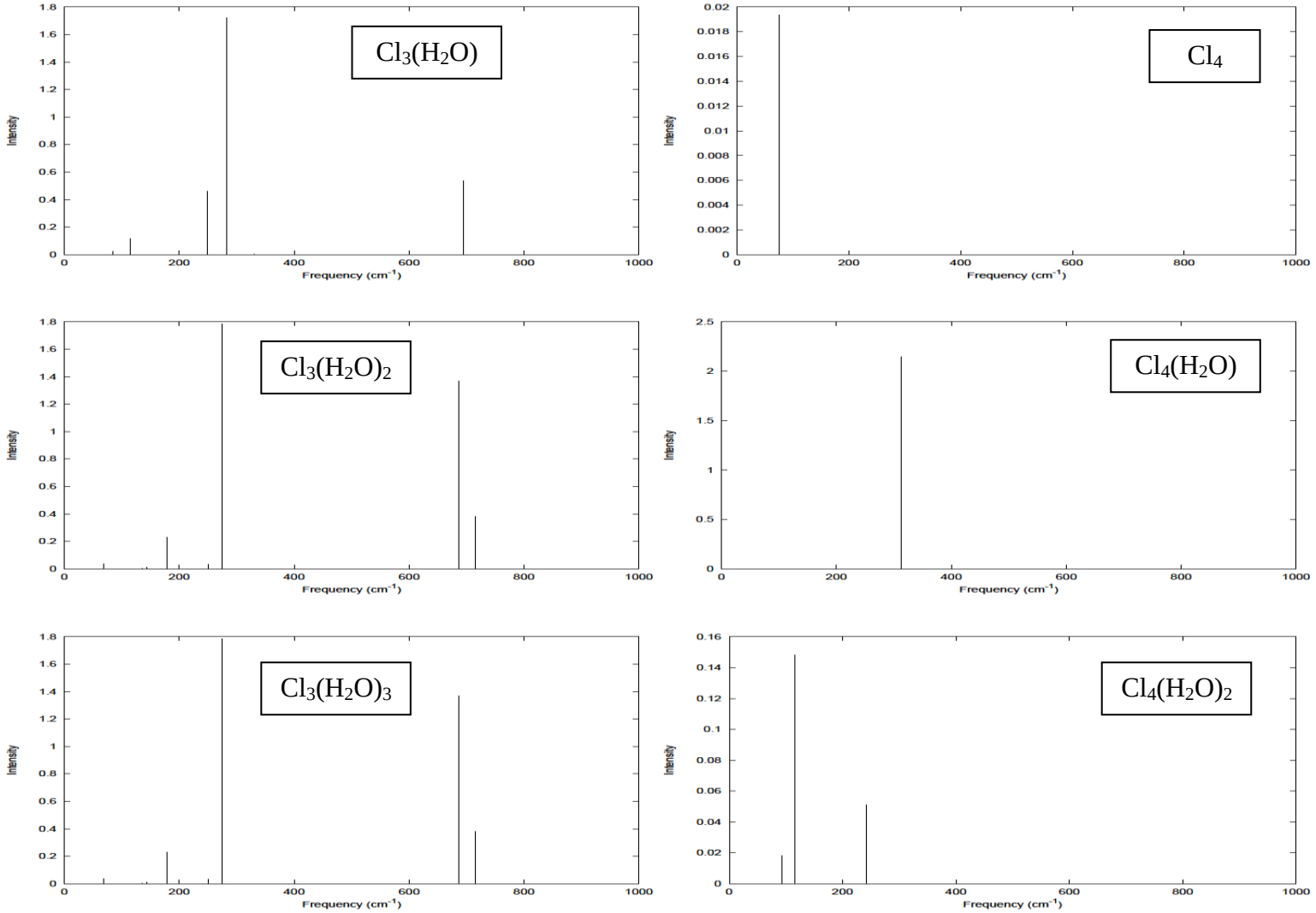


Figure 3A-2: *(continued)*

Table 3A.12: Total energies for all stable geometries of $[Ni(OH)_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

			Total Energy (Hartrees)			
n	**m**	**Point Group**	**HF**	**MP2**	**B3LYP**	**C-PCM†**
1	0	C_s	-1581.78617830	-1582.16967900	-1583.65042140	-1583.88114
1	1	C_s	-1657.81305360	-1658.32815520	-1660.18132620	-1660.33638
		C_1	-1657.91671820	-1658.49799460	-1660.18131800	-1660.335834
1	2	C_1	-1733.99233290	-1734.77048430	-1736.65473950	-1736.791805
1	3	C_1	-1810.05859060	-1811.03292560	-1813.11748700	-1813.235109
1	4	C_1	-1886.11180130	-1887.28411630	-1889.57392140	-1889.686223
1	5	C_1	-1962.16179380	-1963.53395880	-1966.02500970	-1966.136391
2	0	C_{2v} #1	-1657.3901886	-1657.9604689	-1659.8605198	--
		C_{2v} #2	-1657.39765820	-1658.16230100	-1659.83694020	-1659.887261
		C_2	-1657.58540680	-1658.18519690	-1659.86288260	-1659.888691
2	1	C_s	-1733.59122830	-1734.43101770	-1736.3092134	--
		C_1	-1733.63240700	-1734.42940340	-1736.23910850	-1736.342056
2	2	C_1	-1809.67542070	-1810.66730370	-1812.75031400	-1812.774219
2	3	C_1	1885.71102810	-1886.90144590	-1889.1908982	-1889.215298
2	4	C_1 [5+1]	-1961.75162320	-1963.14136190	-1965.63786960	-1965.663983
		cis-C_1	-1961.747273	-1963.140185	-1965.633098	-1965.663156
3	0	C_3	-1733.08091690	-1733.89079280	-1735.76625560	-1735.868499
		C_1	-1733.07935930	-1733.88972640	-1735.76510580	-1735.867483
3	1	C_s [3+1]	-1809.1186792	-1810.1297168	-1812.2167927	--
		C_1 [3+1]	-1809.12613230	-1810.13365490	-1812.21986650	-1812.313077
3	2	C_1 [4+1]	-1885.16276240	-1886.37012630	-1888.65896070	-1888.749692
3	3	fac-C_{3v} #1	-1961.1970624	-1962.60878990	-1965.1021487	--
		C_{3v} #2 [3+3]	-1961.20388760	-1962.60653600	-1965.11598350	-1965.195615
		C_3 [3+3]	-1961.20388760	-1962.59328140	-1965.11599650	-1965.195644
4	0	S_4	-1808.39030340	-1809.41385370	-1811.48410740	-1811.809330
		C_2	-1808.39157600	-1809.41540790	-1811.48645920	-1811.812296
4	1	C_2 [4+1]	-1884.45643380	-1885.67915860	-1887.96030300	-1888.262316
4	2	C_2 [4+2]	-1960.51677980	-1961.93801130	-1964.43020740	-1964.710782

NOT Stable

†Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.13: Ni-O bond lengths, in Angstroms, for energy minimum structures of $[Ni(OH)_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

			Optimized Ni-O Bond Lengths (Å)					
			HF/6-31+G*		MP2/6-31+G*		B3LYP/6-31+G*	
n	**m**	**Symmetry**	**OH**	**H_2O**	**OH**	**H_2O**	**OH**	**H_2O**
1	0	C_s	1.752	N/A	1.734	N/A	1.768	N/A
1	1	C_s	2.118	2.244	2.051	2.150	1.696	1.915
		C_1	1.740	1.969	1.708	1.918	1.693	1.915
1	2	C_1	1.792	2.022 2.039	1.751	1.956 2.024	1.745	1.953 2.051
1	3	C_1	1.814	2.069 2.091 2.086	1.791	2.030 2.062 2.046	1.780	2.040 2.084 2.071
1	4	C_1	1.856	2.111 2.098 2.150 2.164	1.826	2.087 2.071 2.115 2.100	1.811	2.115 2.099 2.140 2.113
1	5	C_1	1.918	2.162 2.149 2.136 2.173 2.170	1.926	2.105 2.094 2.090 2.113 2.119	1.936	2.118 2.110 2.116 2.126 2.138
2	0	C_{2v}#2	1.770	N/A	1.763	N/A	1.763	N/A
		C_2	1.790	N/A	1.761	N/A	1.730	N/A
2	1	C_s	1.815	2.077	1.799	2.060	--	--
		C1	1.836 1.812	2.156	1.782 1.811	2.112	1.786 1.751	2.077
2	2	C_1	1.877 1.881	2.151 2.180	1.860 1.863	2.104 2.134	1.841 1.837	2.138 2.205
2	3	C_1	1.940 1.895	2.213 2.217 2.260	1.950 1.871	2.157 2.157 2.191	1.953 1.842	2.238 2.176 2.216
2	4	C_1 [5+1]	1.925 1.952	2.171 2.230 2.168	1.924 1.957	2.105 2.155 2.102	1.933 1.968	2.109 2.179 2.104
		cis-C_1	1.988 1.976	2.212 2.204 2.182 2.268	1.996 1.981	2.141 2.137 2.118 2.187	2.000 1.987	2.171 2.163 2.138 2.218
3	0	C_3	1.913	N/A	1.886	N/A	1.873	N/A
		C_1	1.932 1.907 1.902	N/A	1.869 1.927 1.862	N/A	1.844 1.944 1.843	N/A

3	1	$C_{1[3+1]}$	1.917 1.911 1.902	--	1.892 1.885 1.869	--	1.886 1.873 1.847	--
3	2	$C_{1[4+1]}$	1.971 1.916 1.967	2.300	1.972 1.887 1.954	2.197	1.988 1.868 1.955	2.213
3	3	C3v#1	--	--	2.017	2.268	--	--
		C_{3v}#2[3+3]	1.909	--	1.879	--	1.866	--
		C3[3+3]	1.909	--	1.839	--	1.866	--
4	0	S_4	2.043	N/A	2.016	N/A	2.013	N/A
		C2	2.050 2.030	N/A	2.028 1.997	N/A	2.041 1.979	N/A
4	1	$C_{2[4+1]}$	2.041 2.026	--	2.013 1.997	--	2.016 1.994	--
4	2	$C_{2[4+2]}$	2.029 2.030	--	2.009 1.997	--	2.017 1.985	--

Table 3A.14: Ni-O vibrational stretching frequencies, in wavenumbers, calculated at HF/6-31+G* for minimum energy structures of $[Ni(OH)_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

n	m	Point Group Symmetry	Freq (cm^{-1})	Irr. Rep. Symm.	OH/H_2O	Notes
1	0	C_s	850.8	a'	OH	
1	1	C_1	422.9	a'	H_2O	
			808.6	a'	OH	
1	2	C_1	358.4	a	H_2O	H_2O wag
			380.2	a	H_2O	H_2O wag
			385.3	a	H_2O	H_2O wag
			670.6	a	OH	H_2O rock
			688.4	a	OH	H_2O rock
			736.6	a	OH	H_2O rock
1	3	C_1 #1	312.8	a	H_2O	
			315.5	a	H_2O	H_2O twist
			326.7	a	H_2O	H_2O wag/twist
			352.7	a	H_2O	
			360.1	a	H_2O	H_2O wag/twist
			673.7	a	OH	H_2O rock
			703.6	a	OH	H_2O rock
1	4	C_1	246.3	a	H_2O	H_2O twist/rock
			274.3	a	H_2O	H_2O twist
			296.8	a	H_2O	H_2O twist
			304.4	a	H_2O	H_2O twist
			329.3	a	H_2O	H_2O twist/wag
			635.5	a	OH	H_2O twist/rock
1	5	C_1	236.0	a	H_2O	H_2O twist
			242.9	a	H_2O	H_2O twist
			265.8	a	H_2O	H_2O twist
			287.7	a	H_2O	H_2O twist
			304.3	a	H_2O	H_2O twist/wag
			306.6	a	H_2O	H_2O twist
			529.7	a	OH	H_2O wag/twist
			570.6	a	OH	H_2O rock
			579.9	a	OH	H_2O rock
			588.0	a	OH	H_2O rock
2	0	C_2	611.9	a	OH	
			784.3	b	OH	
2	1	C_1	278.9	a	H_2O	H_2O twist
			289.6	a	H_2O	H_2O twist
			583.5	a	OH	H_2O rock
			685.4	a	OH	H_2O twist
			730.2	a	OH	H_2O rock

2	2	C_1	272.6 291.1 543.7 630.8	a a a a	H_2O H_2O OH OH	 H_2O wag H_2O wag/twist
2	3	C_1	208.5 244.5 249.5 283.9 508.1 597.4	a a a a a a	H_2O H_2O H_2O H_2O OH OH	 H_2O rock H_2O wag
2	4	C_1 [5+1]	193.4 218.7 270.1 284.3 288.2 474.6 490.5 569.9	a a a a a a a a	H_2O H_2O H_2O H_2O H_2O OH OH OH	 H_2O rock H_2O rock H_2O rock H_2O rock/wag H_2O rock H_2O rock/twist
3	0	C_3	509.4 540.3 540.3	a e e	OH OH OH	
3	1	C_1 [3+1]	511.4 522.9 548.4 566.9	a a a a	OH OH OH OH	 H_2O rock H_2O rock H_2O rock
3	2	C_1 [4+1]	213.7 459.1 484.7 530.9	a a a a a	H_2O OH OH OH OH	 H_2O rock H_2O rock H_2O rock
3	3	C_{3v} #2 [3+3]	506.1 542.0 542.0	a_1 e e	OH OH OH	
4	0	C_2	338.4 375.7 403.1 413.6	a b b a	OH OH OH OH	
4	1	C_2 [4+1]	397.4 407.5 451.0 463.4	a b a b	OH OH OH OH	
4	2	C_2 [4+2]	391.2 400.4 444.6 444.9	a b b a	OH OH OH OH	

Table 3A.15: Ni-O vibrational stretching frequencies, in wavenumbers, calculated at MP2/6-31+G* for minimum energy structures of $[Ni(OH)_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

n	m	Point Group Symmetry	Freq (cm^{-1})	Irr. Rep. Symm.	OH/H_2O	Notes
1	0	C_s	864.6	a'	OH	
1	1	C_1	447.7	a	H_2O	
			811.2	a	OH	
1	2	C_1	375.8	a	H_2O	
			409.7	a	H_2O	
			747.0	a	OH	
1	3	C_1	328.7	a	H_2O	
			353.3	a	H_2O	H_2O twist
			365.3	a	H_2O	H_2O twist
			377.1	a	H_2O	
			667.5	a	OH	H_2O twist
			686.2	a	OH	H_2O twist
1	4	C_1	239.6	a	H_2O	
			268.1	a	H_2O	H_2O twist
			302.3	a	H_2O	H_2O twist
			313.9	a	H_2O	H_2O twist
			327.1	a	H_2O	H_2O twist
			352.3	a	H_2O	H_2O twist/wag
			356.6	a	H_2O	H_2O twist
			632.8	a	OH	H_2O twist
1	5	C_1	262.1	a	H_2O	
			270.3	a	H_2O	
			302.5	a	H_2O	H_2O wag/twist
			323.8	a	H_2O	
			334.7	a	H_2O	H_2O rock/twist
			337.5	a	H_2O	H_2O wag/twist
			509.0	a	OH	H_2O wag
			538.5	a	OH	H_2O wag/twist
			564.5	a	OH	H_2O rock/twist
			572.9	a	OH	H_2O twist
2	0	C_2	613.2	a	OH	
			797.6	b	OH	
2	1	C_s	343.8	a'	H_2O	
			581.6	a'	OH	
			722.7	a"	OH	
2	2	C_1	295.7	a	H_2O	
			313.0	a	H_2O	
			534.2	a	OH	
			618.5	a	OH	H_2O twist

2	3	C_1	240.1 262.0 281.3 295.7 495.4 580.4 588.5	a a a a a a a	H_2O H_2O H_2O H_2O OH OH OH	 H_2O rock H_2O rock H_2O rock H_2O twist H_2O wag H_2O wag/twist
2	4	C_1 [5+1]	210.8 242.4 312.2 325.7 467.7 518.0	a a a a a a	H_2O H_2O H_2O H_2O OH OH	H_2O twist H_2O twist H_2O twist H_2O wag H_2O rock/twist
3	0	C_3	501.9 540.7 540.7	a e e	OH OH OH	
3	1	C_1 [3+1]	500.8 524.3 558.8	a a a	OH OH OH	 H_2O rock H_2O rock
3	2	C_1 [4+1]	247.4 439.2 467.5 472.9 535.2	a a a a a	H_2O OH OH OH OH	 H_2O rock H_2O rock H_2O rock H_2O wag
3	3	C_{3v}#1	152.6 152.7 186.8 431.4 431.5 441.8	e e a_1 e e a_1	H_2O H_2O H_2O OH OH OH	
4	0	C_2	327.8 388.2 429.8 412.0	a b b a	OH OH OH OH	
4	1	C_2 [4+1]	368.8 395.3 418.3 420.0	a b a b	OH OH OH OH	
4	2	C_2 [4+2]	384.9 396.1 423.2 428.1	a b b a	OH OH OH OH	

Table 3A.16: Ni-O vibrational stretching frequencies, in wavenumbers, calculated at B3LYP/6-31+G* for minimum energy structures of $[Ni(OH)_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

n	m	Point Group Symmetry	Freq (cm^{-1})	Irr. Rep. Symm.	OH/H_2O	Notes
1	0	C_s	773.8	a'	OH	
1	1	C_s	438.8	a'	H_2O	
			794.7	a'	OH	
1	2	C_1	347.4	a	H_2O	
			401.8	a	H_2O	
			727.1	a	OH	
1	3	C_1	292.6	a	H_2O	
			333.8	a	H_2O	
			351.9	a	H_2O	
			655.2	a	OH	H_2O twist
			690.5	a	OH	H_2O twist
1	4	C_1	252.4	a	H_2O	
			268.5	a	H_2O	
			295.4	a	H_2O	H_2O twist/wag
			312.9	a	H_2O	H_2O twist
			328.0	a	H_2O	
			635.4	a	OH	H_2O twist
1	5	C_1	202.8	a	H_2O	H_2O twist
			232.8	a	H_2O	H_2O twist
			264.7	a	H_2O	H_2O twist
			256.8	a	H_2O	H_2O twist
			261.0	a	H_2O	
			281.8	a	H_2O	H_2O wag
			304.3	a	H_2O	
			315.1	a	H_2O	H_2O twist
			502.9	a	OH	H_2O wag
			529.6	a	OH	H_2O wag
			562.7	a	OH	H_2O wag/twist
2	0	C_2	665.2	a	OH	
			821.5	b	OH	
2	1	C_1	272.7	a	H_2O	H_2O rock
			284.2	a	OH	H_2O twist
			589.8	a	OH	H_2O scissor
			697.1	a	OH	H_2O wag
			744.5	a	OH	H_2O scissor
2	2	C_1	211.2	a	H_2O	
			277.3	a	H_2O	
			544.3	a	OH	H_2O twist
			617.6	a	OH	H_2O twist

2	3	C_1	165.5 200.4 224.1 246.9 278.3 282.0 495.3 583.0 599.2	a a a a a a a a a	H_2O H_2O H_2O H2O H2O H2O OH OH OH	 H2O twist H2O wag H2O twist H2O rock/twist
2	4	C_1 [5+1]	215.7 233.1 299.7 308.6 313.0 456.6 511.4	a a a a a a a	H_2O H_2O H_2O H_2O H2O OH OH	 H2O rock H2O twist H2O twist H2O twist/rock
3	0	C_3	504.1 530.9 530.9	a e e	OH OH OH	
3	1	C_1 [3+1]	500.9 511.7 561.2	a a a	OH OH OH	 H2O rock
3	2	C_1 [4+1]	191.6 226.8 233.3 417.4 461.4 535.5	a a a a a a	H2O H2O H2O OH OH OH	
3	3	C_3 [3+3]	498.7 539.5 539.5	a e e	OH OH OH	
4	0	C_2	298.1 364.9 407.6 415.5	a b b a	OH OH OH OH	
4	1	C_2 [4+1]	351.4 380.2 407.3 409.6	a b b a	OH OH OH OH	
4	2	C_2 [4+2]	370.8 376.2 420.1 424.5	a b a b	OH OH OH OH	

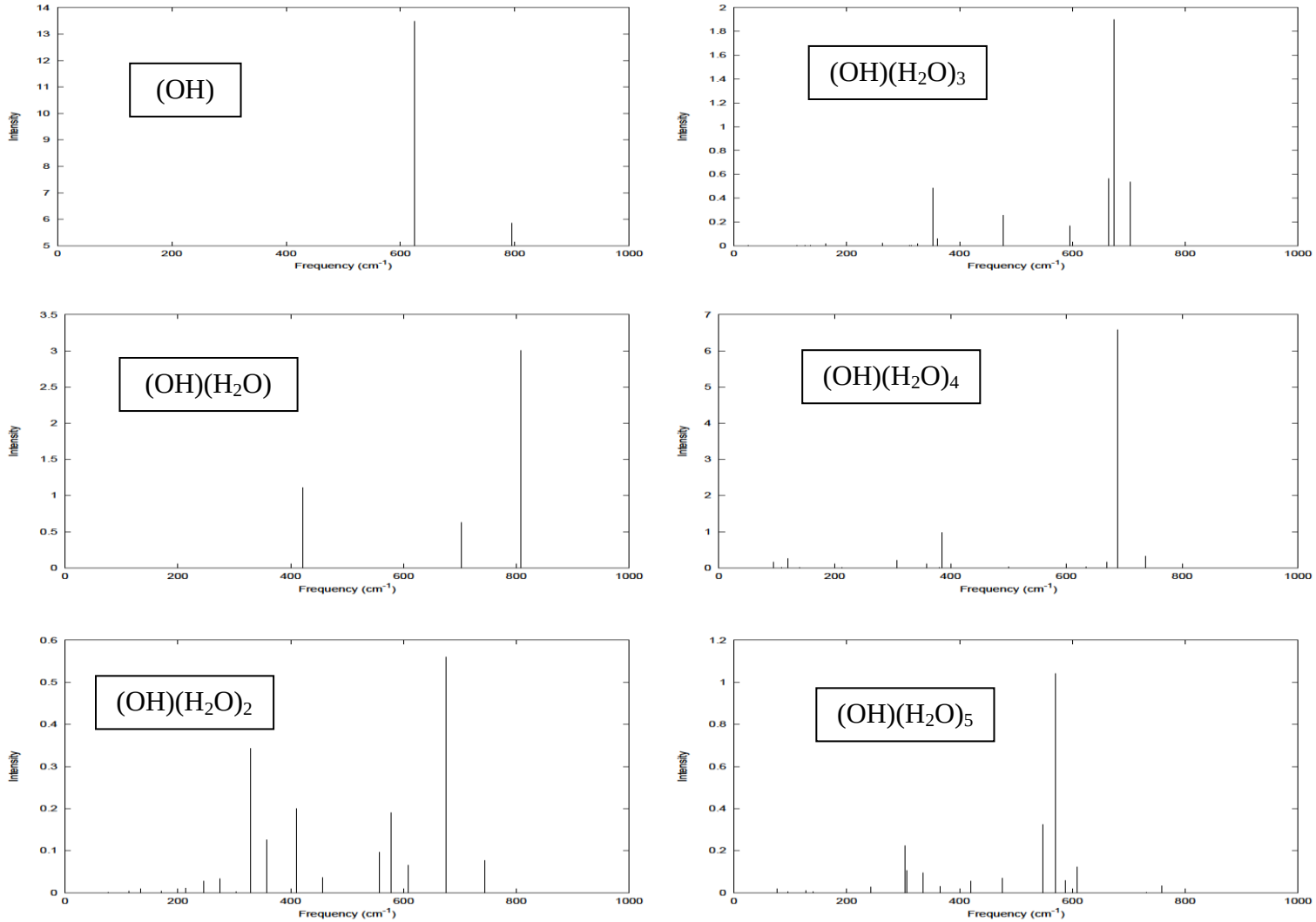


Figure 3A-3: Simulated polarized Raman spectra for $[Ni(OH)_n(H_2O)_m]^{2-n}$, where n=1 – 4, m=0 – (6-n).

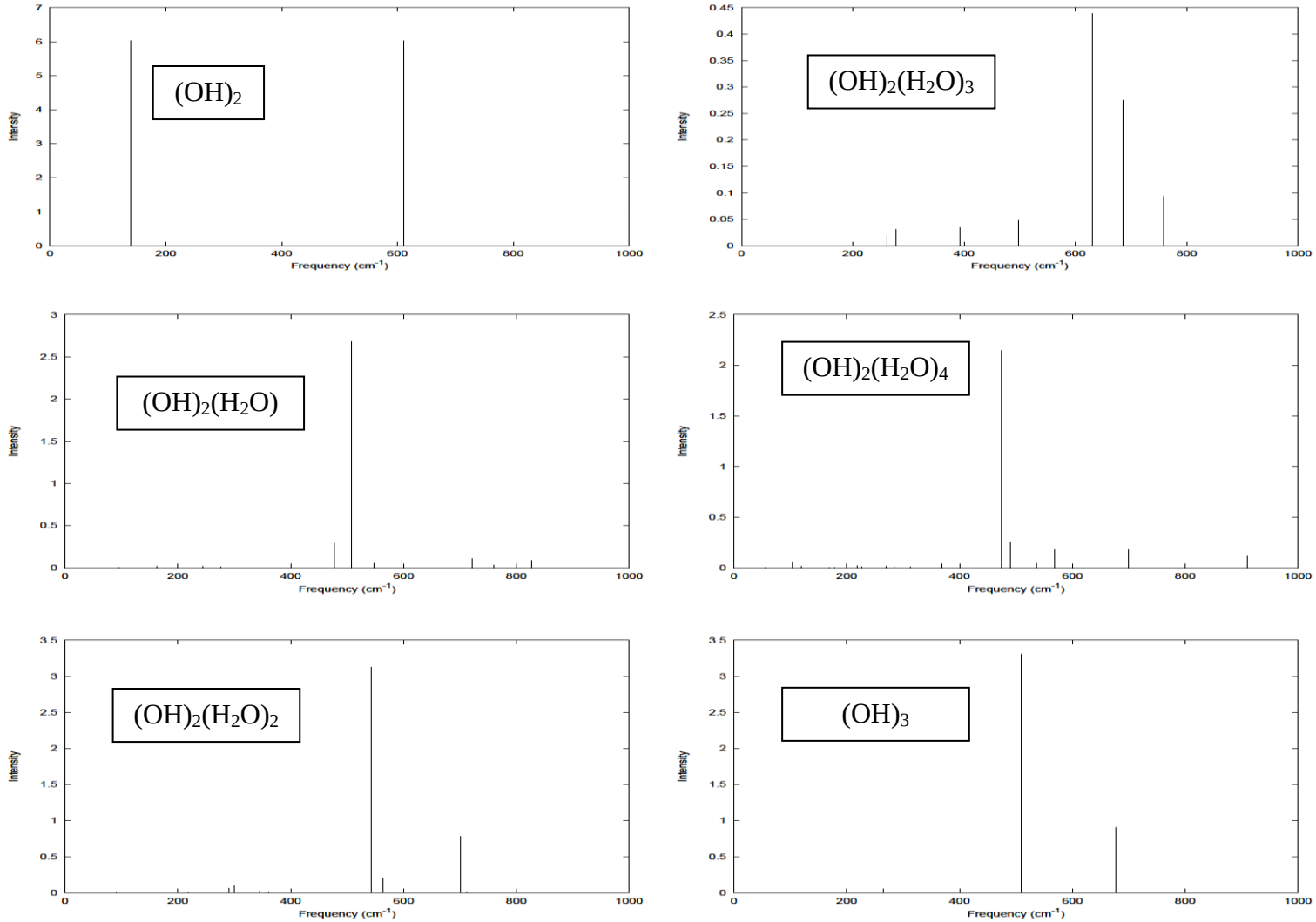


Figure 3A-3: *(continued)*

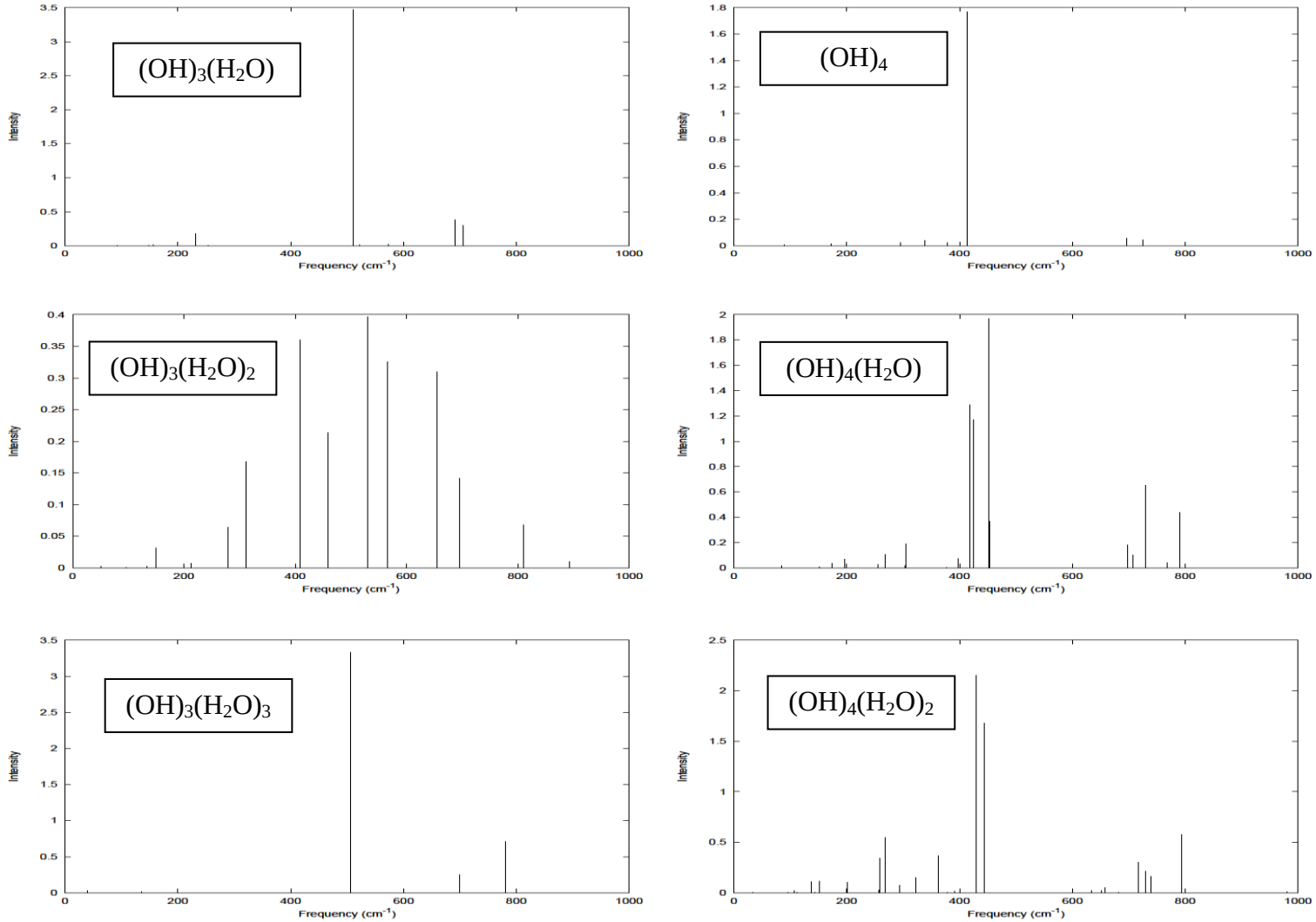


Figure 3A-3: *(continued)*

Table 3A.17: Total energies for the stable geometries of $[Ni(NH_3)_n(H_2O)_m]^{2+}$, where n=1 – 6, m=0 – (6-n).

			Total Energies (Hartrees)			
n	**m**	**Point Group**	**HF**	**MP**	**B3LYP**	**C-PCM†**
1	0	C_{3v}	-1562.0793222	-1562.4182083	-1563.8432339	-1564.468456
1	1	C_s#1	-1638.3023300	-1638.8405963	-1640.4780228	--
		C_s#2	-1638.3023489	-1638.840627	-1640.4780274	--
		C_1	-1638.2043510	-1638.749363	-1640.475559	-1640.914623
1	2	C_s	-1714.3988260	-1715.1367730	-1716.9872854	--
		C_1	-1714.3988260	-1715.1367730	-1716.9892140	-1717.36066
1	3	C_1	-1790.4891710	-1791.4259718	-1793.4831931	-1793.820502
1	4	C_s	-1866.5591567	-1867.6947717	-1869.9584854	-1870.283644
1	5	C_s	-1942.6229310	-1943.9577421	-1946.4261030	-1946.741075
2	0	D_{3d}	-1618.4070224	-1618.9412123	-1620.5602654	-1621.066891
		D_{3h}	-1618.4069912	-1618.9411844	-1620.5602518	-1621.067631
		D_3	-1618.4070224	-1618.4041510	-1620.5602648	-1621.067643
2	1	C_2	-1694.5947926	-1695.319691	-1697.1347733	-1697.478974
		C_1	-1694.5953200	-1695.3205186	-1697.1347945	-1697.478973
2	2	C_s	-1770.6788621	-1771.6027431	-1773.6403616	-1773.967627
		C_2	-1770.6787381	-1771.6027674	-1773.6401977	--
2	3	C_3	-1846.7375238	-1847.8578007	-1850.1028474	--
		C_2	-1846.7427819	-1847.8649630	-1850.1097881	-1850.426654
2	4	C_{2h} (trans)	-1922.8017782	-1924.1229727	-1926.5721979	--
		C_2 #1 (trans)	-1922.8017782	-1924.1229730	-1926.5722223	-1926.881780
		C_2 #2 (trans)	-1922.8013714	-1924.1227461	-1926.5715507	-1926.881295
		C_{2v} (trans)	-1922.8010525	-1924.1221318	-1926.5715171	--
		C_s (cis)	-1922.8041127	-1924.1256554	-1926.5752917	-1926.883128
3	0	C_{3h}	-1674.7418400	-1675.4672144	-1677.2948409	--
		C_3	-1674.7872156	-1675.5008732	-1677.3174846	-1677.665822
3	1	C_s	-1750.8673423	-1751.7782977	-1753.7985293	--
		C_1	-1750.8673351	-1751.7783530	-1753.7985539	-1754.115331
3	2	C_s	-1826.9283469	-1828.0377031	-1830.2640455	-1830.572161
3	3	fac-C_3	-1902.9853364	-1904.2934396	-1906.7244602	-1907.025093
		mer-C_1	-1902.9831195	-1904.2907497	-1906.7213607	-1907.023271
4	0	C_{2v}	-1731.0417055	-1731.9413868	-1733.9450110	-1734.24907
4	1	C_2	-1883.1633175	-1884.4564545	-1886.8678428	--
		C_s	-1807.1107778	-1808.2062837	-1810.4143918	-1810.714345

4	2	C_{2v} (trans)	-1883.1633175	-1884.4564544	-1886.8678428	-1887.163814
		cis-C_s	-1883.1639541	-1884.4575665	-1886.8692235	-1887.164336
5	0	C_s	-1787.2917852	-1788.3725153	-1790.5614495	-1790.856646
		C_1	-1787.2917852	-1788.3726414	-1790.5613346	-1790.856389
5	1	C_s	-1863.3423715	-1864.6213830	-1867.0136406	--
		C_1	-1863.3423715	-1864.6213811	-1867.0136639	-1867.30392
6	0	C_s	-1843.5200116	-1844.7839792	-1847.1566489	-1847.441755
		C_1	-1843.5200530	-1844.7840364	-1847.1566413	-1847.442386

NOT Stable

†Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.18: Optimized Ni-N and Ni-O bond lengths, in Angstroms, for energy minimum structures of $[Ni(NH_3)_n(H_2O)_m]^{2+}$, where n=1 – 6, m=0 – (6-n).

			Ni-N and Ni-O Bond Lengths (Å)					
			HF/6-31+G*		**MP2/6-31+G***		**B3LYP/6-31+G***	
n	**m**	**Symm.**	**Ni-N**	**Ni-O**	**Ni-N**	**Ni-O**	**Ni-N**	**Ni-O**
1	0	C_{3v}	2.044	N/A	2.005	N/A	2.016	N/A
1	1	C_s	2.004	1.938	1.956	1.905	--	--
		C_1	2.032	1.976	1.976	1.927	1.958	1.870
1	2	C_1	2.044	2.026 1.998	1.990	1.974 1.962	1.990	1.965 1.961
1	3	C_1	2.080	2.044 2.057 2.042	2.017	2.001 2.022 2.001	2.019	2.006 2.024 1.999
1	4	C_s	2.103	2.068 2.087 2.136	2.037	2.025 2.043 2.095	2.044	2.031 2.049 2.099
1	5	C_s	2.137	2.145 2.142 2.144 2.149	2.065	2.098 2.097 2.097 2.102	2.075	2.109 2.113 2.103 2.114
2	0	D_3	2.036	N/A	1.980	N/A	1.997	N/A
		D_{3d}	2.036	N/A	1.979	N/A	1.997	N/A
2	1	C_1	2.063 2.061	2.027	2.007 2.009	1.987	1.985 1.985	1.896
2	2	C_s	2.093	2.067 2.077	2.027	2.029 2.043	2.035	2.029 2.046
2	3	C_2	2.112	2.109 2.174	2.047	2.063 2.133	2.057	2.074 2.137
2	4	C_{2h} (trans)	2.148	2.196 2.179	2.151	2.176 2.165	--	--
		C_2 #1 (trans)	2.148	2.197 2.196 2.179	2.075	2.149 2.149 2.135	2.090	2.162 2.172 2.145
		C_2 #2 (trans)	--	--	--	--	2.086	2,170 2.155
		C_s (cis)	2.152 2.160	2.174 2.180 2.176	2.078 2.085	2.128 2.139 2.132	2.087 2.095	2.150 2.158 2.141
3	0	C_3	2.075	N/A	2.014	N/A	2.013	N/A
3	1	C_1	2.116 2.116 2.104	2.083	2.049 2.049 2.045	2.045	2.059 2.059 2.053	2.038

3	2	C_s	2.127 2.136	2.173 2.216	2.066 2.058	2.128 2.177	2.070 2.080	2.130 2.188
3	3	fac-C_3	2.173	2.214	2.096	2.172	2.106	2.198
		mer-C_1	2.168 2.167 2.180	2.216 2.232 2.224	2.099 2.095 2.102	2.161 2.189 2.175	2.105 2.105 2.114	2.188 2.221 2.201
4	0	C_{2v}	2.124 2.124	N/A	2.060 2.060	N/A	2.068 2.069	N/A
4	1	C_s	2.155 2.143 2.185	2.272	2.083 2.073 2.110	2.246	2.095 2.085 2.120	2.272
4	2	trans-C_{2v}	2.202 2.202	2.244 2.244	2.128 2.128	2.194 2.196	2.145 2.145	2.221 2.221
		cis-C_s	2.203 2.192 2.193	2.275 2.252	2.122 2.112 2.116	2.238 2.216	2.135 2.123 2.129	2.289 2.250
5	0	C_1	2.153 2.203 2.209 2.206 2.206	N/A	2.083 2.133 2.136 2.135 2.134	N/A	2.096 2.149 2.154 2.151 2.152	N/A
5	1	C_s	2.213 2.221 2.232 2.216	2.317	2.135 2.137 2.155 2.139	2.287	--	--
		C_1	2.216 2.221 2.232 2.232 2.213	2.317	2.141 2.137 2.155 2.155 2.135	2.285	2.155 2.150 2.175 2.175 2.152	2.329
6	0	C_s	--	--	--	--	2.201 2.204 2.204 2.200 2.195	N/A
		C_1	2.254 2.254 2.254 2.254 2.254 2.254	N/A	2.177 2.175 2.176 2.176 2.175 2.176	N/A	2.200 2.199 2.198 2.200 2.196 2.198	N/A

Table 3A.19: Ni-O and Ni-N stretching frequencies, in wavenumbers, calculated at HF/6-31+G* for minimum energy structures of $[Ni(NH_3)_n(H_2O)_m]^{2+}$, where n=1 – 6, m=0 – (6-n).

n	m	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	NH_3/H_2O	Notes
1	0	C_{3v}	480.4	a_1	NH_3	
1	1	C_s #2	441.5	a'	H_2O/NH_3	
			553.4	a'	H_2O/NH_3	
1	2	C_s	385.8	a'	H_2O	H_2O wag
			398.2	a'	H_2O/NH_3	
			476.6	a'	H_2O/NH_3	H_2O rock
1	3	C_1	348.1	a	H_2O/NH_3	
			364.0	a	H_2O	
			377.0	a	H_2O/NH_3	
			418.6	a	H_2O/NH_3	H_2O wag
1	4	C_s	249.6	a'	H_2O/NH_3	
			317.2	a"	H_2O	H_2O wag
			322.7	a'	H_2O	H_2O twist
			351.9	a'	H_2O	
			391.5	a'	H_2O/NH_3	
1	5	C_s	232.3	a'	H_2O/NH_3	
			234.5	a'	H_2O/NH_3	
			297.9	a"	H_2O	H_2O wag/twist
			302.9	a'	H_2O	H_2O wag
			318.8	a'	H_2O	
			358.7	a'	H_2O/NH_3	H_2O wag
2	0	D_{3d}	410.4	a_{1g}	NH_3	
			532.3	a_{2u}	NH_3	
2	1	C_1	378.6	a	H_2O/NH_3	
			435.7	a	H_2O/NH_3	H_2O wag
			446.4	a	H_2O/NH_3	
2	2	C_s	340.8	a'	H_2O	
			350.5	a'	H_2O/NH_3	
			379.6	a'	H_2O/NH_3	
			415.7	a"	NH_3	H_2O wag
			432.5	a"	NH_3	H_2O wag
2	3	C_2	233.8	a	H_2O/NH_3	
			289.8	b	H_2O	
			313.2	a	H_2O	
			361.3	a	H_2O/NH_3	
			392.5	b	NH_3	H_2O wag
			441.6	b	NH_3	H_2O wag

2	4	cis-C_s	219.4 220.0 277.6 282.9 298.4 334.4 350.8	a' a' a" a" a' a' a'	H_2O/NH_3 H_2O/NH_3 H_2O H_2O H_2O H_2O/NH_3 NH_3	H_2O twist H_2O twist H_2O twist H_2O wag
3	0	C_3	423.5 459.8 459.8	a e e	NH_3 NH_3 NH_3	
3	1	C_s	334.7 363.9 391.5 391.6	a' a' a" a'	H_2O H_2O/NH_3 NH_3 NH_3	 H_2O rock H_2O wag
3	2	C_s	222.2 276.0 340.2 369.1 375.6	a' a' a' a' a"	H_2O/NH_3 H_2O H_2O/NH_3 NH_3 NH_3	 H_2O rock/wag H_2O rock/wag
3	3	fac-C_3	207.8 207.8 275.0 319.6 319.6 340.6 346.7	e e a e e a a	H_2O/NH_3 H_2O/NH_3 H_2O H_2O/NH_3 H_2O/NH_3 NH_3 NH_3	 H_2O twist H_2O twist
4	0	C_{2v}	367.8 371.9 371.9 401.6	a_1 e e a_1	NH_3 NH_3 NH_3 NH_3	
4	1	C_s	210.3 303.0 337.6 357.0 358.7	a' a' a' a' a"	H_2O/NH_3 H_2O/NH_3 NH_3 NH_3 NH_3	 H_2O rock H_2O wag
4	2	cis-C_s	194.1 208.1 279.5 301.2 322.9 333.0	a' a' a' a' a" a'	H_2O H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 NH_3 H_2O/NH_3	 H_2O wag H_2O rock

5	0	C_s	225.7 318.0 318.3 320.6 348.6	a' a' a" a' a'	NH_3 NH_3 NH_3 NH_3 NH_3	
5	1	C_s	188.9 218.5 274.2 292.3 306.6 322.8	a' a' a' a" a' a'	H_2O/NH_3 NH_3 H_2O/NH_3 NH_3 NH_3 H_2O/NH_3	 H_2O rock H_2O wag
6	0	C_1	205.4 205.4 276.2 275.4 276.5 312.1	a a a a a a	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3	

Table 3A.20: Ni-O and Ni-N stretching frequencies, in wavenumbers, calculated at MP2/6-31+G* for minimum energy structures of $[Ni(NH_3)_n(H_2O)_m]^{2+}$, where n=1 – 6, m=0 – (6-n).

n	m	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	NH_3/H_2O	Notes
1	0	C_{3v}	488.9	a_1	NH_3	
1	1	C_s #2	457.8	a'	H_2O/NH_3	
			578.2	a'	H_2O/NH_3	
1	2	C_s	392.8	a'	H_2O/NH_3	H_2O wag
			414.6	a'	H_2O/NH_3	
			425.3	a'	H_2O/NH_3	H_2O wag
			504.3	a'	H_2O	H_2O rock
1	3	C_1	359.2	a	H_2O/NH_3	H_2O wag
			364.7	a	H_2O/NH_3	H_2O wag
			381.2	a	H_2O	H_2O wag
			395.2	a	H_2O	H_2O wag
			397.5	a	H_2O/NH_3	H_2O wag
			458.7	a	H_2O/NH_3	H_2O rock
1	4	C_s	266.0	a'	H_2O/NH_3	
			319.7	a"	H_2O	H_2O wag
			339.2	a'	H_2O	H_2O wag
			348.3	a"	H_2O	H_2O wag
			357.6	a'	H_2O	H_2O wag
			377.7	a'	H_2O/NH_3	H_2O wag
			444.2	a'	H_2O/NH_3	H_2O wag
1	5	C_s	252.6	a'	H_2O/NH_3	H_2O wag
			255.1	a'	H_2O/NH_3	
			310.8	a"	H_2O	H_2O twist/wag
			316.6	a'	H_2O	H_2O wag
			321.4	a"	H_2O/NH_3	H_2O twist/wag
			330.9	a'	H_2O	H_2O wag
			346.6	a'	H_2O	H_2O wag/twist
			367.0	a'	H_2O/NH_3	H_2O wag
			387.6	a'	H_2O/NH_3	H_2O wag/rock
			404.0	a'	H_2O/NH_3	H_2O wag/rock
2	0	D_{3d}	433.2	a_{1g}	NH_3	
			568.6	a_{2u}	NH_3	
2	1	C_1	383.4	a	H_2O	H_2O wag
			404.5	a	H_2O/NH_3	H_2O wag
			462.2	a	NH_3	H_2O wag
			475.0	a	H_2O/NH_3	

2	2	C_2	361.0 362.2 379.1 402.1 460.2	a b a a b	H_2O/NH_3 H_2O H_2O H_2O/NH_3 NH_3	H_2O wag H_2O wag H_2O wag H_2O wag H_2O rock
2	3	C_2	247.1 299.3 335.9 385.9 446.4	a b a a b	H_2O/NH_3 H_2O H_2O/NH_3 H_2O/NH_3 NH_3	H_2O twist H_2O wag H_2O wag H_2O wag H_2O wag/rock
2	4	cis-C_s	221.5 239.5 241.1 278.3 298.7 316.1 321.6 353.4 372.8 389.4	a' a' a' a" a" a' a" a' a' a'	H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O H_2O H_2O/NH_3 H_2O NH_3 NH_3 H_2O/NH_3	H_2O twist/wag H_2O wag H_2O twist H_2O wag/twist H_2O twist H_2O wag H_2O wag/twist H_2O wag H_2O wag H_2O wag/rock
3	0	C_3	423.5 459.8 459.8	a e e	NH_3 NH_3 NH_3	
3	1	C_1	348.7 387.2 421.0 430.9	a' a a a	H_2O NH_3 NH_3 NH_3	 H_2O wag H_2O wag H_2O rock
3	2	C_s	254.2 272.5 340.4 371.5 423.9	a' a" a' a' a'	H_2O/NH_3 H_2O H_2O/NH_3 H_2O/NH_3 NH_3	 H_2O wag H_2O wag H_2O wag
3	3	fac-C_3	220.1 220.1 287.9 355.3 355.3 372.9	e e a e e a	H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O/NH_3	H_2O twist H_2O twist H_2O twist H_2O wag H_2O wag H_2O twist
4	0	C_{2v}	386.8 404.7 404.7 431.8	a_1 e e a_1	NH_3 NH_3 NH_3 NH_3	

4	1	C_s	224.3 333.9 367.6 377.0 386.4	a' a' a' a" a'	H_2O/NH_3 H_2O/NH_3 NH_3 NH_3 NH_3	 H_2O wag H_2O rock
4	2	cis-C_s	209.8 225.4 311.4 337.6 357.2 359.3	a' a' a' a' a" a'	H_2O H_2O/NH_3 H_2O/NH_3 NH_3 NH_3 NH_3	 H_2O wag/rock H_2O twist/rock H_2O wag
5	0	C_1	252.4 346.5 348.3 348.6 376.6	a a a a a	NH_3 NH_3 NH_3 NH_3 NH_3	
5	1	C_s	205.9 249.1 309.9 324.0 338.5 348.0	a' a' a' a" a' a'	H_2O NH_3 H_2O/NH_3 NH_3 NH_3 H_2O/NH_3	 H_2O rock H_2O wag
6	0	C_1	235.0 235.5 304.7 305.8 305.8 335.0	a a a a a a	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3	

Table 3A.21: Ni-O and Ni-N stretching frequencies, in wavenumbers, calculated at B3LYP/6-31+G* for minimum energy structures of $[Ni(NH_3)_n(H_2O)_m]^{2+}$, where n=1 – 6, m=0 – (6-n).

n	m	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	NH_3/H_2O	Notes
1	0	C_{3v}	469.2	a_1	NH_3	
1	1	C_1	450.0	a	H_2O/NH_3	
			579.9	a	H_2O/NH_3	
1	2	C_1	387.4	a	H_2O/NH_3	H_2O wag
			411.2	a	H_2O/NH_3	H_2O wag
			433.0	a	NH_3	H_2O wag
			492.5	a	H_2O/NH_3	H_2O wag
1	3	C_1	348.1	a	H_2O	H_2O wag
			354.6	a	H_2O/NH_3	H_2O wag
			378.9	a	H_2O	H_2O wag
			390.0	a	H_2O/NH_3	H_2O wag
			398.1	a	H_2O/NH_3	H_2O wag
			446.7	a	H_2O/NH_3	H_2O wag/rock
1	4	C_s	257.5	a'	H_2O/NH_3	
			300.6	a"	H_2O	H_2O wag
			319.3	a'	H_2O	H_2O wag
			322.9	a"	H_2O	H_2O wag
			333.4	a"	H_2O	H_2O wag/rock
			336.3	a'	H_2O/NH_3	H_2O wag
			365.7	a'	H_2O/NH_3	H_2O wag/twist
			374.0	a"	H_2O/NH_3	H_2O wag/twist
			427.4	a'	H_2O/NH_3	H_2O wag/rock
1	5	C_s	240.4	a'	H_2O/NH_3	H_2O twist/wag
			243.1	a'	H_2O/NH_3	H_2O twist/wag
			292.7	a'	H_2O	H_2O twist/wag
			299.5	a"	H_2O	H_2O wag
			306.6	a"	H_2O	H_2O twist/wag
			313.3	a'	H_2O	H_2O wag/twist
			327.9	a'	H_2O/NH_3	H_2O wag
			347.2	a'	H_2O/NH_3	H_2O wag
			373.3	a'	NH_3	H_2O wag/rock
			387.1	a'	H_2O/NH_3	H_2O wag/twist
2	0	D_{3d}	423.1	a_{1g}	NH_3	
			547.5	a_{2u}	NH_3	
2	1	C_1	429.3	a	H_2O/NH_3	
			500.5	a	H_2O/NH_3	
			533.0	a	NH_3	

2	2	C_s	352.5 358.4 392.7 443.8	a' a' a' a"	H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 NH_3	H_2O wag H_2O rock
2	3	C_2	244.0 285.9 320.1 321.3 324.0 375.2 426.1	a b a b a a b	H_2O/NH_3 H_2O H_2O/NH_3 H_2O H_2O H_2O/NH_3 NH_3	H_2O twist H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag/rock
2	4	cis-C_s	210.4 222.0 228.0 262.5 289.4 298.4 338.5 358.1 372.3	a' a' a' a" a" a' a' a' a'	H_2O H_2O/NH_3 H_2O H_2O H_2O H_2O NH_3 H_2O/NH_3 NH_3	H_2O twist/wag H_2O twist H_2O twist/wag H_2O twist/wag H_2O twist/wag H_2O wag H_2O wag H_2O wag H_2O twist
3	0	C_3	417.9 447.0 447.0	a e e	NH_3 NH_3 NH_3	
3	1	C_1	344.0 372.2 405.8 411.6	a a a a	H_2O/NH_3 H_2O/NH_3 NH_3 NH_3	 H_2O rock
3	2	C_s	225.7 276.6 337.5 348.9 355.2 386.7 395.1	a' a' a' a" a' a' a"	H_2O/NH_3 H_2O NH_3 NH_3 H_2O/NH_3 NH_3 NH_3	 H_2O wag H_2O wag H_2O wag H_2O rock H_2O wag/rock
3	3	fac-C_3	201.3 201.3 266.3 338.1 338.1 362.8	e e a e e a	H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O/NH_3	 H_2O wag H_2O wag H_2O twist H_2O wag/twist
4	0	C_{2v}	377.5 395.2 395.4 416.6	a_1 b_1 b_2 a_1	NH_3 NH_3 NH_3 NH_3	

4	1	C_s	208.2 314.7 352.7 363.8 371.6 392.2	a' a' a' a" a' a"	H_2O H_2O/NH_3 NH_3 NH_3 NH_3 NH_3	 H_2O wag H_2O rock H_2O wag
4	2	cis-C_s	193.1 203.9 290.2 319.5 337.0 349.1	a' a' a' a' a" a'	H_2O H_2O H_2O/NH_3 H_2O/NH_3 NH_3 NH_3	 H_2O wag/rock H_2O wag
5	0	C_s	236.3 326.7 326.7 331.7 361.2	a' a" a' a' a'	NH_3 NH_3 NH_3 NH_3 NH_3	
5	1	C_1	140.7 192.3 231.2 292.6 297.1 318.1 336.5	a a a a a a a	H_2O H_2O NH_3 H_2O/NH_3 NH_3 NH_3 H_2O/NH_3	 H_2O rock H_2O wag
6	0	C_s	214.0 216.5 275.7 277.5 282.7 320.2	a' a' a' a' a" a'	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3	

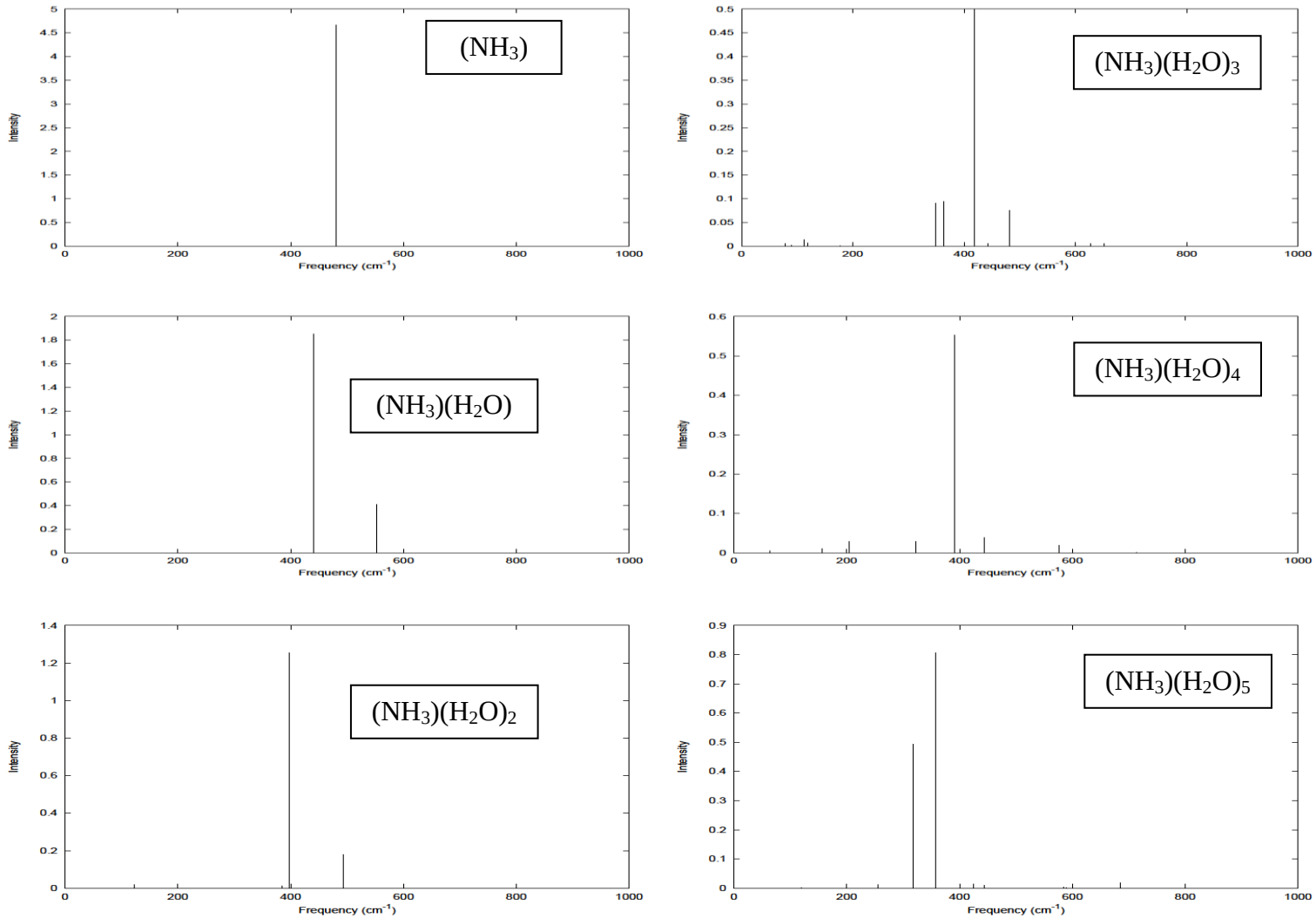


Figure 3A-4: Simulated polarized Raman spectra for $[Ni(NH_3)_n(H_2O)_m]^{2+}$, where n=1 – 6, m=0 – (6-n).

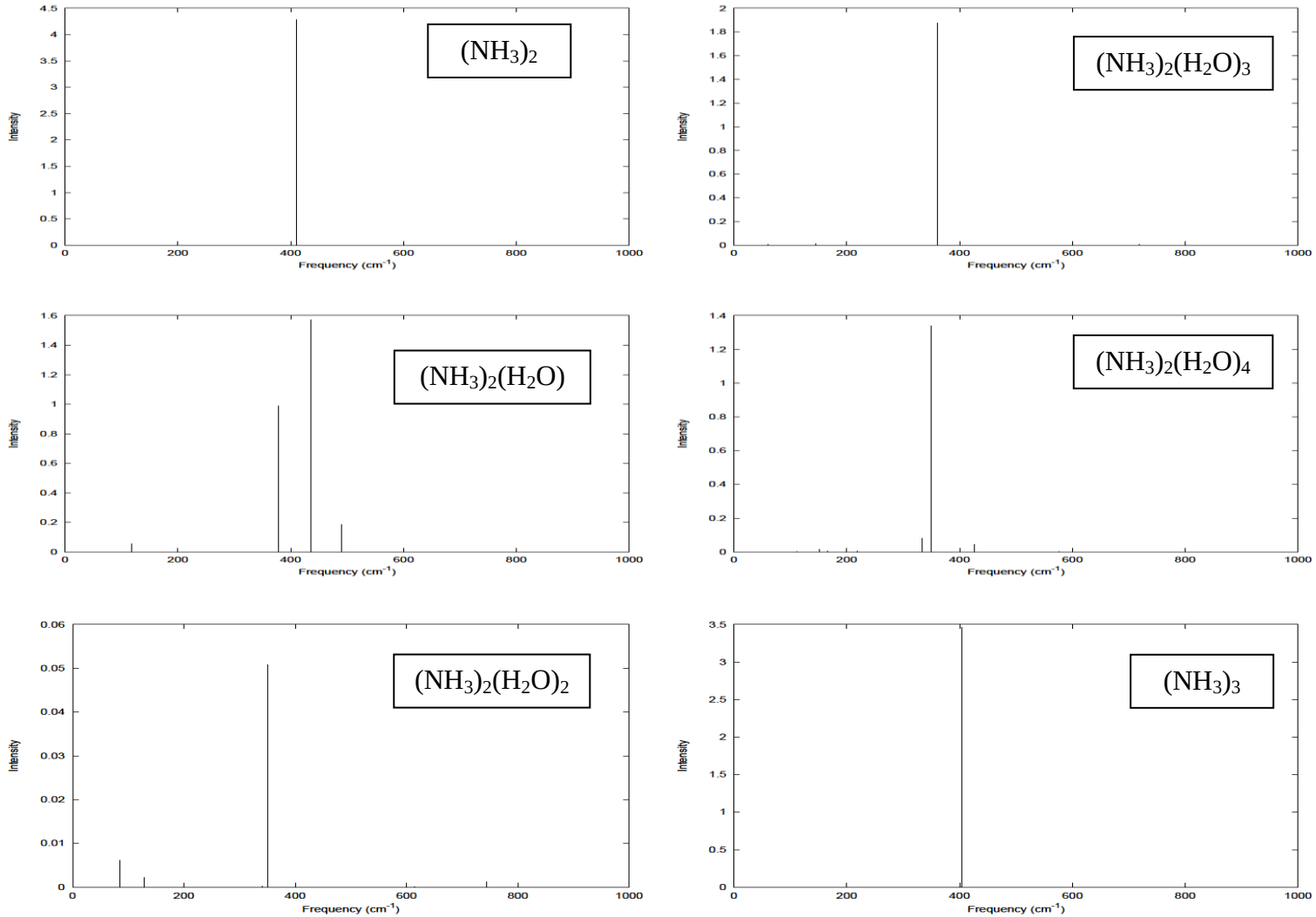


Figure 3A-4: *(continued)*

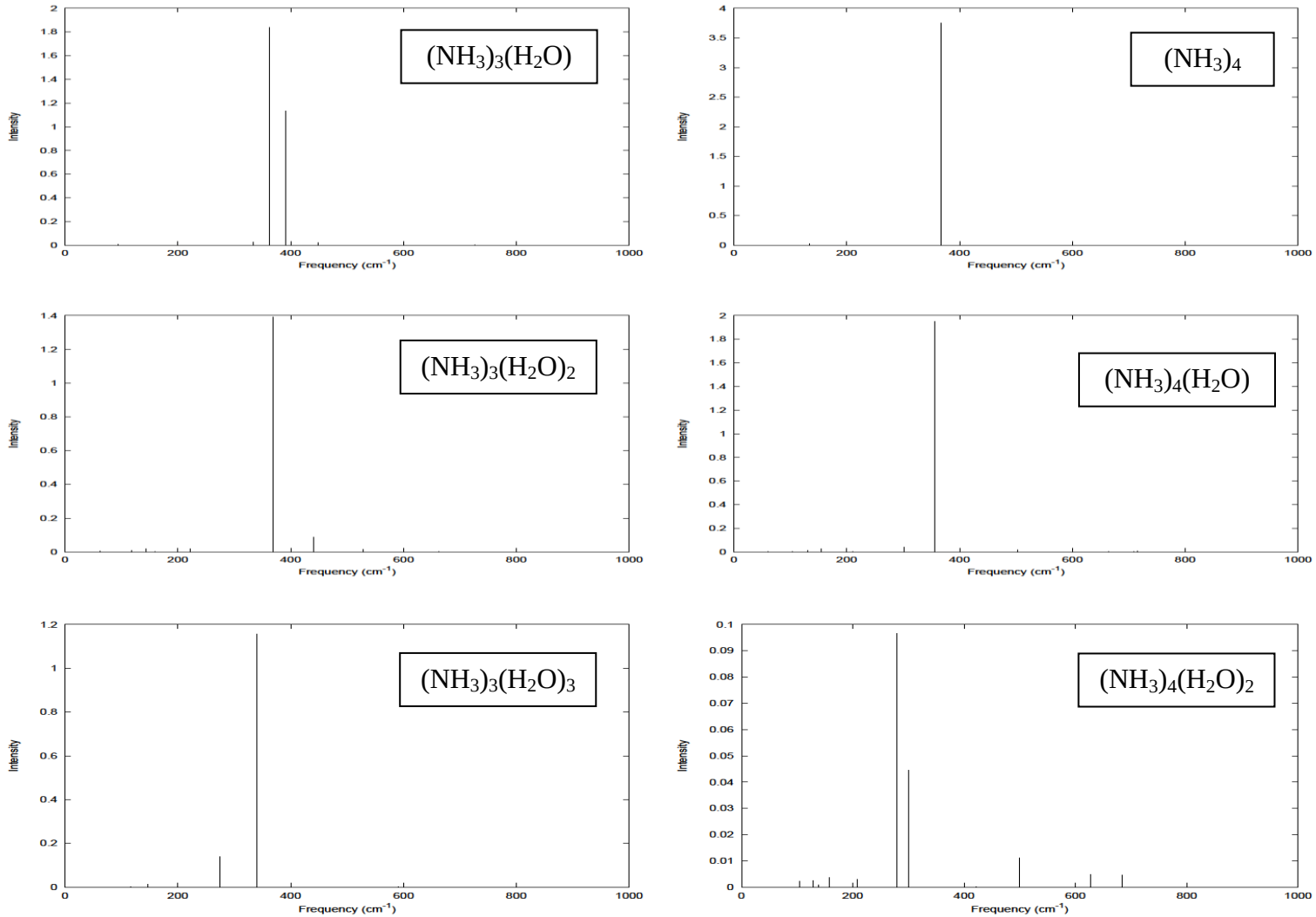


Figure 3A-4: *(continued)*

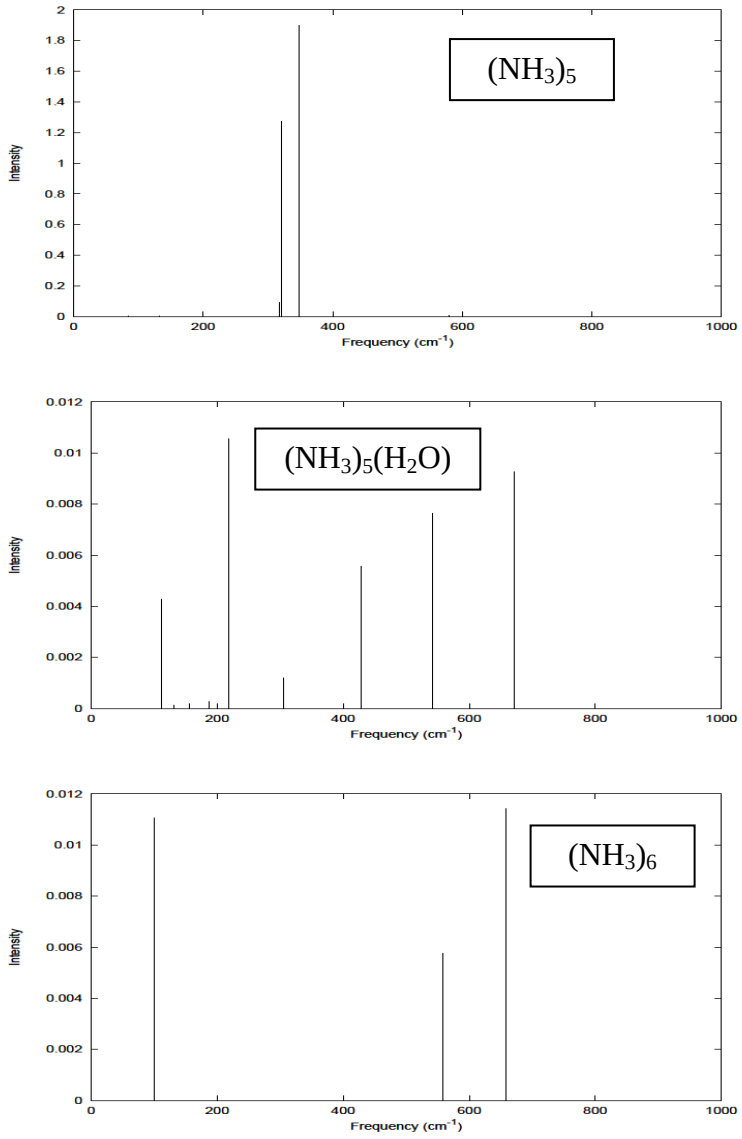


Figure 3A-4: *(continued)*

Table 3A.22: Total energies for all stable geometries of $[NiCl_n(OH)_m(H_2O)_l]^{2-n-m}$, where n=1 – 3, m=1 – (4-n), l=0 – (6-n-m).

				Optimized Energies (Hartrees)			
n	**m**	**l**	**Point Group**	**HF**	**MP2**	**B3LYP**	**C-PCM†**
1	1	0	C_s	-2041.66947940	-2042.1807902	-2044.2422968	-2044.301892
1	1	1	C_1	-2117.71650550	-2118.4460582	-2120.7139267	-2120.750431
1	1	2	C_s	-2193.7615123	-2194.6859971	-2197.1543587	-2197.189945
			C_1	-2193.76678980	-2194.6925508	-2197.1600672	-2197.190205
1	1	3	C_s	-2269.8023058	-2270.9283548	-2273.6021136	--
			C_1 [4+1]	-2269.804125	-2270.928723	-2273.605633	-2273.626944
1	1	4	trans-C_s #1	-2345.8336848	-2347.170189	-2350.048203	-2350.078542
			trans-C_s #2	-2345.842566	-2347.170188	-2350.048203	-2350.078555
			cis-C_1	-2345.840196	-2347.168488	-2350.048074	-2350.080359
1	2	0	C_2	-2117.14919140	-2117.9054956	-2120.192356	--
			C_1	-2117.14919140	-2117.9054956	-2120.19235120	-2120.286044
1	2	1	C_s	-2193.22989990	-2194.1698547	-2196.64598440	-2196.732299
1	2	2	C_2	-2269.26349930	-2270.4040929	-2273.0775598	--
			C_1	-2269.26488270	-2270.4041086	-2273.07769890	-2273.158959
1	2	3	C_1 [5+1]	-2345.30645060	-2346.6455981	-2349.52704130	-2349.606143
1	3	0	C_3	-2192.52218580	-2193.4695964	-2195.93407160	-2196.240935
1	3	1	C_1 [4+1]	-2268.58443500	-2269.7326165	-2272.4062421	-2272.691713
1	3	2	C_s [3+2+1]	-2344.63602040	-2344.6287329	-2348.859308	--
			C_1 [3+2+1]	-2344.64095840	-2345.9778076	-2348.8756447	-2349.134069
2	1	0	C_s #1	-2501.2469244	-2501.9344455	-2501.60773230	-2504.683233
			C_s #2	-2501.24849650	-2501.9385309	-2504.6162314	--
			C_1	-2501.24849650	-2501.9658051	-2504.61798020	-2504.702131
2	1	1	C_1	-2577.33129080	-2578.2042117	-2581.05815300	-2581.138804
2	1	2	C_1	-2653.36426140	-2654.4369142	-2657.49753960	-2657.576358
2	1	3	C_1 [5+1]	-2729.39573260	-2730.6658144	-2733.94055680	-2734.024255
2	2	0	C_2	-2576.64463590	-2577.5217834	-2580.3803982	--
			C_s	-2576.64457510	-2577.5218910	--	--
			C_1	-2576.6446359	-2577.5217834	--	--
2	2	1	C_s [3+2]	-2652.69800370	-2653.7715476	-2656.85143930	-2657.11759
2	2	2	C_{2v} [4+2]	-2728.74417390	-2730.0164648	-2733.29040500	-2733.547031

3	1	0	C_s	-2960.75207160	-2961.5615582	-2964.7987142	--
			C_1	-2960.75769220	-2961.5672031	-2964.80869380	-2965.090155
3	1	1	C_1 [4+1]	-3036.81050170	-3037.8200020	-3041.26990320	-3041.531485
3	1	2	C_s [4+2]	-3112.84904320	-3114.0555961	-3117.71990960	-3117.965422

NOT Stable †Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.23: Ni-O bond lengths for stable geometries of $[NiCl_n(OH)_m(H_2O)_l]^{2-n-m}$, where n=1 – 3, m=1 – (4-n), l=0 – (6-n-m).

				Optimized Ni-O Bond Lengths (Å)					
				HF/6-31+G*		MP2/6-31+G*		B3LYP/6-31+G*	
n	**m**	**l**	**Point Group**	**OH**	**H_2O**	**OH**	**H_2O**	**OH**	**H_2O**
1	1	0	C_s	1.785	N/A	1.765	N/A	1.769	N/A
1	1	1	C_1	1.810	2.123	1.782	2.080	1.765	2.105
1	1	2	C_1	1.873	2.114 2.141	1.853	2.070 2.094	1.829	2.104 2.119
1	1	3	C_1 [4+1]	1.888	2.094 2.124	1.891	2.042 2.074	1.907	2.042 2.095
1	1	4	trans-C_s #1	--	--	1.984	2.298 2.112 2.179	2.000	2.335 2.124 2.228
			trans-C_s #2	1.968	2.383 2.171 2.248	1.983	2.298 2.112 2.179	2.000	2.335 2.124 2.228
			cis-C_1	1.957	2.237 2.217 2.158 2.210	1.967	2.165 2.151 2.101 2.143	1.973	2.181 2.182 2.118 2.157
1	2	0	C_2	1.861	N/A	1.834	N/A	--	N/A
			C_1	1.861 1.861	N/A	1.834 1.834	N/A	1.845 1.843	N/A
1	2	1	C_s	1.919	2.315 2.370	1.897	2.258 2.270	1.844	2.268 [3+1]
1	2	2	C_2	1.935	2.321	--	--	--	--
			C_1	1.936 1.936	2.356 2.357 2.480	1.938 1.923	2.272 2.283 2.365	1.943 1.902	2.316 2.311 2.423
1	2	3	C_1 [5+1]	1.956 1.938	2.327 2.272	1.943 1.942	2.291 2.180	1.937 1.942	2.332 2.209
1	3	0	C_3	1.972	N/A	1.974	N/A	1.951	N/A
1	3	1	C_1 [4+1]	1.968 1.978 1.981	--	1.964 1.963 1.977	--	1.953 1.946 1.960	--
1	3	2	C_s [3+2+1]	1.927 1.936 1.922	--	--	--	--	--
			C_s [3+2+1]	1.924 1.916 1.910	--	1.894 1.890 1.885	--	1.892 1.872 1.867	--

2	1	0	C_s #1	--	--	--	--	1.858	N/A
			C_s #2	1.845	N/A	1.818	N/A	--	N/A
			C_1	1.845	N/A	1.834	N/A	1.815	N/A
2	1	1	C_1 #1		2.251	1.876	2.209	1.847	2.299
			C_1 #2		2.274	1.925	2.223	1.893	2.299
2	1	2	C_1	1.926	2.228	1.930	2.163	1.937	2.167
2	1	3	C_1 [5+1]	1.887	2.265 2.152 2.152	1.864	2.210 2.124 2.102	1.841	2.225 2.155 2.116
2	2	0	C_2	1.929	N/A	1.918	N/A	--	N/A
			C_s	1.930	N/A	1.918	N/A	--	--
2	2	1	C_s [3+2]	1.854	2.048	1.825	2.016	1.806	2.049
2	2	2	C_{2v} [4+2]	1.907	2.173	1.901	2.114	1.892	2.129
3	1	0	C_s	1.960	N/A	--	N/A	--	N/A
			C_1	1.922	N/A	1.912	N/A	1.889	N/A
3	1	1	C_1 [4+1]	1.940	--	1.932	--	1.922	--
3	1	2	C_s [4+2]	1.885	2.121	1.877	2.071	1.865	2.084

Table 3A.24: Ni-Cl bond lengths for stable geometries of $[NiCl_n(OH)_m(H_2O)_l]^{2-n-m}$, where n=1 – 3, m=1 – (4-n), l=0 – (6-n-m).

				Optimized Ni-Cl Bond Lengths (Å)		
n	**m**	**l**	**Point Group**	**HF/6-31+G***	**MP2/6-31+G***	**B3LYP/6-31+G***
1	1	0	C_s	2.171	2.093	2.098
1	1	1	C_1	2.222	2.152	2.164
1	1	2	C_1	2.264	2.203	2.233
1	1	3	C_1 [4+1]	2.275	2.199	2.205
1	1	4	trans-C_s #1	--	2.298	2.335
			trans-C_s #2	2.383	2.298	2.335
			cis-C_1	2.409	2.319	2.371
1	2	0	C_2	2.312	2.211	--
			C_1	2.313	2.210	2.272
1	2	1	C_s	2.370	2.270	2.268
1	2	2	C_2	2.518	--	--
			C_1	2.480	2.365	2.423
1	2	3	C_1 [5+1]	2.470	2.347	2.400
1	3	0	C_3	2.909	2.491	2.808
1	3	1	C_1 [4+1]	--	--	--
1	3	2	C_s [3+2+1]	--	--	--
1	3	2	C_s [3+2+1]	--	--	--
2	1	0	C_s #1	--	--	2.275 2.253
			C_s #2	2.280	2.183	--
			C_1	2.281 2.281	2.216 2.249	2.223 2.276
2	1	1	C_1	2.358 2.330	2.267 2.240	2.294 2.261
2	1	2	C_1	2.397 2.446	2.298 2.351	2.340 2.390
2	1	3	C_1 [5+1]	2.471	2.376	2.453
2	2	0	C_2	2.635	2.455	--
			C_s	2.686 2.575	2.505 2.406	--
2	2	1	C_s [3+2]	--	--	--
2	2	2	C_{2v} [4+2]	--	--	--

3	1	0	C_s	2.437 2.480	--	--
			C_1	2.497 2.494 2.450	2.375 2.376 2.336	2.432 2.455 2.360
3	1	1	C_1 [4+1]	2.459 2.464 2.447	2.347 2.346 2.334	2.404 2.389 2.362
3	1	2	C_s [4+2]	2.360	2.271	2.318

Table 3A.25: Ni-O and Ni-Cl stretching frequencies of $[NiCl_n(OH)_m(H_2O)_l]^{2-n-m}$, where n=1 – 3, m=1 – (4-n), l=0 – (6-n-m) calculated at HF/6-31+G*.

n	m	l	Point Group Symmetry	Freq. (cm^{-l})	Irr. Rep. Symm.	OH/H_2O/Cl	Notes
1	1	0	C_s	395.0 734.6	a' a'	Cl OH	
1	1	1	C_1	292.7 364.7 609.6 695.9	a a a a	H_2O Cl OH OH	 H_2O wag H_2O rock H_2O rock
1	1	2	C_1	291.4 300.9 316.4 337.6 600.4 629.7	a a a a a a	H_2O H_2O H_2O/ H_2O/Cl OH OH	 H_2O rock H_2O rock H_2O rock H_2O rock H_2O rock
1	1	3	C_1 [4+1]	305.0 334.1 337.6 347.3 596.4	a a a a a	H_2O H_2O/Cl Cl H_2O OH	 H_2O rock H_2O wag H_2O twist/rock H_2O twist
1	1	4	C_s #2	173.1 206.4 245.1 263.5 283.2 297.8 504.0	a" a' a" a' a" a' a'	H_2O H_2O/Cl H_2O H_2O/Cl H_2O H_2O/Cl OH	 H_2O wag/twist
1	2	0	C_2	305.7 576.8 618.6	a a b	Cl OH OH	
1	2	1	C_s	229.3 264.9 272.0 515.4 548.9	a' a' a' a' a"	H_2O Cl Cl OH OH	
1	2	2	C_1	119.9 156.2 219.8 485.8 542.0	a a a a a	H_2O H_2O Cl OH OH	

1	2	3	C_1 [5+1]	145.2 176.4 207.7 230.5 265.2 452.7 484.6 572.5	a a a a a a a a	H_2O/Cl H_2O H_2O/Cl H_2O/Cl H_2O OH OH OH	 H_2O rock H_2O wag
1	3	0	C_3	44.5 458.0 458.1 463.9	a e e a	Cl OH OH OH	
1	3	1	C_1 [4+1]	102.2 451.4 452.8 467.0	a a a a	Cl OH OH OH	
1	3	2	C_1 [3+2+1]	504.5 532.3 540.0	a a a	OH OH OH	
2	1	0	C_s #2	303.3 345.6 623.4	a' a" a'	Cl Cl OH	
2	1	1	C_1	201.3 270.1 306.1 539.5	a a a a	H_2O H_2O/Cl H_2O/Cl OH	
2	1	2	C_1	146.5 169.7 197.4 234.6 246.9 257.2 272.1 528.7	a a a a a a a a	H_2O H_2O/Cl H_2O Cl H_2O/Cl H_2O/Cl H_2O/Cl OH	
2	1	3	C_1 [5+1]	190.2 223.7 247.5 272.8 320.3 563.1 571.5	a a a a a a a	H_2O/Cl H_2O/Cl H_2O/Cl H_2O H_2O/Cl OH OH	 H_2O twist H_2O twist

2	2	0	C_2	87.6 107.2 130.5 147.9 488.7 533.1	b a b a a b	Cl Cl Cl Cl OH OH	
2	2	1	C_s [3+2]	379.8 554.5 653.9	a' a' a"	H_2O OH OH	 H_2O rock
2	2	2	C_{2v} [4+2]	249.4 302.9 515.5 578.5	b_1 a_1 a_1 b_2	H_2O H_2O OH OH	
3	1	0	C_1	186.9 194.3 213.8 524.0	a a a a	Cl Cl Cl OH	
3	1	1	C_1 [4+1]	211.7 215.1 218.4 492.6 530.5	a a a a a	Cl Cl Cl OH OH	
3	1	2	C_s [4+2]	276.2 290.3 344.1 582.5	a' a" a' a'	Cl H_2O H_2O OH	

Table 3A.26: Ni-O and Ni-Cl stretching frequencies of $[NiCl_n(OH)_m(H_2O)_l]^{2-n-m}$, where n=1 – 3, m=1 – (4-n), l=0 – (6-n-m) calculated at MP2/6-31+G*.

n	m	l	Point Group Symmetry	Freq (cm^{-1})	Irr. Rep. Symm.	OH/H_2O	Notes
1	1	0	C_s	417.4 735.7	a' a'	Cl OH	
1	1	1	C_1	319.9 381.6 638.2 719.0	a a a a	H_2O Cl OH OH	 H_2O rock H_2O rock
1	1	2	C_1	320.0 338.1 359.0 598.8	a a a a	H_2O H_2O H_2O/Cl OH	 H_2O rock/wag
1	1	3	C_1 [4+1]	326.9 350.8 375.1 382.0 573.8	a a a a a	H_2O H_2O/Cl H_2O/Cl H_2O OH	 H_2O rock H_2O rock H_2O twist
1	1	4	C_s #1	200.8 228.0 247.7 280.0 296.0 324.1 328.1 442.6 495.4	a" a' a' a" a' a" a' a' a'	H_2O H_2O/Cl H_2O H_2O H_2O/Cl H_2O H_2O/Cl OH OH	
1	2	0	C_2	338.8 598.5 629.4	a a b	Cl OH OH	
1	2	1	C_s	176.4 226.4 272.9 307.7 504.4 548.4	a' a' a' a' a' a"	H_2O H_2O H_2O/Cl Cl OH OH	

1	2	2	C_1	157.1 183.2 247.4 263.4 272.9 471.0 532.0	a a a a a a a	H_2O/Cl H_2O H_2O/Cl H_2O/Cl H_2O/Cl OH OH	 H_2O rock H_2O rock
1	2	3	C_1 [5+1]	148.1 168.5 244.8 257.0 268.1 272.5 456.7 513.5	a a a a a a a a	H_2O H_2O Cl H_2O H_2O/Cl Cl OH OH	 H_2O rock H_2O rock
1	3	0	C_3	165.0 430.2 430.2 446.9	a e e a	Cl OH OH OH	
1	3	1	C_1 [4+1]	180.9 429.3 441.6 453.2	a a a a	Cl OH OH OH	
1	3	2	C_1 [3+2+1]	502.7 537.3 541.4	a a a	OH OH OH	
2	1	0	C_1	309.1 348.4 595.9	a a a	Cl Cl OH	
2	1	1	C_1	268.4 291.6 348.9 513.7	a a a a	H_2O/Cl H_2O/Cl Cl OH	 H_2O rock H_2O rock
2	1	2	C_1	197.7 222.3 269.2 279.2 283.1 303.3 516.0	a a a a a a a	H_2O/Cl H_2O H_2O/Cl H_2O/Cl H_2O/Cl H_2O/Cl OH	

2	1	3	C_1	214.8 259.9 280.8 291.7 342.0 561.4	a a a a a a	H_2O/Cl H_2O/Cl H_2O/Cl H_2O H_2O/Cl OH	
2	2	0	C_s	162.4 210.9 465.2 515.2	a' a' a' a"	Cl Cl OH OH	
2	2	1	C_s [3+2]	396.2 546.9 660.4	a' a' a"	H_2O OH OH	
2	2	2	C_{2v} [4+2]	286.9 333.9 493.1 544.3	b_1 a_1 a_1 b_2	H_2O H_2O OH OH	
3	1	0	C_1	222.8 237.5 245.3 275.2 503.6	a a a a a	Cl Cl Cl Cl OH	
3	1	1	C_1 [4+1]	242.6 258.3 263.0 482.7	a a a a	Cl Cl Cl OH	
3	1	2	C_s [4+2]	304.6 324.2 373.0 552.0	a' a" a' a'	Cl H_2O H_2O OH	 H_2O rock

Table 3A.27: Ni-O and Ni-Cl stretching frequencies of $[NiCl_n(OH)_m(H_2O)_l]^{2-n-m}$, where n=1 – 3, m=1 – (4-n), l=0 – (6-n-m) calculated at B3LYP/6-31+G*.

n	m	l	Point Group Symmetry	Freq (cm^{-1})	Irr. Rep. Symm.	OH/H_2O	Notes
1	1	0	C_s	417.4 735.7	a' a'	Cl OH	
1	1	1	C_1	319.9 381.6 638.2 719.0	a a a a	H_2O Cl OH OH	
1	1	2	C_1	320.0 359.0 598.8	a a a	H_2O H_2O/Cl OH	 H_2O rock H_2O rock/wag
1	1	3	C_1 [4+1]	276.2 288.0 321.5 341.2 373.6 547.6	a a a a a a	H_2O/Cl H_2O/Cl H_2O H_2O/Cl H_2O OH	 H_2O rock H_2O rock
1	1	4	C_s #1	188.5 208.1 235.4 264.2 304.5 314.9 459.1 494.5	a' a' a' a' a' a' a' a'	H_2O H_2O/Cl Cl H_2O/Cl H_2O H_2O/Cl OH OH	 H_2O rock H_2O rock H_2O twist
1	2	0	C_1	282.7 544.4 559.5	a a a	Cl OH OH	
1	2	1	C_s [3+1]	290.6 533.2 581.1	a' a' a"	Cl OH OH	
1	2	2	C_1	135.2 149.0 226.6 469.1 526.5	a a a a a	H_2O/Cl H_2O H_2O/Cl OH OH	
1	2	3	C_1 [5+1]	129.8 227.3 234.9 453.5 502.8	a a a a a	H_2O H_2O/Cl H_2O/Cl OH OH	 H_2O rock

1	3	0	C_3	48.6 447.0 447.1 458.4	a e e a	Cl OH OH OH	
1	3	1	C_1 [4+1]	103.0 430.7 442.9 455.2 465.1	a a a a a	Cl OH OH OH OH	
1	3	2	C_1 [3+2+1]	503.1 521.2 537.9	a a a	OH OH OH	
2	1	0	C_1	284.8 319.4 600.8	a a a	Cl Cl OH	
2	1	1	C_1	232.1 255.5 271.0 316.6 499.6	a a a a a	H_2O H_2O/Cl H_2O/Cl H_2O/Cl OH	
2	1	2	C_1	174.8 203.1 248.0 261.9 269.0 508.8	a a a a a a	H_2O/Cl H_2O H_2O/Cl H_2O H_2O/Cl OH	 H_2O rock
2	1	3	C_1 [5+1]	236.2 225.2 259.4 313.6 572.1	a a a a a	H_2O/Cl H_2O/Cl H_2O H_2O/Cl OH	 H_2O rock H_2O twist
2	2	0	--	--	--	--	
2	2	1	C_s [3+2]	359.0 564.1 665.0 675.2	a' a' a" a"	H_2O OH OH OH	 H_2O rock H_2O rock
2	2	2	C_{2v} [4+2]	266.9 312.5 489.9 524.2	b_1 a_1 a_1 b_2	H_2O H_2O OH OH	 H_2O rock
3	1	0	C_1	180.2 189.2 234.6 502.9	a a a a	Cl Cl Cl OH	

3	1	1	C_1 [4+1]	207.8 214.7 236.6 470.4	a a a a	Cl Cl Cl OH	
3	1	2	C_s [4+2]	243.3 268.6 301.3 353.1 545.8	a' a' a" a' a'	Cl Cl H_2O H_2O OH	H_2O rock

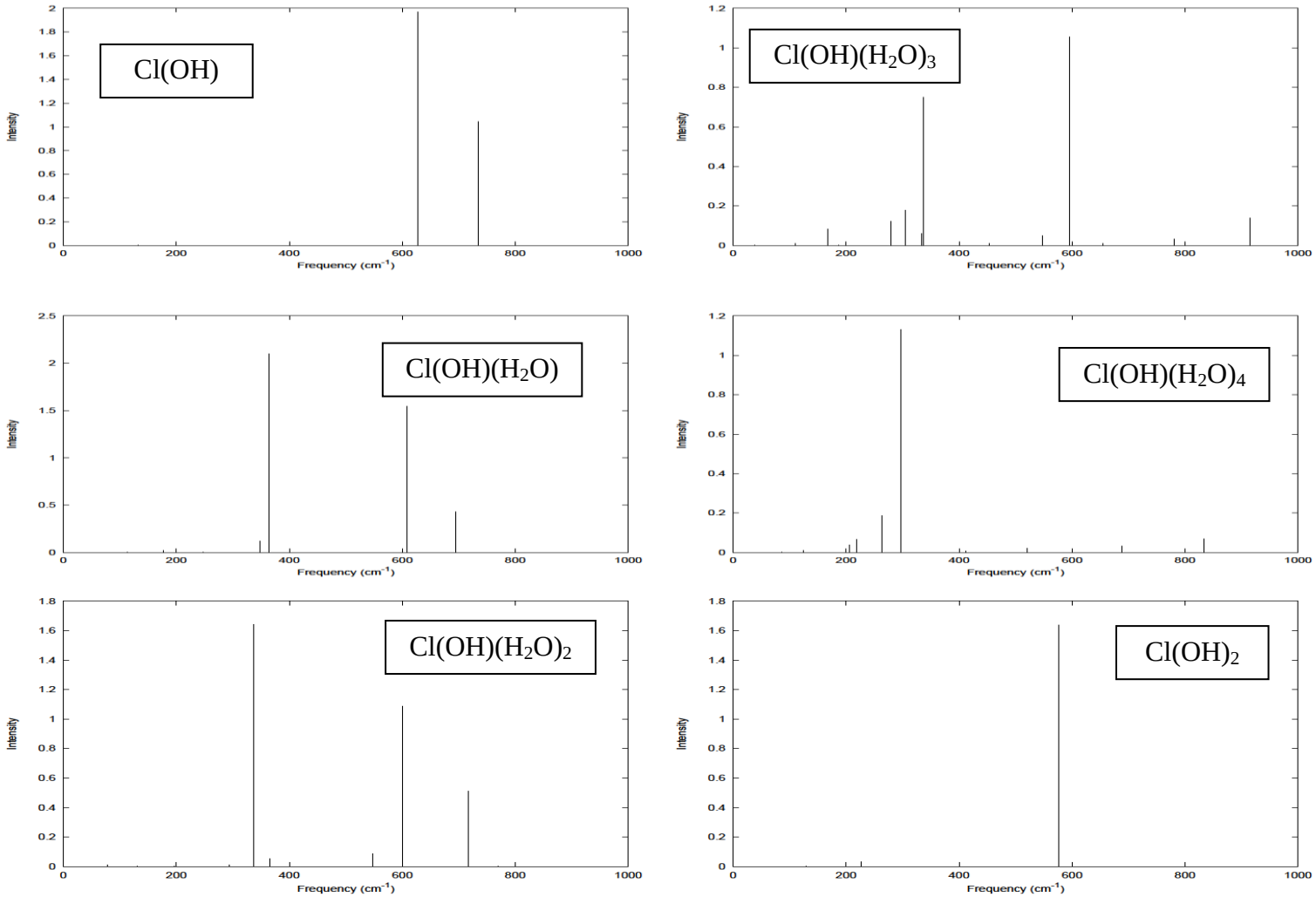


Figure 3A-5: Simulated polarized Raman spectra for $[NiCl_n(OH)_m(H_2O)_l]^{2-n-m}$, where n=1 – 3, m=1 – (4-n) and l=0 – (6-n-m)

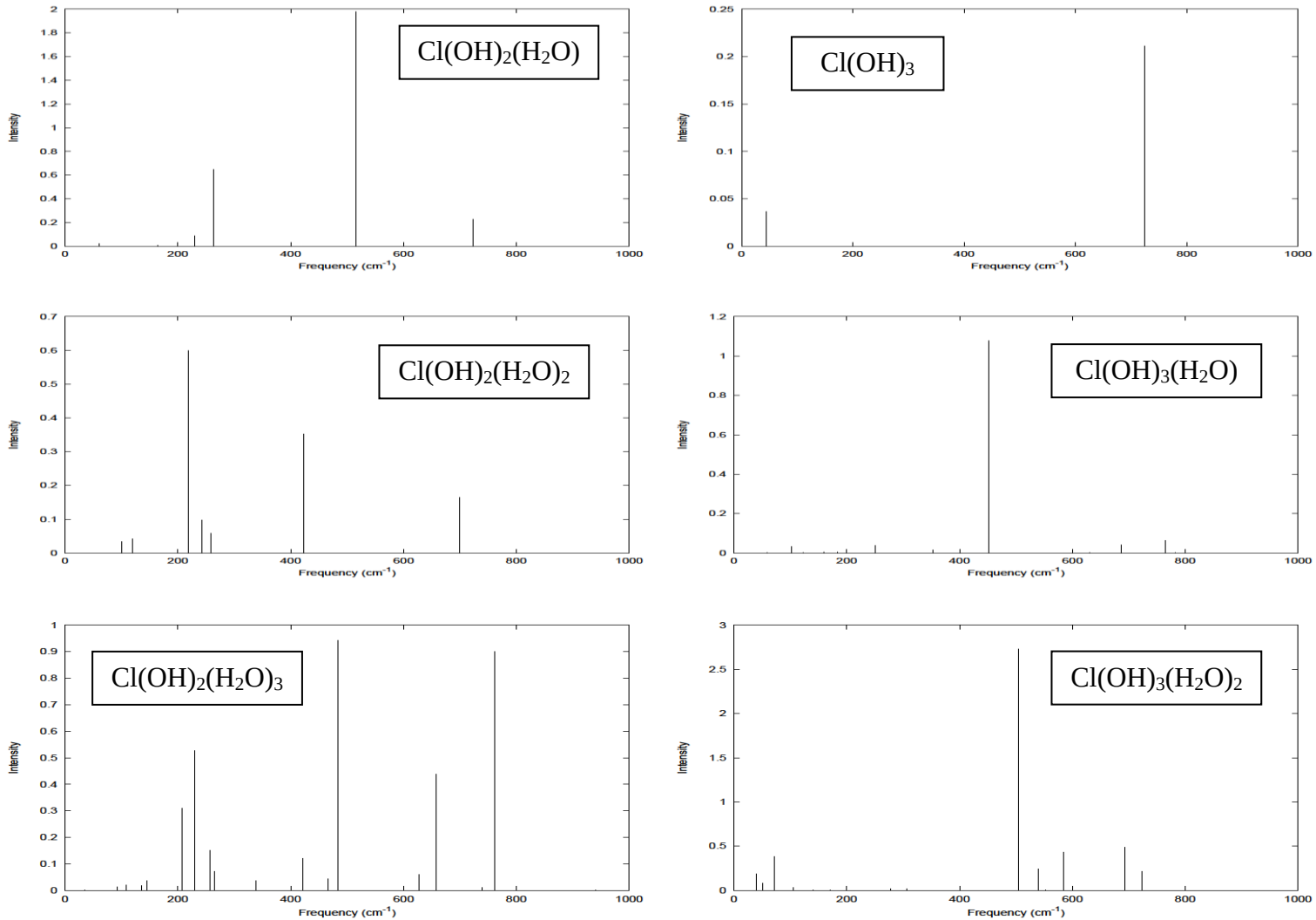


Figure 3A-5: *(continued)*

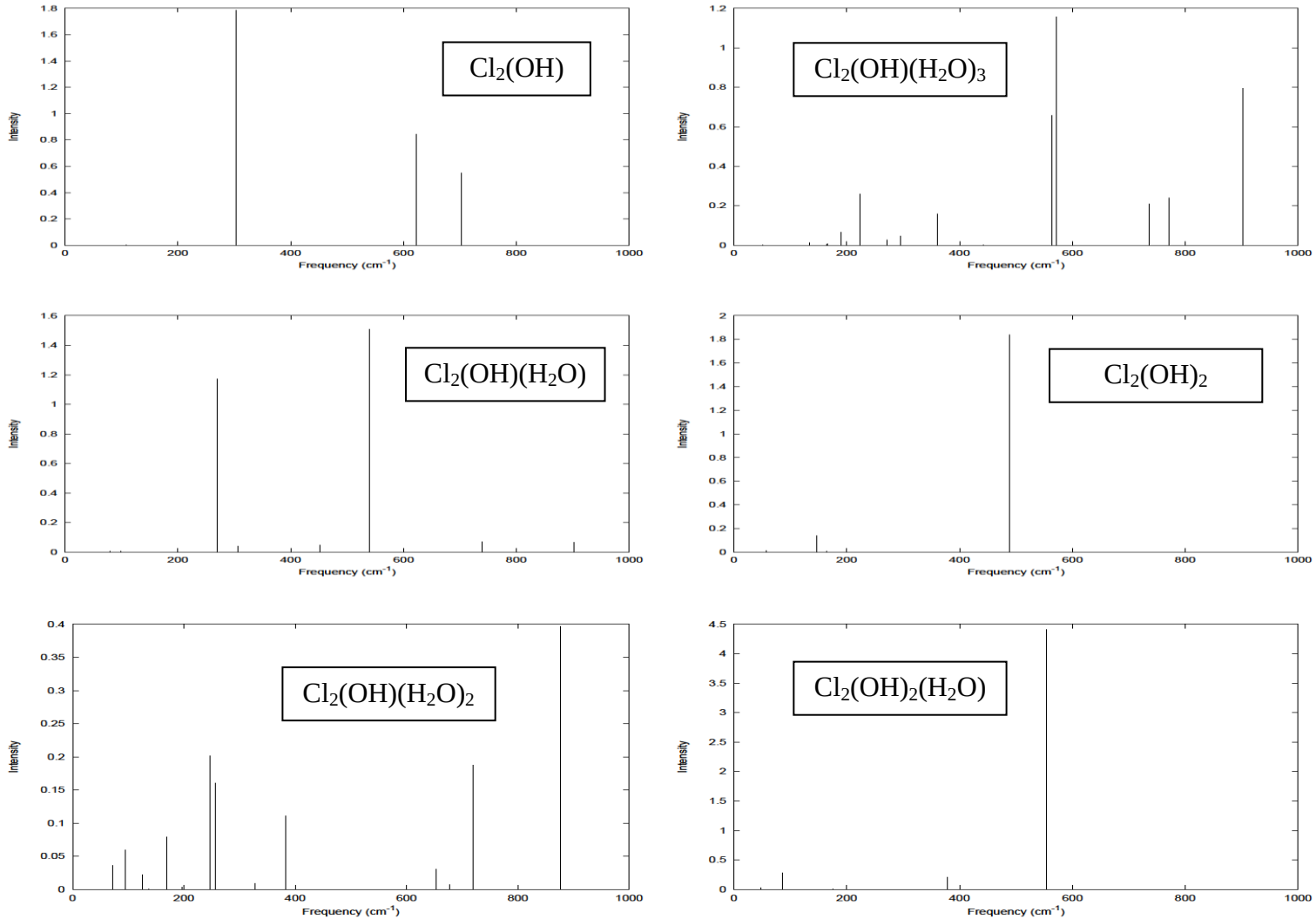


Figure 3A-5: *(continued)*

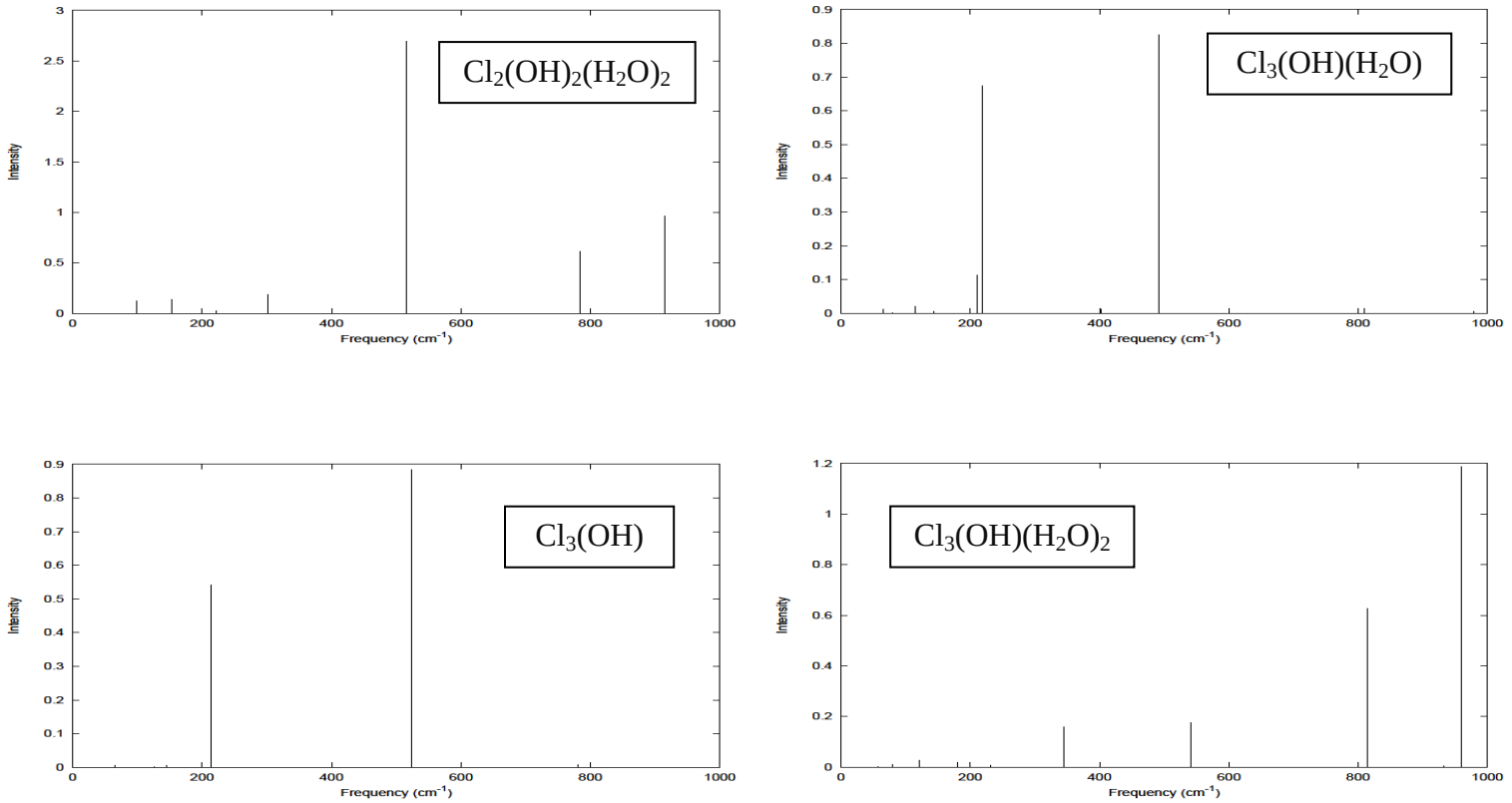


Figure 3A-5: *(continued)*

Table 3A.28: Total energies for all stable geometries of $[NiCl_n(NH_3)_m(H_2O)_l]^{2-n}$, where n=1 – 4, m=1 – (6-n), l=0 – (6-n-m).

				Optimized Energies (Hartrees)			
n	**m**	**l**	**Point Group**	**HF**	**MP2**	**B3LYP**	**C-PCM†**
1	1	0	C_{3v}	-2022.0980564	-2022.6041428	-2024.7279077	--
			C_1	-2022.1883406	-2022.6860537	-2024.7151254	-2024.877645
1	1	1	C_s #1	-2098.2131827	-2098.9270800	-2101.1910704	--
			C_s #2	-2098.2131642	-2098.9269617	-2101.1910438	-2101.305085
			C_s #3	-2098.2600669	-2098.9576410	-2101.2062985	--
			C_1	-2098.2630663	-2098.9576409	-2101.2070834	-2101.333125
1	1	2	C_s	-2174.3276946	-2175.2226221	-2177.669693	--
			C_1	-2174.3276330	-2175.2235796	-2177.6717744	-2177.78607
1	1	3	C_s	-2250.3797989	-2251.4741945	-2254.1275377	--
			C_1	-2250.3796168	-2251.4741932	-2254.1275960	-2254.241266
1	1	4	trans-C_1	-2326.4293401	-2327.7240739	-2330.5817946	-2330.696261
			cis-C_1	-2326.427845	-2327.722271	-2330.579878	-2330.695757
1	2	0	C_{2v}	-2078.4034719	-2079.1339232	-2081.3565099	--
			C_2	-2078.4034719	-2079.1041295	-2081.3475190	-2081.450697
			C_s	-2078.4382613	-2079.1041295	-2081.3475172	--
			C_1	-2078.4506871	-2079.1349343	-2081.3638443	-2081.482464
1	2	1	C_1	-2154.5134195	-2155.3955160	-2157.8239233	-2157.932329
1	2	2	C_2	-2230.5609366	-2231.6420052	-2234.2764732	-2234.382417
1	2	3	mer-C_2	-2306.6063231	-2307.8852423	-2310.7240271	--
			mer-C_1	-2306.6087815	-2307.8890036	-2310.7274536	-2310.834643
			fac-C_s	-2306.606911	-2307.886436	-2310.725247	-2310.834483
1	3	0	C_{3v}	-2134.6976760	-2135.5655365	-2137.9747161	--
			C_s	-2134.6976761	-2135.5656659	-2137.9749818	-2138.07835
			C_1	-2134.6976761	-2135.5656659	-2137.9749972	-2138.078245
1	3	1	C_s	-2210.7406736	-2211.8070288	-2214.4220821	--
			C_1	-2210.7406736	-2211.8071171	-2214.4224854	-2214.523325
1	3	2	mer-C_s	-2286.7860630	-2288.0501281	-2290.8695286	-2290.972438
			mer-C_1 #1	-2286.7860630	-2288.0501342	-2290.8695009	-2290.973156
			mer-C_1 #2	-2286.78399	-2288.048109	-2290.867593	-2290.972374
			fac-C_1	-2286.787263	-2288.052535	-2290.871856	-2290.974232
1	4	0	C_4	-2190.9179084	-2191.9695394	-2194.5649489	-2194.665632
1	4	1	trans-C_2	-2266.9592327	-2268.2079399	-2271.0069362	--
			trans-C_1	-2266.9592052	-2268.2079331	-2271.0076066	-2271.110998
			cis-C_1	-2266.963828	-2268.213431	-2271.013151	-2271.111722
1	5	0	C_s	-2247.1384287	-2248.3715745	-2251.1521094	-2251.249910
			C_1	-2247.1384321	-2248.3716948	-2251.1521093	-2251.249923

2	1	0	C_s #1	-2481.9898892	-2482.6404218	-2485.2723637	--
			C_s #2	-2481.989883	-2482.6404067	-2485.2723576	-2485.302716
			C_1	-2481.9898895	-2482.6404218	-2485.2723574	-2485.302719
2	1	1	C_s	-2558.0405850	-2558.8879777	-2561.7203077	-2561.754151
2	1	2	C_s	-2634.0831933	-2635.1303271	-2638.1687266	-2638.200500
			C_1	-2634.0831933	-2635.1303208	-2638.1687227	-2638.200517
2	1	3	mer-C_1	-2710.1096648	-2711.3573060	-2714.6038273	-2714.636472
			fac-C_1	-2710.10878	-2711.3563	-2714.602517	-2714.638134
2	2	0	C_{2v}	-2538.2193655	-2539.0521149	-2541.8649231	--
			C_2	-2538.219225	-2539.0521150	-2541.8650448	--
			C_1	-2538.2193658	-2539.0521150	-2541.8650788	-2541.897504
2	2	1	C_1	-2614.2530432	-2615.2837623	-2618.3031744	-2618.338217
2	2	2	all-trans-C_i	-2690.2919760	-2691.5237651	-2694.7462132	-2694.785727
			all-cis-C_1	-2690.285521	-2691.518167	-2694.744756	-2694.778252
			H_2O-trans-C_{2v}	-2690.285284	-2691.517167	-2694.744139	-2694.778380
			NH_3-trans-C_2	-2690.283041	-2691.515087	-2694.741682	-2694.777933
			Cl-trans-C_1	-2690.293135	-2691.525096	-2694.747787	-2694.786928
2	3	0	C_s	-2594.4317890	-2595.4479139	-2598.4474248	--
			C_1	-2594.4317891	-2595.4479139	-2598.4474315	-2598.481764
2	3	1	mer-C_1	-2670.4563966	-2671.6723212	-2674.8792690	-2674.916844
			fac-C_s	-2670.458282	-2671.674434	-2674.881381	-2674.916571
			fac-C_1	-2670.458282	-2671.674478	-2674.8813873	-2674.917358
2	4	0	trans-C_{4h}	-2650.6411940	-2651.8408884	-2655.0241477	-2655.064122
			trans-C_{2v}	-2650.6411571	-2651.8413701	-2655.0239758	--
			trans-C_2	-2650.6411941	-2651.8413699	-2655.0240196	-2655.063148
			cis-C_{2v}	-2650.6283634	-2651.8270651	-2655.0145476	-2655.054129
			cis-C_2	-2650.6283614	-2651.8271261	-2655.0145476	-2655.054138
3	1	0	C_{3v}	-2941.6057872	-2942.3949595	-2945.6145710	-2945.703019
			C_s	-2941.6062327	-2942.3961493	-2945.6162124	-2945.705135
3	1	1	C_1	-3017.6386861	-3018.6287553	-3022.0563875	-3022.139619
3	1	2	C_s [5+1]	-3093.6684086	-3094.8555353	-3098.4932607	-3098.57533
3	2	0	C_{3h}	-2997.8157774	-2998.7874416	-3002.1955805	--
			C_{2v} #1	-2997.8156408	-2998.7889534	-3002.1951338	--
			C_{2v} #2	-2997.8161501	-2998.7886257	-3002.1967848	-3002.285954
			C_s	-2997.8161494	-2998.7889534	-3002.1968114	-3002.285986
3	2	1	C_1 [5+1]	-3073.8481268	-3075.0205447	-3078.6408278	-3078.726809
3	3	0	fac-C_{3v}	-3053.9922929	-3055.1513991	-3058.7455920	-3058.853373
			fac-C_3	-3053.9922929	-3055.1515773	-3058.7455842	-3058.853332
			C_1 [5+1]	-3054.0165752	-3055.1738445	-3058.7727412	-3058.868521

4	1	0	C_{3v} #1	-3401.0571941	-3401.9828599	-3405.7988242	--
			C_{3v} #2	-3401.0565443	-3401.9816377	-3405.7995623	-3406.074909
			C_3	-3401.05719	-3401.9828601	-3405.7987992	-3406.077956
			C_s	-3401.0577058	-3401.9842551	-3405.8003769	--
4	1	1	C_1 [4+2]	-3477.1342146	-3478.2541651	-3482.2856329	-3482.52012
4	2	0	C_{2v} [5+1]	-3457.2729464	-3458.3795192	-3462.3842043	-3462.66446

NOT Stable †Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.29: Ni-Cl and Ni-N bond lengths, in Angstroms, for stable geometries of $[NiCl_n(NH_3)_m(H_2O)_l]^{2-n}$, where n=1 – 4, m=1 – (6-n), l=0 – (6-n-m).

				Optimized Ni-Cl and Ni-N Bond Lengths (Å)					
				HF/6-31+G*		MP2/6-31+G*		B3LYP/6-31+G*	
n	**m**	**l**	**Point Group**	**Ni-Cl**	**Ni-N**	**Ni-Cl**	**Ni-N**	**Ni-Cl**	**Ni-N**
1	1	0	C_{3v}	2.120	2.060	2.070	1.997	--	--
			C_1	2.126	2.036	2.076	1.986	2.083	2.005
1	1	1	C_s #1	2.139	2.056	2.057	1.982	--	--
			C_s #2	--	--	--	--	2.093	1.989
			C_s #3	2.159	2.069	2.086	2.015	--	--
			C_1	2.162	2.073	2.086	2.015	2.086	2.018
1	1	2	C_s	2.204	2.099	--	--	--	--
			C_1	2.202	2.100	2.132	2.034	2.125	2.040
1	1	3	C_s	2.260	2.110	2.194	2.048	--	--
			C_1	2.260	2.119	2.194	2.048	2.216	2.048
1	1	4	trans-C_1	2.350	2.154	2.285	2.085	2.329	2.102
			cis-C_1	2.336	2.149	2.265	2.070	2.307	2.082
1	2	0	C_{2v}	2.149	2.062	--	--	--	--
			C_2	2.149	2.063	--	--	2.088	2.001
			C_s	2.157	2.096	2.064	1.985	--	--
			C_1	2.170	2.094 2.094	2.099	2.020 2.020	2.103	2.024 2.024
1	2	1	C_1	2.211	2.119 2.115	2.144	2.051 2.043	2.149	2.074 2.055
1	2	2	C_2	2.293	2.125	2.232	2.050	2.275	2.060
1	2	3	mer-C_2	2.362	2.168	--	--	--	--
			mer-C_1	2.367	2.173 2.172	2.302	2.099 2.090	2.351	2.117 2.103
			fac-C_s	2.357	2.166	2.285	2.086	2.331	2.095
1	3	0	C_{3v}	2.218	2.133	--	--	--	--
			C_s	2.218	2.133 2.133	2.148	2.067 2.059	2.157	2.093 2.073
1	3	1	C_s	2.298	2.153 2.175	--	--	--	--
			C_1	2.298	2.153 2.153 2.170	2.237	2.100 2.067 2.069	2.282	2.107 2.078 2.083

1	3	2	mer-C_s	2.389	2.187 2.199 2.197	--	--	2.377	2.119 2.141 2.135
			mer-C_1 #1	2.389	2.187 2.199 2.197	2.326	2.112 2.120 2.119	2.376	2.119 2.142 2.134
			mer-C_1 #2	2.373	2.192 2.187 2.191	2.299	2.110 2.097 2.105	2.347	2.119 2.115 2.106
			fac-C_1	2.383	2.188 2.188 2.187	2.318	2.110 2.105 2.104	2.367	2.129 2.116 2.115
1	4	0	C_4	2.312	2.203	2.247	2.121	2.301	2.136
1	4	1	trans-C_2	2.388	2.234 2.213	2.305	2.147 2.122	--	--
			trans-C_1	2.385	2.232 2.231 2.215 2.212	2.304	2.147 2.148 2.123 2.122	2.363	2.166 2.164 2.139 2.147
			cis-C_1	2.398	2.210 2.211 2.213 2.214	2.333	2.130 2.128 2.129 2.118	2.388	2.141 2.152 2.147 2.130
1	5	0	C_s	2.419	2.233 2.248 2.253	--	--	2.412	2.176 2.179 2.183
			C_1	2.418	2.247 2.233 2.254 2.250 2.250	2.354	2.164 2.149 2.162 2.165 2.161	2.412	2.182 2.176 2.179 2.182 2.179
2	1	0	C_s #1	2.218 2.217	2.098	2.156 2.154	2.030	--	--
			C_s #2	--	--	--	--	2.153	2.040
			C_1	2.220 2.220	2.111	2.147 2.148	2.032	2.153 2.153	2.041
2	1	1	C_s	2.269	2.118	2.200	2.037	2.222	2.042
2	1	2	C_s	2.334	2.117	2.258	2.034	2.291	2.042
			C_1	2.334 2.334	2.117	2.258 2.257	2.033	2.292 2.291	2.042
2	1	3	mer-C_1	2.410 2.430	2.168	2.326 2.349	2.082	2.372 2.403	2.091
			fac-C_1	2.425 2.411	2.152	2.339 2.324	2.071	2.393 2.380	2.079

2	2	0	C_{2v}	2.281	2.139	2.211	2.052	--	--
			C_2	--	--	2.211	2.052	--	--
			C_1	2.281 2.281	2.139 2.139	2.211 2.211	2.052 2.052	2.238 2.235	2.064 2.059
2	2	1	C_1	2.380 2.380	2.153 2.173	2.307 2.307	2.070 2.089	2.319 2.377	2.077 2.096
2	2	2	all-trans-C_i	2.432	2.173	2.345	2.093	2.401	2.096
			all-cis-C_1	2.462 2.415	2.199 2.160	2.382 2.329	2.105 2.076	2.446 2.379	2.117 2.086
			H_2O-trans-C_{2v}	2.447	2.220	2.366	2.127	2.420	2.138
			NH_3-trans-C_2	2.441	2.164	2.351	2.085	2.413	2.089
			Cl-trans-C_1	2.430 2.430	2.183 2.163	2.343 2.342	2.092 2.078	2.386 2.389	2.106 2.087
2	3	0	C_s	2.390 2.383	2.158 2.183	2.315 2.308	2.065 2.098	--	--
			C_1	2.390 2.383	2.158 2.183 2.183	2.315 2.308	2.065 2.098 2.098	2.357 2.353	2.077 2.105 2.104
2	3	1	mer-C_1	2.430 2.492	2.223 2.198 2.178	2.338 2.414	2.123 2.117 2.097	2.398 2.489	2.140 2.122 2.104
			fac-C_s	2.464	2.182 2.243	--	--	2.441	2.108 2.157
			fac-C_1	2.465 2.464	2.243 2.243 2.182	2.386 2.378	2.144 2.141 2.096	2.443 2.442	2.157 2.157 2.109
2	4	0	trans-C_{4h}	2.473	2.217	--	--	2.432	2.144
			trans-C_{2v}	--	--	2.385 2.385	2.126 2.125	--	--
			trans-C_2	2.472 2.472	2.218 2.218	2.384 2.384	2.125 2.127	2.432 2.432	2.145 2.145
			cis-C_{2v}	2.488	2.211 2.272	--	--	2.473	2.137 2.183
			cis-C_2	2.484	2.212 2.274	2.403	2.133 2.164	2.473	2.137 2.183

3	1	0	C_{3v}	--	--	--	--	2.299	2.050
			C_s	2.343 2.353	2.142	2.265 2.266	2.055	2.294 2.294	2.052
3	1	1	C_1	2.384 2.432 2.453	2.158	2.285 2.339 2.356	2.069 2.186	2.325 2.383 2.412	2.071 2.203
3	1	2	C_s [5+1]	2.346 2.405	2.149	2.265 2.324	2.067	2.296 2.357	2072
3	2	0	C_{3h}	2.463	2.154	--	--	--	--
			C_{2v} #1	--	--	2.336 2.360	2.070	--	--
			C_{2v} #2	2.440 2.471	2.155	--	--	2.394 2.422	2.073
			C_s	2.472 2.441 2.470	2.155	2.360 2.336 2.360	2.070	2.421 2.424 2.393	2.074
3	2	1	C_1 [5+1]	2.421 2.416	2.174 2.131	2.321 2.329	2.090 2.058	2.369 2.385	2.091 2.059
3	3	0	fac-C_{3v}	2.545	2.265	--	--	2.525	2.159
			fac-C_3	2.546	2.265	--	--	2.525	2.159
			mer-C_1 [5+1]	2.426 2.426	2.129 2.207 2.208	2.336 2.336	2.051 2.122 2.123	2.378 2.378	2.061 2.134 2.134
4	1	0	C_{3v} #1	2.384 2.621	2.152	2.323 2.466	2.104	--	--
			C_{3v} #2	--	--	--	--	2.326 2.558	2.080
			C_3	--	--	--	--	2.325 2.558	2.076
			C_s	--	--	2.319 2.388 2.504	2.098	--	--
4	1	1	C_1 [4+2]	2.359 2.382 2.382	2.109	2.258 2.302 2.307	2.029	2.283 2.342 2.338	2.189
4	2	0	C_{2v} [5+1]	2.387 2.568	2.204	2.308 2.459	2.113	2.342 2.503	2.124

Table 3A.30: Ni-O bond lengths, in Angstroms, for stable geometries of $[NiCl_n(NH_3)_m(H_2O)_l]^{2-n}$, where n=1 – 4, m=1 – (6-n), l=0 – (6-n-m).

				Optimized Ni-O Bond Lengths (Å)		
n	**m**	**l**	**Point Group**	**HF/6-31+G***	**MP2/6-31+G***	**B3LYP/6-31+G***
1	1	1	C_s #1	2.001	1.941	--
			C_s #2	--	--	1.954
			C_s #3	2.076	2.009	--
			C_1	2.048	2.009	2.010
1	1	2	C_s	2.087	--	--
			C_1	2.093 2.088	2.055 2.053	2.090 2.076
1	1	3	C_s	2.112 2.176	2.062 2.137	--
			C_1	2.181 2.181 2.105	2.137 2.137 2.062	2.132 2.134 2.102
1	1	4	trans-C_1	2.171 2.172 2.173 2.173	2.117 2.117 2.119 2.117	2.132 2.133 2.134 2.132
			cis-C_1	2.172 2.171 2.183 2.180	2.121 2.127 2.128 2.132	2.135 2.158 2.144 2.144
1	2	1	C_1	2.111	2.068	2.083
1	2	2	C_2	2.201	2.151	2.162
1	2	3	mer-C_2	2.221 2.200	--	--
			mer-C_1	2.205 2.191 2.209	2.153 2.139 2.152	2.171 2.153 2.170
			fac-C_s	2.213 2.211	2.169 2.158	2.201 2.179
1	3	1	C_s	2.272	--	--
			C_1	2.272	2.243	2.267
1	3	2	mer-C_s	2.232	--	2.193
			mer-C_1 #1	2.232 2.232	2.151 2.151	2.193 2.193
			mer-C_1 #2	2.258 2.243	2.232 2.197	2.274 2.244
			fac-C_1	2.272 2.226	2.216 2.175	2.252 2.191

1	4	1	trans-C_2	2.279	2.246	--
			trans-C_1	2.286	2.246	2.285
			cis-C_1	2.331	2.279	2.312
2	1	1	C_s	2.127	2.074	2.042
2	1	2	C_s	2.177 2.173	2.121 2.119	2.134 2.131
			C_1	2.173 2.177	2.117 2.124	2.134 2.131
2	1	3	mer-C_1	2.276 2.172 2.182	2.204 2.122 2.133	2.229 2.139 2.149
			fac-C_1	2.250 2.214 2.187	2.179 2.151 2.141	2.206 2.169 2.154
2	2	1	C_1	2.146	2.087	2.119
2	2	2	all-trans-C_i	2.204	2.146	2.191
			all-cis-C_1	2.212 2.300	2.168 2.223	2.183 2.251
			H_2O-trans-C_{2v}	2.185	2.135	2.156
			NH_3-trans-C_2	2.286	2.214	2.247
			Cl-trans-C_1	2.201 2.217	2.153 2.165	2.184 2.194
2	3	1	mer-C_1	2.377	2.289	2.317
			fac-C_s	2.223	--	2.198
			fac-C_1	2.223	2.184	2.198
3	1	1	C_1	2.232	2.069	2.071
3	1	2	C_s [5+1]	2.236	2.188	2.217
3	2	1	C_1 [5+1]	2.150	2.116	2.129
4	1	1	C_1 [4+2]	--	--	--

Table 3A.31: Ni-N, Ni-Cl and Ni-N stretching frequencies of $[NiCl_n(NH_3)_m(H_2O)_l]^{2-n}$, where n=1 – 4, m=1 – (6-n), l=0 – (6-n-m) calculated at HF/6-31+G*.

n	m	l	Point Group Symmetry	Freq. (cm^{-l})	Irr. Rep. Symm.	$Cl/NH_3/H_2O$	Notes
1	1	0	C_1	395.0	a	Cl/NH_3	
				526.0	a	Cl/NH_3	
1	1	1	C_1	373.9	a	$Cl/NH_3/H_2O$	
				433.2	a	$Cl/NH_3/H_2O$	H_2O wag
				450.4	a	Cl/H_2O	H_2O wag
				478.0	a	Cl/NH_3	H_2O wag
1	1	2	C_s	319.7	a"	H_2O	
				326.8	a'	NH_3/H_2O	
				354.0	a'	Cl/NH_3	
				428.8	a'	Cl/NH_3	H_2O rock
1	1	3	C_s	221.6	a'	Cl/H_2O	
				260.2	a"	H_2O	H_2O wag/twist
				308.9	a"	H_2O	H_2O twist
				312.4	a'	Cl/H_2O	
				362.6	a'	Cl/NH_3H_2O	
				382.0	a'	$Cl/NH_3/H_2O$	H_2O rock
1	1	4	trans-C_1	224.6	a	$Cl/NH_3/H_2O$	
				233.7	a	H_2O	H_2O twist
				290.1	a	H_2O	H_2O twist
				291.3	a	H_2O	H_2O twist
				317.8	a	$Cl/NH_3/H_2O$	
				354.0	a	Cl/NH_3	H_2O twist
1	2	0	C_1	369.0	a	Cl/NH_3	
				391.7	a	NH_3	
				454.6	a	Cl/NH_3	
1	2	1	C_1	307.9	a	H_2O	
				347.2	a	Cl/NH_3	H_2O twist
				367.6	a	NH_3	H_2O wag
				411.8	a	Cl/NH_3	H_2O rock
1	2	2	C_2	205.8	a	Cl/H_2O	H_2O twist
				230.2	a	Cl/NH_3	H_2O twist
				268.6	b	H_2O	
				330.4	a	Cl/NH_3	
				352.4	a	$Cl/NH_3/H_2O$	
				377.5	b	NH_3	H_2O twist

1	2	3	mer-C_1	199.0 216.6 231.3 231.9 271.4 303.7 331.2 336.9	a a a a a a a a	Cl/H_2O $Cl/NH_3/H_2O$ H_2O H_2O H_2O $Cl/NH_3/H_2O$ Cl/NH_3 Cl/NH_3	H_2O twist/rock H_2O twist H_2O rock H_2O twist H_2O rock H_2O wag
1	3	0	C_{3v}	347.0 351.9 351.9 401.1	a_1 e e a_1	Cl/NH_3 NH_3 NH_3 Cl/NH_3	
1	3	1	C_s	204.7 302.1 326.0 347.7 356.0	a' a' a' a' a"	H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/NH_3 NH_3	 H_2O twist H_2O rock H_2O wag
1	3	2	fac-C_1	215.5 228.0 246.7 311.8 316.7 326.7	a a a a a a	$Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ H_2O Cl/NH_3 $Cl/NH_3/H_2O$ NH_3/H_2O	H_2O twist H_2O twist H_2O twist H_2O rock
1	4	0	C_4	226.3 303.1 314.9 314.9 341.5	b a e e a	NH_3 Cl/NH_3 NH_3 NH_3 Cl/NH_3	
1	4	1	cis-C_1	183.8 219.1 280.4 302.2 305.2 320.1	a a a a a a	H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/NH_3 Cl/NH_3 $Cl/NH_3/H_2O$	H_2O wag H_2O wag H_2O rock H_2O rock H_2O twist
1	5	0	C_1	205.2 209.1 273.8 274.1 287.3 310.5	a a a a a a	Cl/NH_3 NH_3 NH_3 NH_3 Cl/NH_3 Cl/NH_3	
2	1	0	C_s #1	319.6 374.8 431.7	a' a' a'	Cl NH_3 Cl	

2	1	1	C_s	293.5 310.5 366.8 385.4	a' a' a' a'	Cl/H_2O Cl/H_2O NH_3 Cl	 H_2O wag H_2O twist
2	1	2	C_s	217.4 289.0 292.7 320.4 350.9 367.5	a' a' a' a" a" a'	Cl/H_2O H_2O Cl/H_2O Cl/ Cl/ NH_3	 H_2O rock H_2O rock H_2O wag
2	1	3	mer-C_1	183.4 221.0 265.6 293.1 294.4 323.5 342.8	a a a a a a a	$Cl/NH_3/H_2O$ Cl/H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ NH_3 NH_3	 H_2O rock/twist H_2O rock H_2O rock H_2O rock
2	2	0	C_{2v}	294.7 345.0 345.7 373.7	a_1 b_2 a_1 b_1	Cl NH_3 NH_3 Cl	
2	2	1	C_1	214.8 278.3 301.6 316.9 333.3 375.1	a a a a a a	Cl/NH_3 NH_3/H_2O Cl $Cl/NH_3/H_2O$ NH_3 NH_3	 H_2O rock H_2O wag H_2O wag
2	2	2	Cl-trans-C_1	193.3 213.4 267.5 270.3 295.7 323.5 334.5	a a a a a a a	$Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ NH_3/H_2O NH_3	 H_2O rock H_2O wag H_2O wag H_2O wag H_2O wag
2	3	0	C_s	210.9 298.4 300.8 326.4 330.9	a' a' a' a" a'	Cl/NH_3 Cl/NH_3 Cl/NH_3 NH_3 Cl/NH_3	
2	3	1	fac-C_s	176.4 186.5 213.6 264.5 273.0 289.4 316.9	a' a' a' a' a" a' a'	Cl/H_2O Cl/NH_3 $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/NH_3 $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$	 H_2O twist H_2O rock

2	4	0	trans-C_{4h}	187.5 219.5 248.9 297.5 297.5 304.5	a_g b_g a_u e_u e_u a_g	Cl/NH_3 NH_3 Cl NH_3 NH_3 Cl/NH_3	
3	1	0	C_s	258.3 294.0 296.3 344.2	a' a" a' a'	Cl/NH_3 Cl Cl NH_3	
3	1	1	C_1	169.3 177.1 236.2 262.3 268.4 335.5	a a a a a a	H_2O Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O NH_3	 H_2O rock H_2O rock
3	1	2	C_s [5+1]	196.9 258.3 280.0 304.0 349.0	a' a" a' a' a'	$Cl/NH_3/H_2O$ H_2O $Cl/NH_3/H_2O$ Cl/H_2O NH_3	 H_2O rock
3	2	0	C_{2v} #2	185.9 222.6 236.2 313.6 361.7	a_1 b1 a_1 a_1 b_2	Cl/NH_3 Cl Cl NH_3 NH_3	
3	2	1	C_1 [5+1]	210.8 241.9 258.7 300.6 338.5 374.1	a a a a a a	$Cl/NH_3/H_2O$ Cl/H_2O Cl/H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ NH_3	 H_2O rock
3	3	0	C_1 [5+1]	188.0 238.4 262.1 295.9 316.6 364.1	a a a a a a	Cl/NH_3 Cl Cl Cl/NH_3 NH_3 Cl/NH_3	
4	1	0	C_{3v} #1	115.3 195.9 251.2 345.0	a_1 a_1 a_1 a_1	Cl/NH_3 Cl Cl/NH_3 Cl/NH_3	

4	1	1	C_1 [4+2]	251.0 262.9 285.9 380.6	a a a a	Cl Cl Cl NH_3	
4	2	0	C_{2v} [5+1]	140.9 195.3 256.0 312.1 334.4	b_1 b_1 a_1 b_2 a_1	Cl Cl Cl NH_3 Cl/NH_3	

Table 3A.32: Ni-N, Ni-Cl and Ni-N stretching frequencies of $[NiCl_n(NH_3)_m(H_2O)_l]^{2-n}$, where n=1 – 4, m=1 – (6-n), l=0 – (6-n-m) calculated at MP2/6-31+G*.

n	m	l	Point Group Symmetry	Freq. (cm^{-l})	Irr. Rep. Symm.	$Cl/NH_3/H_2O$	Notes
1	1	0	C_1	409.0	a	Cl/NH_3	
				548.0	a	Cl/NH_3	
1	1	1	C_s #3	346.5	a'	Cl/H_2O	
				419.1	a'	$Cl/NH_3/H_2O$	
				489.3	a'	$Cl/NH_3/H_2O$	
1	1	2	C_1	342.0	a	H_2O	
				355.8	a	H_2O	
				377.1	a	Cl/NH_3	
				464.2	a	Cl/NH_3	H_2O wag
1	1	3	C_s	233.4	a'	$Cl/NH_3/H_2O$	H_2O twist
				261.2	a'	$Cl/NH_3/H_2O$	H_2O twist
				284.3	a"	H_2O	H_2O twist
				337.9	a"	H_2O	H_2O twist
				349.7	a'	H_2O	
				358.0	a"	$Cl/NH_3/H_2O$	
				424.9	a'	$Cl/NH_3/H_2O$	H_2O rock
1	1	4	trans-C_1	250.3	a	$Cl/NH_3/H_2O$	H_2O twist
				255.5	a	$Cl/NH_3/H_2O$	H_2O twist
				259.3	a	H_2O	
				319.3	a	H_2O	H_2O twist
				322.3	a	H_2O	
				324.6	a	H_2O	H_2O twist
				335.3	a	$Cl/NH_3/H_2O$	
				386.2	a	Cl/NH_3	H_2O twist
1	2	0	C_1	398.5	a	Cl/NH_3	
				438.9	a	NH_3	
				474.7	a	Cl/NH_3	
1	2	1	C_1	330.8	a	H_2O	
				366.9	a	$Cl/NH_3/H_2O$	
				406.3	a	Cl/NH_3	H_2O wag
				444.4	a	Cl/NH_3	H_2O twist
1	2	2	C_2	225.6	a	H_2O	
				272.0	a	H_2O	
				298.3	b	H_2O	
				357.8	a	Cl/NH_3	
				377.1	a	$Cl/NH_3/H_2O$	
				416.3	b	NH_3	H_2O wag

1	2	3	mer-C_1	220.3 243.5 250.2 259.2 294.5 324.3 365.0 370.9	a a a a a a a a	H_2O $Cl/NH_3/H_2O$ H_2O NH_3/H_2O H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$	 H_2O wag H_2O twist H_2O rock
1	3	0	C_s	361.1 386.6 394.3 431.0	a' a' a" a'	Cl/NH_3 NH_3 NH_3 Cl/NH_3	
1	3	1	C_1	217.9 337.0 353.9 372.9 401.5	a a a a a	H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/NH_3 NH_3	 H_2O rock H_2O wag
1	3	2	fac-C_1	215.1 249.4 264.2 274.9 335.8 359.7	a a a a a a	$Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$	 H_2O twist H_2O twist H_2O twist
1	4	0	C_4	257.5 335.3 353.0 353.2 361.4	a a e e a	NH_3 Cl/NH_3 NH_3 NH_3 Cl/NH_3	
1	4	1	cis-C_1	201.4 248.6 315.7 334.5 339.9 347.9	a a a a a a	H_2O Cl/NH_3 $Cl/NH_3/H_2O$ Cl/NH_3 Cl/NH_3 Cl/NH_3	 H_2O wag H_2O rock H_2O rock H_2O rock H_2O rock
1	5	0	C_1	233.0 241.5 307.2 307.2 315.8 334.6	a a a a a a	Cl/NH_3 NH_3 NH_3 NH_3 Cl/NH_3 Cl/NH_3	
2	1	0	C_s #1	335.6 418.7 457.8	a' a' a'	Cl/NH_3 NH_3 Cl	

2	1	1	C_s	317.3 336.7 410.3 414.9	a' a' a" a'	Cl/H_2O H_2O Cl NH_3	 H_2O twist H_2O wag
2	1	2	C_s	244.4 313.0 320.5 369.9 417.1	a' a' a' a" a'	$Cl/NH_3/H_2O$ Cl/H_2O H_2O Cl NH_3	 H_2O rock H_2O wag H_2O rock
2	1	3	mer-C_1	243.5 250.2 259.2 294.5 324.3 365.0 370.9	a a a a a a a	$Cl/NH_3/H_2O$ H_2O NH_3/H_2O H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$	H_2O rock H_2O twist H_2O rock/twist H_2O twist H_2O twist H_2O twist
2	2	0	C_{2v}	313.5 389.0 397.4 398.2	a_1 a_1 b_2 b_1	Cl NH_3 NH_3 Cl	
2	2	1	C_1	239.2 311.9 319.3 340.7 346.8 396.4	a a a a a a	$Cl/NH_3/H_2O$ Cl NH_3/H_2O Cl $Cl/NH_3/H_2O$ NH_3	 H_2O rock H_2O rock H_2O wag
2	2	2	Cl-trans-C_1	220.6 240.2 298.9 312.5 349.5 370.1 397.5	a a a a a a a	$Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl NH_3/H_2O NH_3/H_2O NH_3	 H_2O wag H_2O rock H_2O wag H_2O wag H_2O wag
2	3	0	C_s	235.9 326.0 333.7 370.0 380.0	a' a' a' a" a'	Cl/NH_3 Cl Cl/NH_3 NH_3 NH_3	
2	3	1	fac-C_1	222.0 232.2 296.4 310.0 328.2 352.5	a a a a a a	Cl/NH_3 $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/NH_3 NH_3/H_2O NH_3/H_2O	H_2O rock H_2O rock H_2O rock

2	4	0	trans-C_{2v}	215.3 258.7 278.5 337.1 341.1 341.7	a_1 a_1 a_1 a_1 b_2 b_1	Cl/NH_3 Cl/NH_3 Cl/NH_3 Cl/NH_3 NH_3 NH_3	
3	1	0	C_s	279.0 324.9 332.2 392.1	a' a' a" a'	Cl Cl Cl NH_3	
3	1	1	C_1	184.3 202.6 262.6 277.1 288.3 313.7 378.3	a a a a a a a	H_2O $Cl/NH_3/H_2O$ Cl Cl/H_2O Cl/H_2O Cl/H_2O NH_3	H_2O wag H_2O rock H_2O rock H_2O rock H_2O rock
3	1	2	C_s [5+1]	216.9 302.8 331.2 332.8 391.2	a' a' a' a" a'	$Cl/NH_3/H_2O$ Cl/H_2O $Cl/NH_3/H_2O$ H_2O $Cl/NH_3/H_2O$	 H_2O rock
3	2	0	C_{2v} #1	217.3 271.0 277.9 342.2 408.0	a_1 b_1 a_1 a_1 b_2	Cl/NH_3 Cl Cl Cl/NH_3 NH_3	
3	2	1	C_1 [5+1]	244.6 273.1 294.7 333.3 370.0 415.0	a a a a a a	$Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ NH_3	 H_2O rock
3	3	0	C_1 [5+1]	220.7 265.3 288.2 333.4 357.4	a a a a a	Cl/NH_3 Cl Cl Cl/NH_3 NH_3	
4	1	0	C_s	230.8 239.1 267.0 363.9	a" a' a' a'	Cl Cl Cl/NH_3 Cl/NH_3	
4	1	1	C_1 [4+2]	269.2 288.4 323.5 434.3	a a a a	Cl Cl Cl NH_3	

4	2	0	C_{2v} [5+1]	170.2 227.5 281.6 367.2 372.6	a_1 b_1 a_1 a_1 b_2	Cl/NH_3 Cl Cl Cl/NH_3 NH_3	

Table 3A.33: Ni-N, Ni-Cl and Ni-N stretching frequencies of $[NiCl_n(NH_3)_m(H_2O)_l]^{2-n}$, where n=1 – 4, m=1 – (6-n), l=0 – (6-n-m) calculated at B3LYP/6-31+G*.

n	m	l	Point Group Symmetry	Freq. (cm^{-l})	Irr. Rep. Symm.	$Cl/NH_3/H_2O$	Notes
1	1	0	C_1	394.1	a	Cl/NH_3	
				526.3	a	Cl/NH_3	
1	1	1	C_1	352.7	a	Cl/H_2O	
				407.3	a	$Cl/NH_3/H_2O$	
				465.3	a	$Cl/NH_3/H_2O$	
1	1	2	C_1	298.6	a	H_2O	
				324.7	a	H_2O	
				389.6	a	$Cl/NH_3/H_2O$	H_2O wag
				430.2	a	$Cl/NH_3/H_2O$	H_2O rock
1	1	3	C_1	230.8	a	$Cl/NH_3/H_2O$	
				277.9	a	H_2O	H_2O twist
				311.0	a	H_2O	H_2O twist
				361.8	a	$Cl/NH_3/H_2O$	H_2O rock
				396.8	a	Cl/NH_3	
1	1	4	trans-C_1	230.8	a	$Cl/NH_3/H_2O$	H_2O twist
				232.4	a	$Cl/NH_3/H_2O$	H_2O twist
				250.0	a	H_2O	H_2O twist
				303.4	a	H_2O	
				305.4	a	H_2O	H_2O twist
				318.8	a	$Cl/NH_3/H_2O$	H_2O twist
				328.2	a	$Cl/NH_3/H_2O$	H_2O rock
				360.8	a	Cl/NH_3	H_2O twist
1	2	0	C_1	398.4	a	Cl/NH_3	
				424.9	a	NH_3	
				446.7	a	Cl/NH_3	
1	2	1	C_1	307.9	a	H_2O	
				345.3	a	$Cl/NH_3/H_2O$	
				389.8	a	Cl/NH_3	H_2O wag
				416.8	a	$Cl/NH_3/H_2O$	
1	2	2	C_2	217.5	a	$Cl/NH_3/H_2O$	H_2O rock
				266.6	a	H_2O	H_2O twist
				284.5	b	H_2O	H_2O twist
				315.4	a	Cl/NH_3	H_2O twist
				364.8	a	$Cl/NH_3/H_2O$	
				400.2	b	NH_3	H_2O wag
				475.8	b	NH_3	H_2O wag

1	2	3	mer-C_1	217.4 225.0 259.7 265.0 286.6 306.6 313.3 343.3 353.1	a a a a a a a a a	$Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ H_2O H_2O H_2O $Cl/NH_3/H_2O$ Cl/NH_3 Cl/NH_3 $Cl/NH_3/H_2O$	H_2O twist H_2O twist H_2O twist H_2O twist H_2O twist H_2O twist
1	3	0	C_s	332.3 368.9 372.6 403.5	a' a' a" a'	Cl/NH_3 Cl/NH_3 NH_3 Cl/NH_3	
1	3	1	C_1	306.1 327.3 362.0 382.8 420.3	a a a a a	Cl/NH_3 $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ NH_3 NH_3	 H_2O rock H_2O rock H_2O rock H_2O wag
1	3	2	fac-C_1	186.7 205.9 232.7 233.4 313.8 327.0 347.7	a a a a a a a	Cl $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$	 H_2O twist H_2O wag H_2O twist
1	4	0	C_4	239.9 291.0 332.5 332.5 348.1	b a e e a	NH_3 Cl/NH_3 NH_3 NH_3 NH_3	
1	4	1	cis-C_1	190.3 226.1 293.3 308.0 319.2 337.9	a a a a a a	H_2O Cl/NH_3 $Cl/NH_3/H_2O$ Cl/NH_3 $Cl/NH_3/H_2O$ Cl/NH_3	 H_2O wag H_2O wag H_2O wag H_2O rock H_2O rock
1	5	0	C_s	181.9 214.6 226.0 282.3 284.7 285.2 323.9	a' a' a" a' a' a" a'	Cl/NH_3 Cl/NH_3 NH_3 Cl/NH_3 NH_3 NH_3 Cl/NH_3	
2	1	0	C_s #2	320.9 403.5 434.5	a' a' a"	Cl NH_3 Cl	

2	1	1	C_s	295.5 327.0 377.7 404.4	a' a' a" a'	Cl/H_2O H_2O Cl NH_3	 H_2O twist H_2O wag
2	1	2	C_s	225.1 300.3 306.0 308.4 346.3 403.2	a' a' a' a" a" a'	$Cl/NH_3/H_2O$ Cl/H_2O H_2O Cl Cl NH_3	 H_2O rock H_2O rock H_2O rock H_2O wag
2	1	3	mer-C_1	193.1 228.5 265.9 299.7 301.7 342.1 361.7	a a a a a a a	H_2O Cl/H_2O Cl/H_2O Cl/H_2O $Cl/NH_3/H_2O$ NH_3 NH_3	 H_2O rock H_2O rock
2	2	0	C_1	289.2 361.3 376.5 384.1	a a a a	Cl Cl NH_3 NH_3	
2	2	1	C_1	218.3 276.3 297.5 320.3 338.4 383.1	a a a a a	$Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/NH_3 $Cl/NH_3/H_2O$ NH_3	 H_2O twist H_2O twist H_2O wag
2	2	2	Cl-trans-C_1	197.6 217.1 261.9 279.3 335.2 357.2	a a a a a a	Cl/H_2O $Cl/NH_3/H_2O$ Cl/H_2O Cl/H_2O NH_3/H_2O NH_3	 H_2O rock H_2O wag H_2O wag
2	3	0	C_1	211.8 288.5 322.9 354.3 364.3	a a a a a	Cl/NH_3 Cl Cl/NH_3 NH_3 NH_3	
2	3	1	fac-C_1	206.8 215.9 273.8 286.1 308.0 339.1	a a a a a a	Cl/NH_3 $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/NH_3 Cl/NH_3 NH_3/H_2O	

2	4	0	trans-C_{4h}	193.2 241.0 247.9 318.3 318.3 325.5	a_g b_g a_u e_u e_u a_g	Cl/NH_3 NH_3 Cl NH_3 NH_3 Cl/NH_3	
3	1	0	C_s	256.6 291.7 296.7 388.8	a' a' a" a'	Cl Cl Cl NH_3	
3	1	1	C_1	173.7 236.7 266.8 271.7 374.8	a a a a a	Cl/H_2O Cl/H_2O Cl/H_2O Cl/H_2O NH_3	
3	1	2	C_s [5+1]	195.3 222.9 282.0 282.6 300.6 378.0	a' a' a' a" a' a'	$Cl/NH_3/H_2O$ Cl $Cl/NH_3/H_2O$ H_2O Cl/H_2O NH_3	
3	2	0	C_s	186.6 223.2 235.6 343.6 398.0	a' a' a' a' a"	Cl/NH_3 Cl Cl NH_3 NH_3	
3	2	1	C_1 [5+1]	213.7 244.4 262.2 317.0 356.1 406.5	a a a a a a	$Cl/NH_3/H_2O$ Cl/H_2O Cl/H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$	H_2O wag
3	3	0	C_1 [5+1]	198.3 252.1 268.9 309.8 338.3 390.7	a a a a a a	Cl/NH_3 Cl Cl Cl/NH_3 NH_3 NH_3	
4	1	0	C_{3v} #2	150.1 152.8 219.4 223.6 263.3 375.1	a_1 a_1 a_1 a_1 a_1 a_1	Cl Cl/NH_3 Cl Cl Cl/NH_3 Cl/NH_3	

4	1	1	C_1 [4+2]	243.3 255.8 285.9 417.0	a a a a	Cl Cl Cl NH_3	
4	2	0	C_{2v} [5+1]	148.4 197.4 254.7 342.9 355.2	a_1 b_1 a_1 a_1 b_2	Cl/NH_3 Cl Cl Cl/NH_3 NH_3	

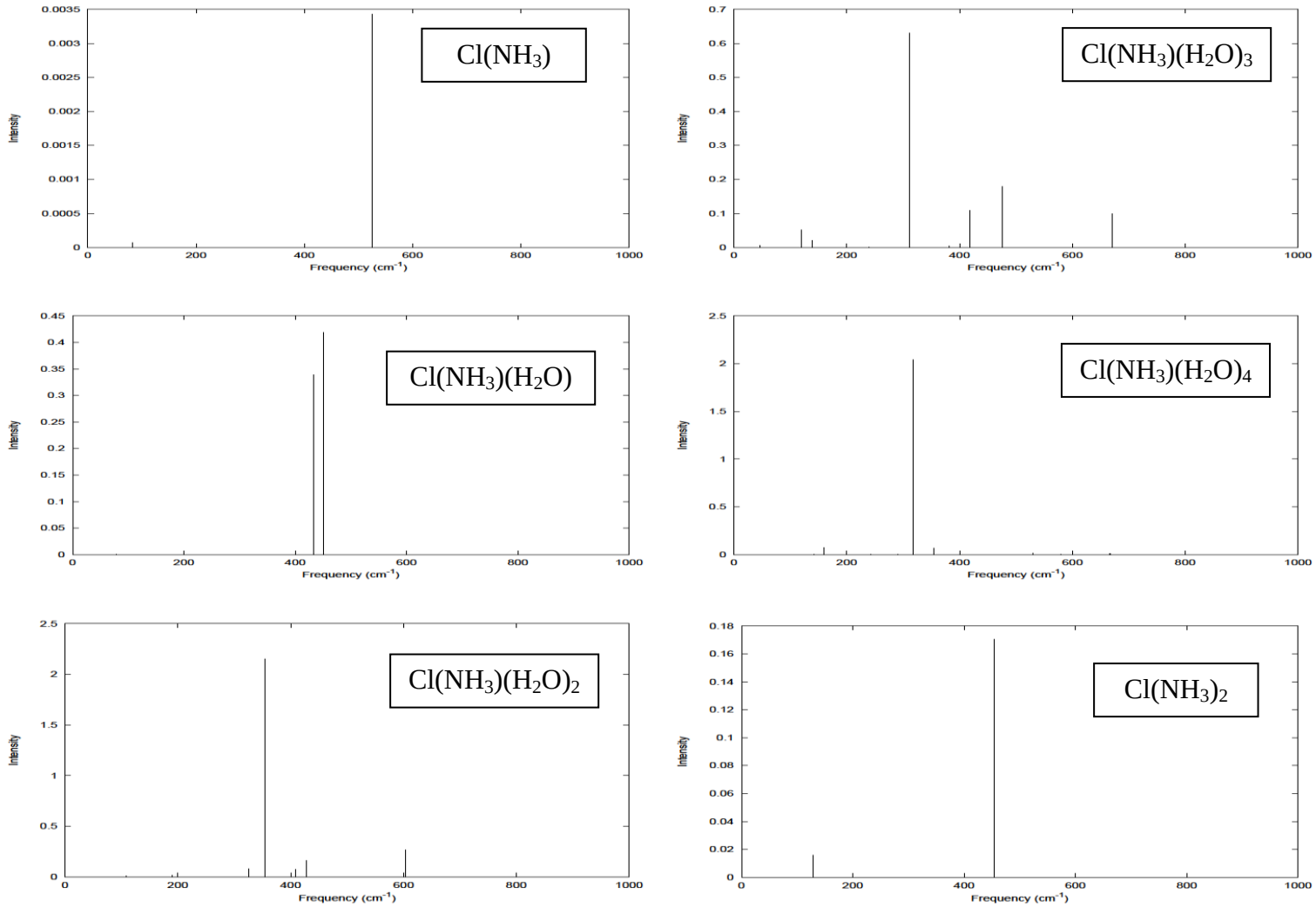


Figure 3A-6: Simulated polarized Raman spectra for $[NiCl_n(NH_3)_m(H_2O)_l]^{2-n}$, where n=1 – 4, m=1 – (6-n) and l=0 – (6-n-m)

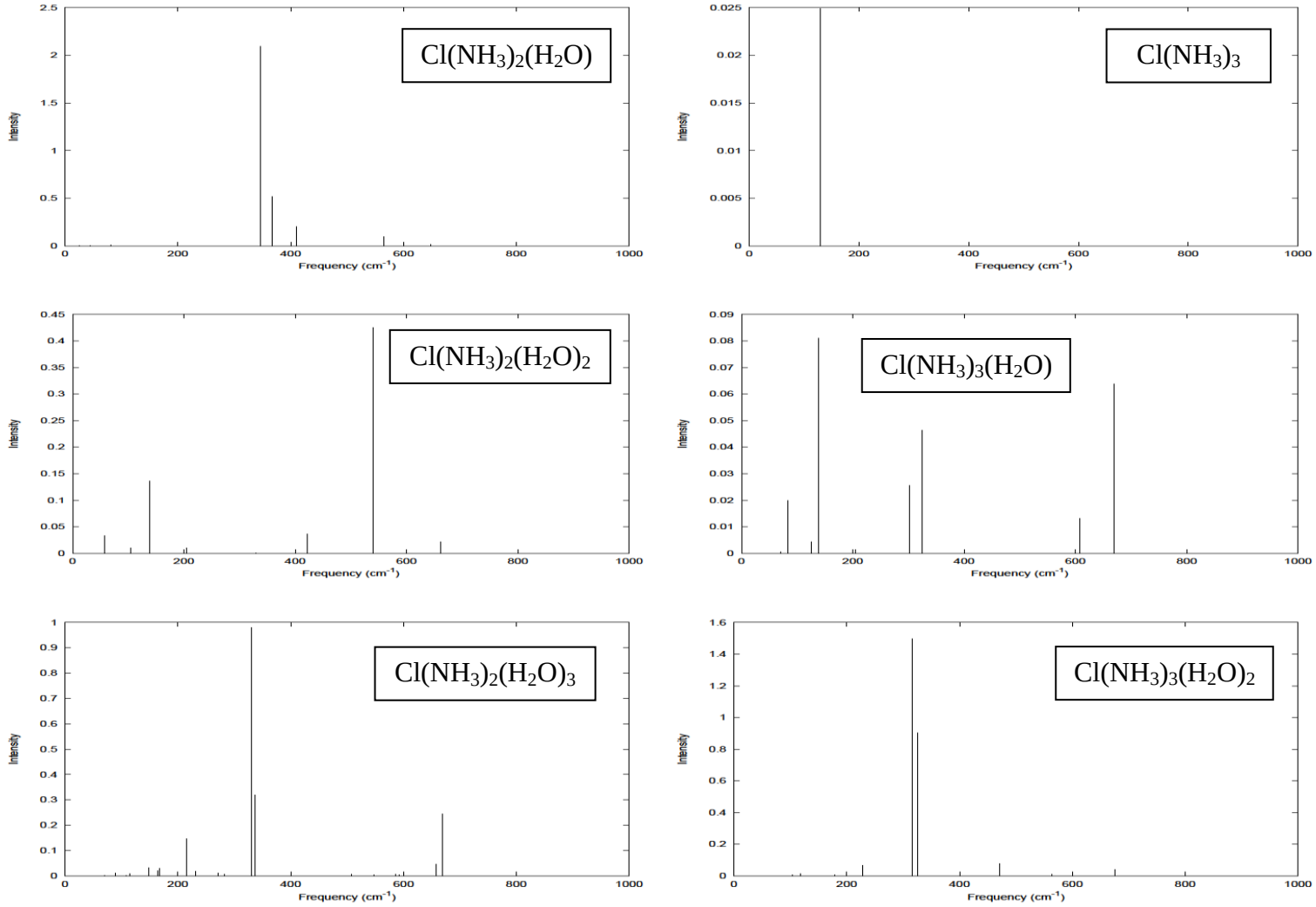


Figure 3A-6: *(continued)*

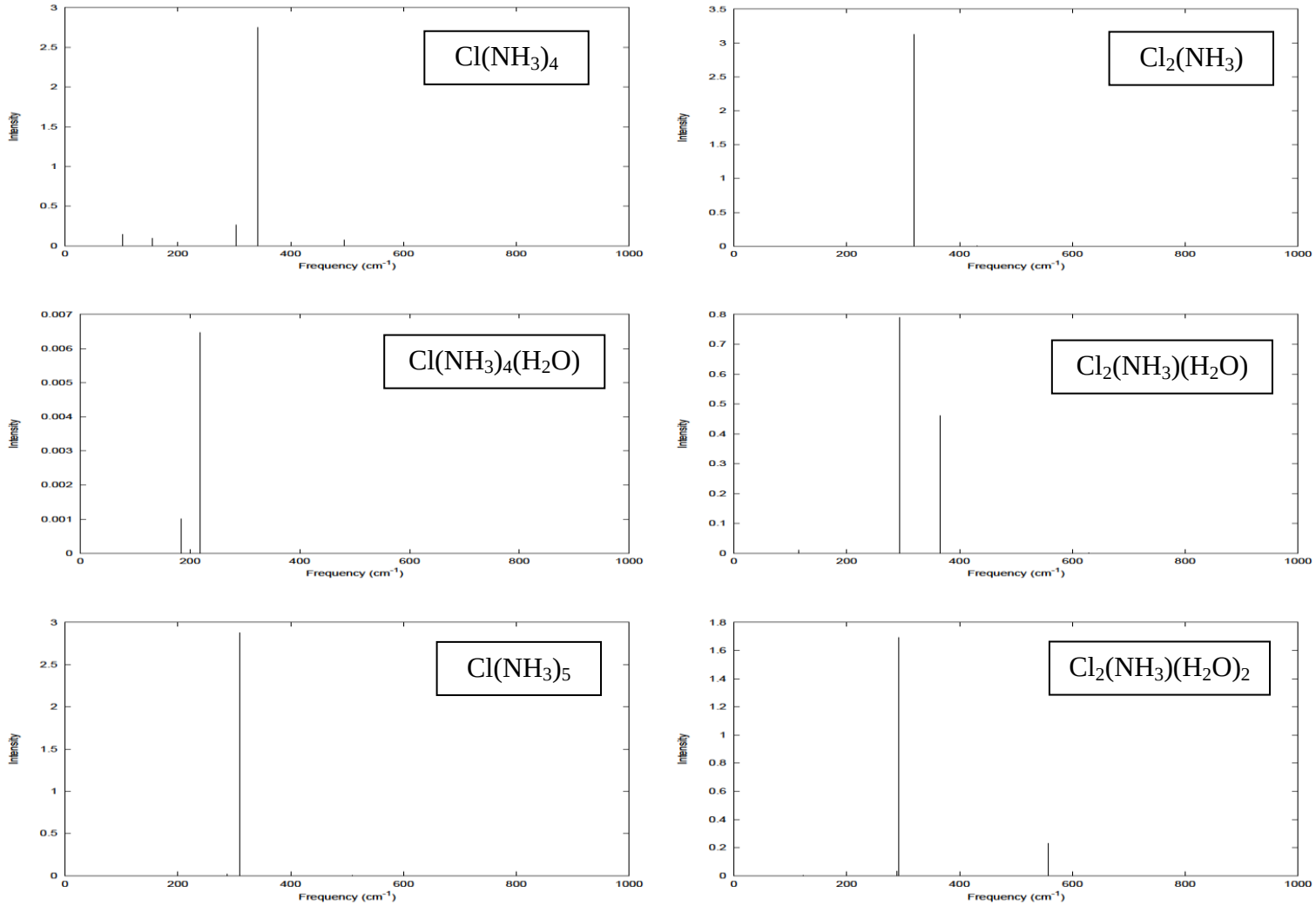


Figure 3A-6: *(continued)*

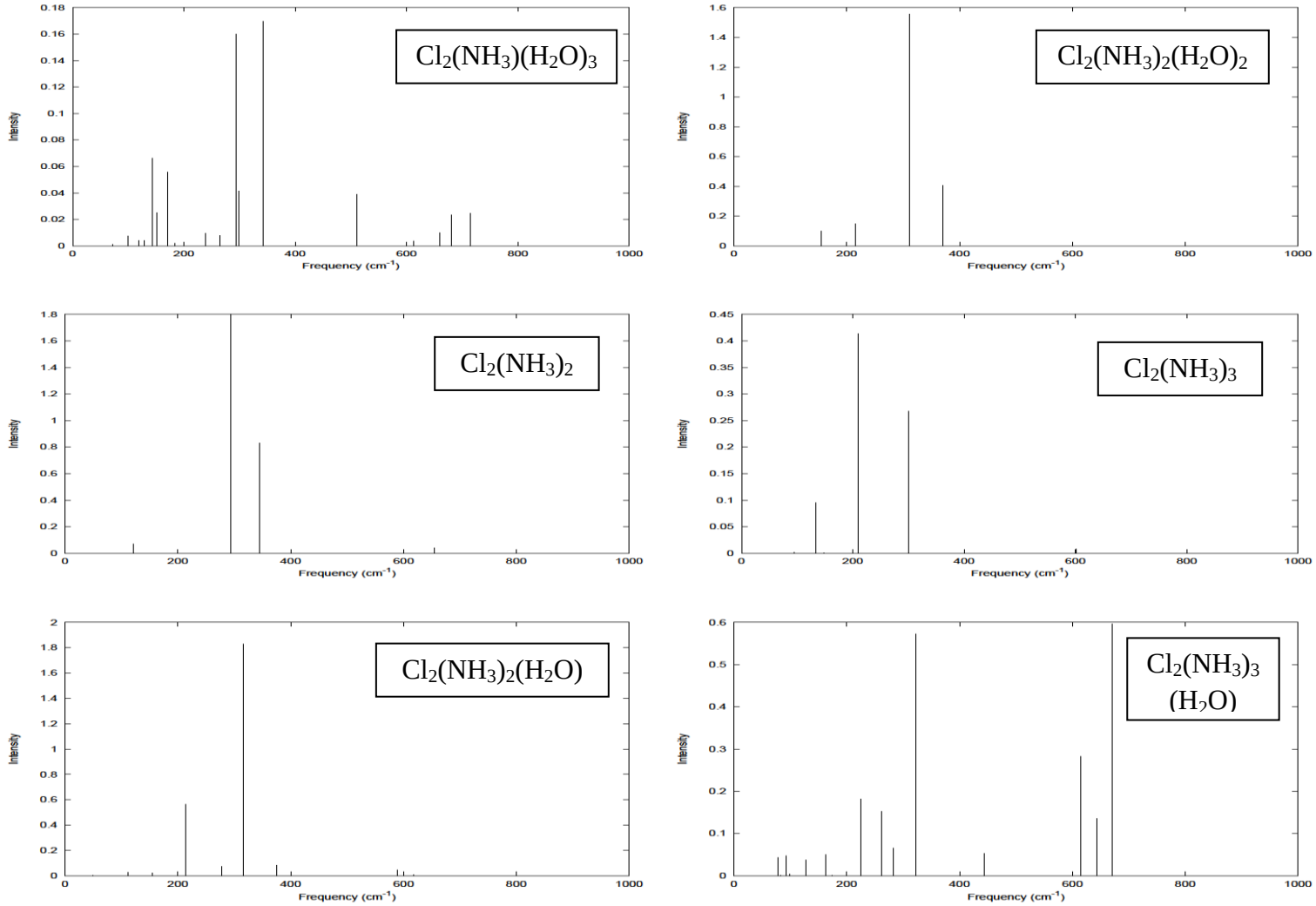


Figure 3A-6: *(continued)*

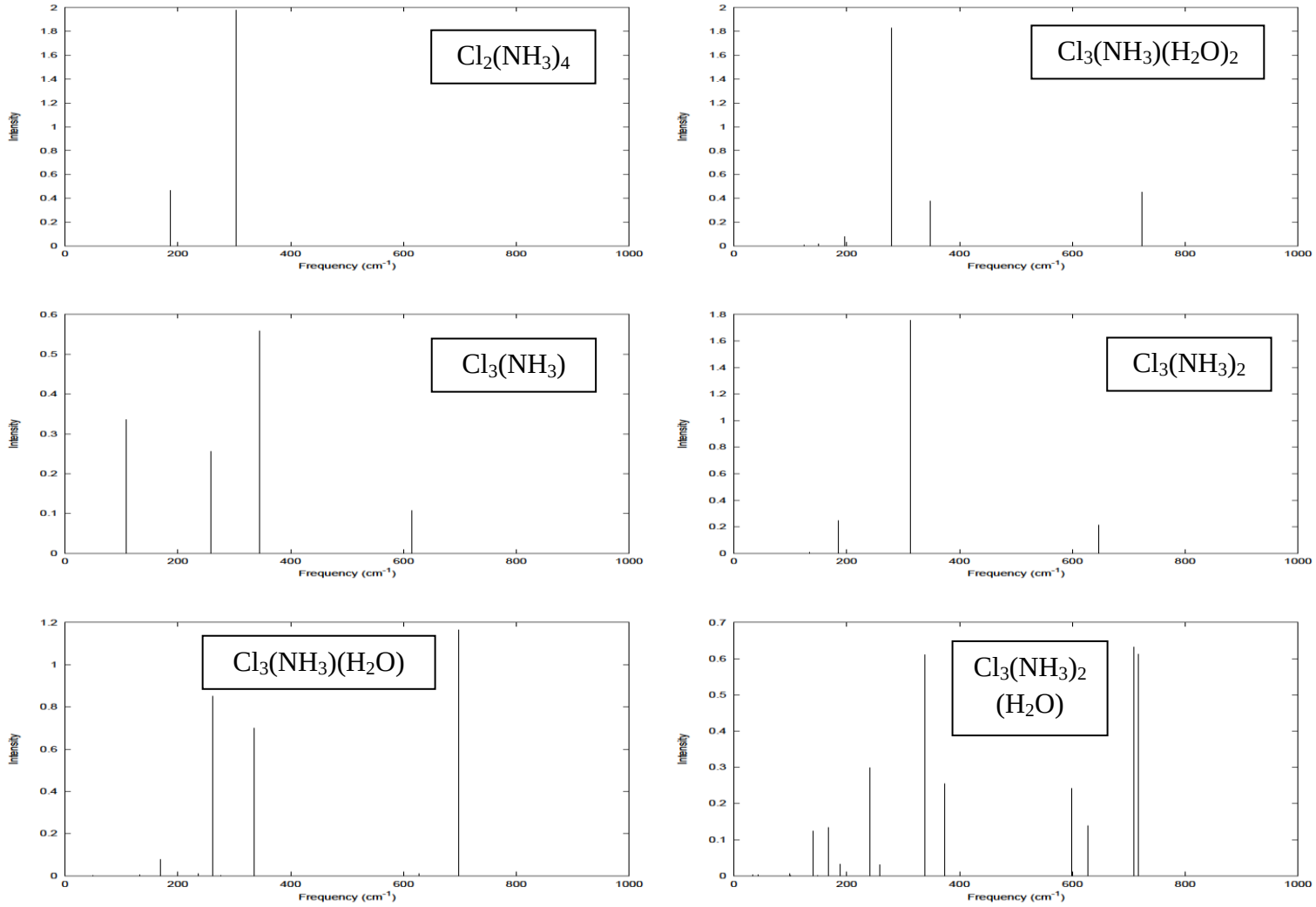


Figure 3A-6: *(continued)*

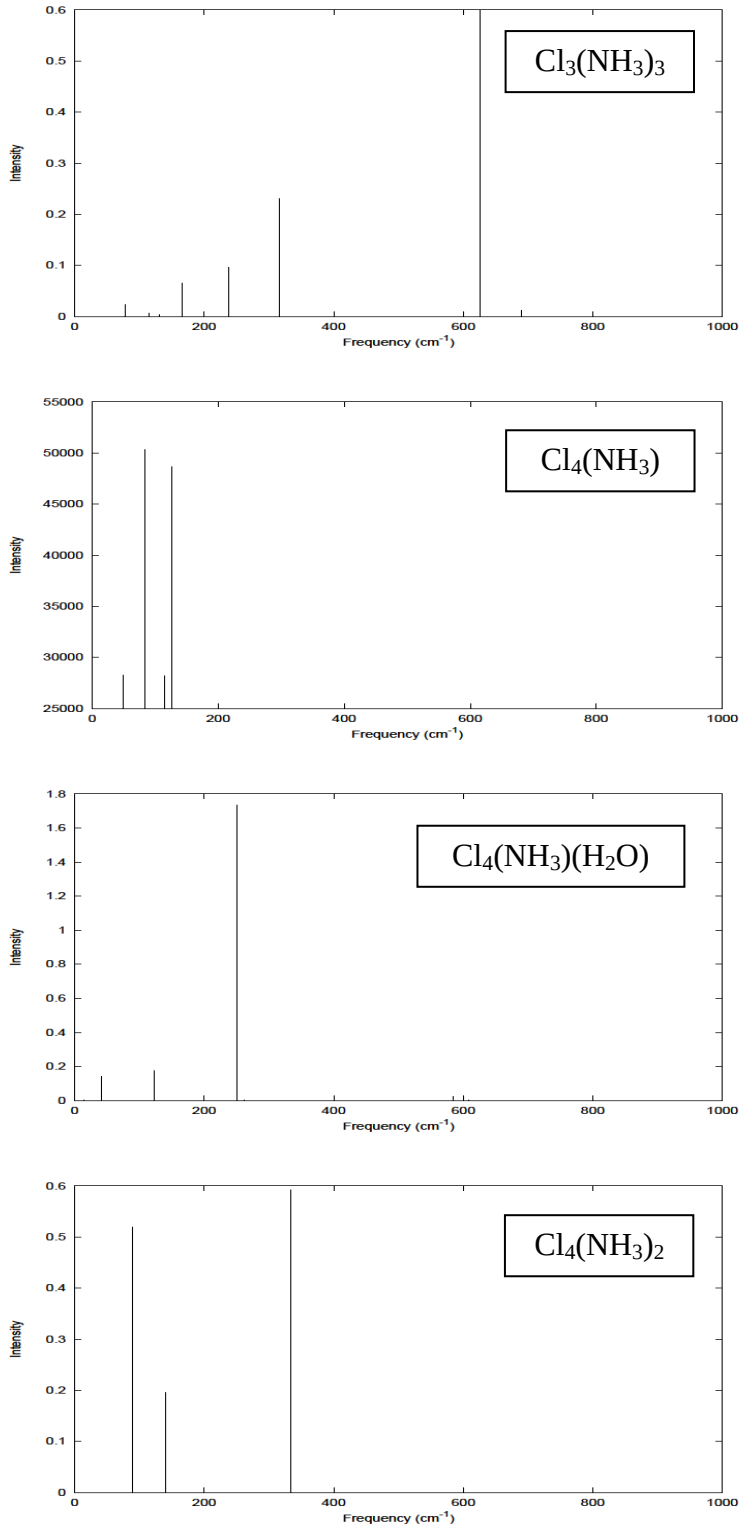


Figure 3A-6: *(continued)*

Table 3A.34: Total energies for all stable geometries of $[Ni(NH_3)_n(OH)_m(H_2O)_l]^{2-m}$, where n=1 – 5, m=1 – (5-n), l=0 – (6-n-m).

				Optimized Energies (Hartrees)			
n	**m**	**l**	**Point Group**	**HF**	**MP2**	**B3LYP**	**C-PCM**
1	1	0	C_s #1	-1638.1115331	-1638.6760294	-1640.341047	--
			C_s #2	-1638.1110108	-1638.6735649	-1640.3410463	--
			C_s #3	-1638.1105885	-1638.6784111	-1640.3411337	-1640.483099
			C_1	-1638.1115331	-1638.6779930	-1640.3411021	-1640.482715
1	1	1	C_1	-1714.1835433	-1714.9471138	-1716.8105499	-1716.933127
1	1	2	C_1	-1790.2414581	-1791.2014443	-1793.2668743	-1793.378169
1	1	3	C_1	-1866.2949191	-1867.4527584	-1869.7219400	-1869.827581
1	1	4	cis-C_1	-1942.3395207	-1943.6973962	-1946.1689652	-1946.274199
			trans-C_1	-1942.343364	-1943.701762	-1946.172935	-1946.276065
1	2	0	C_s	-1713.8133101	-1714.5973938	-1716.4560240	-1716.485368
1	2	1	C_s	-1789.8396337	-1790.820199	-1792.8875606	-1792.921315
			C_1	-1789.8533802	-1790.8312127	-1792.8939565	-1792.916505
1	2	2	C_1	-1865.8923141	-1867.0684521	-1869.3350377	-1869.358178
1	2	3	C_1 [5+1]	-1941.9299590	-1943.3048764	-1945.7795186	-1945.807904
1	3	0	C_1	-1789.2815635	-1790.2735552	-1792.3315876	-1792.437472
1	3	1	C_1 [4+1]	-1865.3332317	-1866.5254259	-1868.7900132	-1868.888053
1	3	2	C_1 [4+2]	-1941.3750600	-1942.7654102	-1945.2404004	-1945.329462
1	4	0	C_1 [4+1]	-1864.6059882	-1865.8084879	-1868.0700193	-1868.373073
1	4	1	C_1 [4+2]	-1940.6683494	-1942.0691966	-1944.5421388	-1944.823888
2	1	0	C_1	-1694.3683590	-1695.1195629	-1696.9634337	-1697.074362
2	1	1	C_1	-1770.4299986	-1771.3764745	-1773.4201989	-1773.521675
2	1	2	C_s	-1846.4768089	-1847.6204168	-1849.8690617	--
			C_1	-1846.4771232	-1847.6207932	-1849.8698747	-1849.969568
2	1	3	mer-C_1	-1922.5170839	-1923.8600675	-1926.3132765	-1926.411118
			fac-C_1	-1922.520932	-1923.865111	-1926.317687	-1926.415524
2	2	0	C_2	-1770.0234009	-1770.9883615	-1773.0348679	-1773.058164
2	2	1	C_1 [4+1]	-1846.0698683	-1847.2316311	-1849.4805936	-1849.504426
2	2	2	C_2 #1 [4+2]	-1922.102169	-1923.459897	-1925.924416	-1925.948835
			C_2 #2 [4+2]	-1922.11271	-1923.47397	-1925.930728	-1925.953281
			C_s	-1922.0902146	-1923.4502356	-1925.9016848	--
			C_1 #1	-1922.0902126	-1923.4571439	-1925.9212236	-1925.943536
			C_1 #2	-1922.098649	-1923.462257	-1925.914264	-1925.938640
			C_1 #3 [4+2]	-1922.11271	-1923.473968	-1925.930662	-1925.955311
			C_1 #4	-1922.092813	-1923.456548	-1925.909254	-1925.935783
2	3	0	C_1 [4+1]	-1845.4886462	-1846.6621366	-1848.9069586	-1849.004987
2	3	1	C_1 [4+2]	-1921.5353558	-1922.9058519	-1925.3612471	-1925.449684
2	4	0	C_2 [4+2]	-1920.8154586	-1922.1974349	-1924.6521230	-1924.934545

3	1	0	C_s	-1750.6105235	-1751.5429185	-1753.5671037	-1753.663455
			C_1	-1750.6105872	-1751.5429184	-1753.5671871	-1753.66356
3	1	1	C_s	-1826.650074	-1827.7775819	-1830.0057648	--
			C_1	-1826.6500735	-1827.7775798	-1830.0057908	-1830.102439
3	1	2	mer-C_s	-1902.6974299	-1904.0266555	-1906.4588598	-1906.550955
			mer-C_1 #1	-1902.6974670	-1904.0267419	-1906.4591277	-1906.551047
			mer-C_1 #2	-1902.695739	-1904.024671	-1906.457587	-1906.551840
			fac-C_s	-1902.702923	-1904.033046	-1906.46562	-1906.555400
3	2	0	C_1	-1826.2308886	-1827.3752745	-1829.6014597	-1829.624969
3	2	1	C_1 [5+1]	-1902.2616305	-1903.6077124	-1906.0424578	-1906.069677
			fac-C_s	-1902.2172212	-1903.5074179	-1906.046216	-1906.069625
3	3	0	C_1 [4+2]	-1901.691825	-1903.044585	-1905.47877	-1905.566068
			C_3 [3+3]	-1901.6865249	-1903.0258589	-1905.4790893	-1905.556265
4	1	0	C_s	-1806.8302152	-1807.9436937	-1810.1517359	-1810.241731
4	1	1	cis-C_1	-1882.8758320	-1884.1901127	-1886.6025303	-1886.689757
			trans-C_s	-1882.86704	-1884.179005	-1886.591465	-1886.684389
			trans-C_1	-1882.867042	-1884.179005	-1886.591456	-1886.684278
4	2	0	trans-C_2	-1882.4308006	-1883.7601248	-1886.1688146	-1886.182461
			C_1 [5+1]	-1882.4307972	-1883.7583792	-1886.1746470	-1886.193421
			cis-C_2	-1882.432593	-1883.762831	-1886.172773	-1886.194117
5	1	0	C_s	-1863.0460474	-1864.3427909	-1866.7348329	-1866.82058
			C_1	-1863.0460475	-1864.3429145	-1866.7348103	-1866.820652

NOT Stable

†Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.35: Ni-O bond lengths for stable geometries of $[Ni(NH_3)_n(OH)_m(H_2O)_l]^{2-m}$, where n=1 – 5, m=1 – (5-n), l=0 – (6-n-m).

				Optimized Ni-O Bond Lengths (Å)					
				HF/6-31+G*		MP2/6-31+G*		B3LYP/6-31+G*	
n	**m**	**l**	**Point Group**	**OH**	**H_2O**	**OH**	**H_2O**	**OH**	**H_2O**
1	1	0	C_s #1	1.755	N/A	--	N/A	--	N/A
			C_s #2	1.761	N/A	1.742	N/A	--	N/A
			C_s #3	1.743	N/A	1.710	N/A	1.699	N/A
			C_1	1.755	N/A	1.712	N/A	1.699	N/A
1	1	1	C_1	1.802	2.055	1.763	2.029	1.755	2.057
1	1	2	C_1	1.827	2.095 2.112	1.797	2.085 2.064	1.788	2.115 2.086
1	1	3	C_1	1.860	2.127 2.205 2.180	1.839	2.088 2.155 2.145	1.822	2.129 2.179 2.166
1	1	4	cis-C_1	1.921	2.201 2.161 2.169 2.222	1.931	2.144 2.114 2.110 2.166	1.942	2.161 2.147 2.121 2.196
			trans-C_1	1.933	2.180 2.175 2.204 2.201	1.949	2.119 2.116 2.141 2.148	1.960	2.133 2.128 2.162 2.169
1	2	0	C_s	1.838 1.835	N/A	1.811 1.808	N/A	1.800 1.798	N/A
1	2	1	C_s	--	--	--	--	1.815	2.377
			C_1	1.879 1.898	2.210	1.857 1.884	2.169	1.837 1.862	2.275
1	2	2	C_1	1.926 1.922	2.278 2.284	1.954 2.894	2.214 2.198	1.975 1.872	2.231 2.226
1	2	3	C_1 [5+1]	1.920 1.935	2.328 2.246	1.921 1.930	2.242 2.174	1.939 1.927	2.261 2.194
1	3	0	C_1	1.952 1.983 1.965	N/A	1.917 1.951 1.979	N/A	1.922 1.922 1.950	N/A
1	3	1	C_1 [4+1]	1.950 1.979 1.971	--	1.933 1.962 1.953	--	1.929 1.971 1.952	--
1	3	2	C_1 [4+2]	1.965 1.977 1.953	--	1.945 1.972 1.937	--	1.953 1.977 1.926	--

1	4	0	C_1 [4+1]	2.038 2.038 2.028 2.050	N/A	1.983 2.002 2.021 2.029	N/A	1.967 1.991 2.021 2.042	N/A
1	4	1	C_1 [4+2]	2.025 2.028 2.042 2.038	--	1.985 2.010 1.996 2.022	--	1.974 2.019 1.989 2.030	--
2	1	0	C_1	1.796	N/A	1.771	N/A	1.766	N/A
2	1	1	C_1	1.836	2.122	1.816	2.086	1.805	2.109
2	1	2	C_s	--	--	1.902	2.124	--	--
			C_1	1.876	2.201 2.208	1.856	2.173 2.164	1.839	2.199 2.200
2	1	3	mer-C_1	1.936	2.201 2.217 2.237	1.953	2.145 2.172 2.175	1.969	2.175 2.227 2.190
			fac-C_1	1.941	2.270 2.196 2.227	1.953	2.207 2.176 2.140	1.955	2.248 2.198 2.179
2	2	0	C_2	1.878	N/A	1.857	N/A	1.845	N/A
2	2	1	C_1 [4+1]	1.934 1.885	--	1.933 1.864	--	1.939 1.847	--
2	2	2	C_2 #1 [4+2]	1.909	--	1.892	--	1.881	--
			C_2 #2 [4+2]	1.923	--	1.912	--	1.911	--
			C_s	1.929	2.022 2.400	1.931	2.057 2.283	--	--
			C_1 #1	1.929 2.022	2.415 2.387	1.866 1.924	[4+2]	1.850 1.918	[4+2]
			C_1 #2	1.999 1.972	2.300 2.349	1.975 2.014	2.225 2.238	1.980 2.009	2.257 2.320
			C_1 #3 [4+2]	1.923 1.923	--	1.911 1.912	--	1.911 1.912	--
			C_1 #4	1.992 1.987	2.302 2.352	2.006 2.000	2.212 2.232	2.011 2.007	2.234 2.266
2	3	0	C_1 [4+1]	1.973 1.971 1.962	N/A	1.947 1.950 1.956	N/A	1.949 1.945 1.958	N/A
2	3	1	C_1 [4+2]	1.980 1.944 1.975	--	1.960 1.924 1.961	--	1.965 1.921 1.964	--
2	4	0	C_2 [4+2]	2.029 2.042	N/A	1.990 2.023	N/A	1.981 2.028	N/A

3	1	0	C_s	--	N/A	1.819	N/A	1.811	N/A
			C_1	1.839	N/A	1.819	N/A	1.811	N/A
3	1	1	C_s	1.901	2.199	--	--	--	--
			C_1	1.901	2.198	1.907	2.152	1.920	2.192
3	1	2	mer-C_s	1.953	2.241	1.984	2.176	2.000	2.197
			mer-C_1 #1	1.953	2.232 2.246	1.982	2.175 2.177	1.995	2.196 2.201
			mer-C_1 #2	1.942	2.346 2.241	1.957	2.274 2.181	1.956	2.364 2.240
			fac-C_s	1.955	2.296	1.978	2.229	1.978	2.281
3	2	0	C_1	1.933 1.948	N/A	1.916 1.976	N/A	1.888 1.997	N/A
3	2	1	C_1 [5+1]	1.964 1.938	--	1.981 1.930	--	1.994 1.920	--
			fac-C_s	1.995	2.326	2.003	2.259	2.009	2.288
3	3	0	C_3 [3+3]	1.911	N/A	1.880	N/A	1.888	N/A
			C_1 [4+2]	1.983 1.959 1.969	N/A	1.939 1.953 1.963	N/A	1.939 1.959 1.950	N/A
4	1	0	C_s	1.911	N/A	1.922	N/A	1.934	N/A
4	1	1	cis-C_1	1.953	2.396	1.977	2.303	1.971	2.442
			trans-C_s	--	--	1.951	2.207	1.959	2.279
			trans-C_1	1.938	2.274	1.951	2.207	1.958	2.288
4	2	0	trans-C_2	1.992	N/A	2.010	N/A	2.025	N/A
			C_1 [5+1]	1.991 1.991	N/A	1.926 1.985	N/A	1.902 2.003	N/A
			cis-C_2	1.999	N/A	2.013	N/A	2.022	N/A
5	1	0	C_s	1.955	N/A	--	N/A	1.988	N/A
			C_1	1.955	N/A	1.976	N/A	1.986	N/A

Table 3A.36: Ni-N bond lengths for stable geometries of $[Ni(NH_3)_n(OH)_m(H_2O)_l]^{2-m}$, where n=1 – 5, m=1 – (5-n), l=0 – (6-n-m).

				Optimized Ni-N Bond Lengths (Å)		
n	**m**	**l**	**Point Group**	**HF/6-31+G***	**MP2/6-31+G***	**B3LYP/6-31+G***
1	1	0	C_s #1	2.035	--	--
			C_s #2	2.036	1.984	--
			C_s #3	2.046	1.987	1.983
			C_1	2.035	1.983	1.983
1	1	1	C_1	2.069	2.005	2.008
1	1	2	C_1	2.108	2.041	2.054
1	1	3	C_1	2.125	2.054	2.068
1	1	4	cis-C_1	2.166	2.084	2.092
			trans-C_1	2.139	2.066	2.084
1	2	0	C_s	2.137	2.057	2.074
1	2	1	C_s	--	--	2.107
			C_1	2.147	2.065	2.079
1	2	2	C_1	2.146	2.058	2.076
1	2	3	C_1 [5+1]	2.167	2.071	2.074
1	3	0	C_1	2.198	2.099	2.186
1	3	1	C_1 [4+1]	2.184	2.080	2.087
1	3	2	C_1 [4+2]	2.209	2.096	2.101
1	4	0	C_1 [4+1]	--	--	--
1	4	1	C_1 [4+2]	--	--	--
2	1	0	C_1	2.098 2.094	2.034 2.025	2.053 2.028
2	1	1	C_1	2.124 2.129	2.058 2.061	2.079 2.084
2	1	2	C_s	--	2.055 2.071	--
			C_1	2.135 2.147	2.067 2.072	2.089 2.095
2	1	3	mer-C_1	2.175 2.183	2.083 2.099	2.088 2.107
			fac-C_1	2.175 2.170	2.093 2.085	2.098 2.094
2	2	0	C_2	2.243	2.149	2.175
2	2	1	C_1 [4+1]	2.158 2.171	2.072 2.087	2.082 2.120

2	2	2	C_2 #1 [4+2]	2.199	2.095	2.121
			C_2 #2 [4+2]	2.150	2.067	2.077
			C_s	2.189 2.277	2.097 2.154	--
			C_1 #1	2.190 2.277	2.072 2.118	2.096 2.151
			C_1 #2	2.211 2.190	2.115 2.094	2.130 2.104
			C_1 #3 [4+2]	2.150 2.150	2.067 2.067	2.078 2.077
			C_1 #4	2.213 2.236	2.114 2.132	2.131 2.154
2	3	0	C_1 [4+1]	2.181	2.078	2.087
2	3	1	C_1 [4+2]	2.180	2.078	2.085
2	4	0	C_2 [4+2]	--	--	--
3	1	0	C_s	--	2.074 2.080	2.089 2.105
			C_1	2.144 2.153 2.147	2.074 2.080 2.080	2.088 2.105 2.105
3	1	1	C_s	2.150 2.195	--	--
			C_1	2.150 2.195 2.195	2.072 2.106 2.107	2.083 2.115 2.112
3	1	2	mer-C_s	2.203 2.185 2.221	2.111 2.103 2.134	2.123 2.129 2.152
			mer-C_1 #1	2.210 2.188 2.214	2.120 2.106 2.130	2.135 2.131 2.144
			mer-C_1 #2	2.190 2.191 2.202	2.107 2.102 2.120	2.111 2.109 2.128
			fac-C_s	2.187 2.176	2.102 2.097	2.110 2.116
3	2	0	C_1	2.294 2.299 2.198	2.166 2.181 2.107	2.177 2.194 2.162

3	2	1	C_1 [5+1]	2.242 2.206 2.271	2.137 2.103 2.154	2.156 2.135 2.164
			fac-C_s	2.217 2.255	2.111 2.145	2.122 2.172
3	3	0	C_3 [3+3]	--	--	--
			C_1 [4+2]	1.896	1.872	1.866
4	1	0	C_s	2.194 2.167 2.231	2.113 2.087 2.141	2.142 2.102 2.149
4	1	1	cis-C_1	2.202 2.203 2.235 2.230	2.120 2.112 2.148 2.139	2.146 2.115 2.163 2.151
			trans-C_s	--	2.129 2.160 2.159	2.145 2.171 2.176
			trans-C_1	2.250 2.223 2.249 2.242	2.160 2.129 2.160 2.159	2.170 2.144 2.171 2.175
4	2	0	trans-C_2	2.309 2.309	2.183 2.183	2.203 2.203
			trans-C_1	2.312 2.310 2.313 2.310	2.200 2.120 2.118 [5+1]	2.228 2.135 2.164 [5+1]
			cis-C_2	2.281 2.284	2.172 2.167	2.185 2.200
5	1	0	C_s	2.283 2.223 2.269 2.259	--	2.220 2.167 2.190 2.178
			C_1	2.283 2.223 2.269 2.269 2.259	2.187 2.136 2.190 2.161 2.163	2.194 2.168 2.216 2.180 2.186

Table 3A.37: Ni-N and Ni-O vibrational stretching frequencies for optimized geometries of $[Ni(NH_3)_n(OH)_m(H_2O)_l]^{2-m}$, where n=1 – 5, m=1 – (5-n), l=0 – (6-n-m) calculated at HF/6-31+G*.

n	m	l	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	OH/H_2O/NH_3	Mixing
1	1	0	C_s #1	445.1	a'	NH_3	
				598.6	a'	OH	
				770.7	a'	OH	
				795.5	a'	OH	
1	1	1	C_1	354.5	a	H_2O	
				409.3	a	NH_3	H_2O rock
				709.4	a	OH	
				720.5	a	OH	
1	1	2	C_1	296.5	a	H_2O	
				322.5	a	H_2O	
				327.9	a	H_2O	H_2O wag
				375.0	a	NH_3	H_2O wag
				402.5	a	NH_3	H_2O wag
				661.6	a	OH	H_2O rock
				667.3	a	OH	
				711.8	a	OH	H_2O rock
1	1	3	C_1	215.7	a	H_2O	H_2O twist
				250.0	a	H_2O	H_2O wag/rock
				277.3	a	H_2O	H_2O wag
				305.2	a	H_2O/NH_3	H_2O twist
				323.5	a	H_2O	H_2O twist
				357.6	a	H_2O/NH_3	H_2O rock/wag
				369.9	a	H_2O/NH_3	H_2O wag
				565.0	a	OH	H_2O wag
				617.5	a	OH	H_2O twist
				655.9	a	OH	H_2O rock
1	1	4	trans-C_1	189.1	a	H_2O	H_2O twist
				212.8	a	H_2O	H_2O twist
				226.2	a	H_2O	H_2O twist
				234.8	a	H_2O/NH_3	H_2O twist
				254.8	a	H_2O	H_2O twist
				263.3	a	H_2O	H_2O twist
				278.7	a	H_2O	H_2O twist
				294.4	a	H_2O	H_2O twist
				321.1	a	H_2O	H_2O twist
				345.2	a	H_2O/NH_3	H_2O wag
				515.6	a	OH	H_2O wag/rock
				559.5	a	OH	H_2O wag/rock

1	2	0	C_1	349.0 572.8 633.7 702.1	a a a a	NH_3 OH OH OH	
1	2	1	C_1	218.4 265.7 338.6 345.1 533.6 607.7 646.9	a a a a a a a	H_2O H_2O NH_3 NH_3 OH OH OH	 H_2O wag H_2O rock H_2O twist H_2O wag
1	2	2	C_1	175.6 206.6 260.8 284.0 338.9 496.4 500.5 523.6 562.8 592.1 617.6	a a a a a a a a a a a	H_2O H_2O H_2O H_2O NH_3 OH OH OH OH OH OH	 H_2O twist H_2O twist H_2O twist H_2O wag H_2O wag
1	2	3	C_1 [5+1]	151.5 153.1 166.8 221.6 298.9 308.1 319.9 332.7 480.2 489.9 545.7 556.0 575.7	a a a a a a a a a a a a a	H_2O H_2O H_2O H_2O H_2O/NH_3 NH_3 NH_3 NH_3 OH OH OH OH OH	 H_2O rock H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag
1	3	0	C_1	274.1 299.1 316.2 445.0 475.6 484.1	a a a a a a	NH_3 NH_3 NH_3 OH OH OH	
1	3	1	C_1 [4+1]	289.1 309.3 447.1 468.3 492.8	a a a a a	NH_3 NH_3 OH OH OH	

1	3	2	C_1 [4+2]	281.3 454.0 465.3 489.6	a a a a	NH_3 OH OH OH	
1	4	0	C_1 [4+1]	352.5 365.8 377.2 389.4 399.0 420.4	a a a a a a	OH OH OH OH OH OH	
1	4	1	C_1 [4+2]	364.4 377.1 382.5 399.1 424.9	a a a a a	OH OH OH OH OH	
2	1	0	C_1	376.3 392.3 400.3 697.3 710.3 742.1	a a a a a a	NH_3 NH_3 NH_3 OH OH OH	
2	1	1	C_1	307.3 348.0 365.0 374.1 651.2	a a a a a	H_2O NH_3 NH_3 NH_3 OH	 H_2O wag H_2O wag H_2O wag H_2O wag
2	1	2	C_1	207.8 233.2 256.8 300.3 328.7 346.9 355.1 596.6 612.5	a a a a a a a a a	H_2O H_2O H_2O H_2O NH_3 NH_3 NH_3 OH OH	H_2O twist H_2O twist H_2O wag H_2O wag H_2O wag H_2O wag H_2O wag H_2O rock H_2O twist

2	1	3	fac-C_1	127.5 207.9 222.2 232.2 261.8 305.5 325.8 336.8 524.9 540.3	a a a a a a a a a a	H_2O H_2O H_2O/NH_3 H_2O H_2O/NH_3 H_2O/NH_3 NH_3 H_2O/NH_3 OH OH	 H_2O twist H_2O twist H_2O twist H_2O twist H_2O wag H_2O twist H_2O wag H_2O twist
2	2	0	C_2	245.3 289.6 514.8 587.3 591.2 655.4	a b a b a b	NH_3 NH_3 OH OH OH OH	
2	2	1	C_1 [4+1]	316.5 319.9 339.6 492.1 561.1 588.4	a a a a a a	NH_3 NH_3 NH_3 OH OH OH	
2	2	2	C_2 #2 [4+2]	334.6 356.0 484.5 532.2 564.5 566.1	b a a b b a	NH_3 NH_3 OH OH OH OH	
2	3	0	C_1 [4+1]	296.7 309.8 450.4 468.9 482.0	a a a a a	NH_3 NH_3 OH OH OH	
2	3	1	C_1 [4+2]	305.1 315.1 438.4 452.4 468.3 502.0	a a a a a a	NH_3 NH_3 OH OH OH OH	
2	4	0	C_2 [4+2]	356.1 360.8 375.5 381.4 395.9 420.8	b a b a b a	OH OH OH OH OH OH	

3	1	0	C_1	325.2 342.0 353.9 641.7	a a a a	NH_3 NH_3 NH_3 OH	
3	1	1	C_s	214.4 281.8 295.7 298.2 334.0 341.5 568.2	a' a' a" a' a" a' a'	H_2O/NH_3 H_2O/NH_3 NH_3 H_2O/NH_3 NH_3 NH_3 OH	 H_2O wag H_2O rock H_2O wag H_2O rock H_2O wag
3	1	2	fac-C_s	197.7 281.0 297.7 307.7 326.8 507.5 523.7	a' a' a' a' a" a' a'	H_2O/NH_3 NH_3 H_2O/NH_3 H_2O/NH_3 NH_3 OH OH	H_2O twist H_2O wag H_2O rock H_2O rock H_2O rock H_2O rock
3	2	0	C_1	183.1 198.0 234.2 268.8 283.4 475.9 532.9 634.4	a a a a a a a a	NH_3 NH_3 NH_3 NH_3 NH_3 OH OH OH	
3	2	1	C_1 [5+1]	207.8 219.4 267.9 283.7 472.1 478.4 494.7 518.1	a a a a a a a a	NH_3 NH_3 NH_3 NH_3 OH OH OH OH	
3	3	0	C_1 [4+2]	293.1 321.1 436.2 462.0 480.6 505.8	a a a a a a	NH_3 NH_3 OH OH OH OH	

4	1	0	C_s	229.2 276.4 306.6 330.2 337.1 556.5	a' a" a' a' a" a'	NH_3 NH_3 NH_3 NH_3 NH_3 OH	
4	1	1	cis-C_1	88.4 193.1 226.9 248.6 278.1 287.6 299.6 312.1 502.1 519.2	a a a a a a a a a a	H_2O H_2O H_2O/NH_3 NH_3 NH_3 H_2O/NH_3 NH_3 NH_3 OH OH	H_2O twist H_2O wag H_2O wag H_2O twist H_2O rock H_2O rock H_2O rock
4	2	0	cis-C_2	174.5 228.7 232.9 267.0 439.7 464.6	a a b a b a	NH_3 NH_3 NH_3 NH_3 OH OH	
5	1	0	C_s	195.4 219.9 225.5 250.4 266.1 296.0 471.5 502.4 530.4	a' a' a' a' a" a' a' a' a'	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3 OH OH OH	

Table 3A.38: Ni-N and Ni-O vibrational stretching frequencies for optimized geometries of $[Ni(NH_3)_n(OH)_m(H_2O)_l]^{2-m}$, where n=1 – 5, m=1 – (5-n), l=0 – (6-n-m) calculated at MP2/6-31+G*.

n	m	l	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	$OH/H_2O/NH_3$	Mixing
1	1	0	C_s #3	458.2	a'	NH_3	
				809.8	a'	OH	
1	1	1	C_1	371.6	a	H_2O	
				422.9	a	NH_3	H_2O wag
				442.8	a	NH_3	H_2O twist
				712.3	a	OH	H_2O rock
				719.3	a	OH	H_2O rock
				726.8	a	OH	H_2O rock
1	1	2	C_1	304.7	a	H_2O	
				341.5	a	H_2O	H_2O wag
				400.5	a	NH_3	H_2O wag
				426.6	a	NH_3	H_2O wag
				440.1	a	H_2O/NH_3	H_2O wag
				657.9	a	OH	
				714.8	a	OH	
1	1	3	C_1	237.2	a	H_2O	H_2O twist
				253.3	a	H_2O	H_2O wag
				282.6	a	H_2O	H_2O rock
				293.6	a	H_2O	H_2O wag
				300.0	a	H_2O	H_2O twist
				327.5	a	H_2O/NH_3	H_2O wag
				384.7	a	H_2O/NH_3	H_2O wag
				394.7	a	NH_3	H_2O wag
				615.5	a	OH	H_2O rock
1	1	4	trans-C_1	227.1	a	H_2O	H_2O twist
				254.4	a	H_2O	H_2O twist
				261.9	a	H_2O/NH_3	H_2O twist
				270.9	a	H_2O	H_2O twist
				305.6	a	H_2O/NH_3	H_2O rock
				309.5	a	H_2O	H_2O wag
				336.7	a	H_2O	H_2O wag
				378.2	a	H_2O/NH_3	H_2O twist
				381.7	a	H_2O/NH_3	H_2O twist
				520.0	a	OH	H_2O wag
				540.5	a	OH	H_2O twist
				560.8	a	OH	H_2O wag
1	2	0	C_1	392.5	a	NH_3	
				566.8	a	OH	
				644.0	a	OH	
				709.5	a	OH	

1	2	1	C_1	241.1 255.6 285.9 384.8 523.3 594.0 603.4	a a a a a a a	H_2O H_2O H_2O NH_3 OH OH OH	 H_2O twist H_2O wag
1	2	2	C_1	198.1 236.4 264.8 282.3 384.9 388.5 481.5 529.6 539.7 559.1	a a a a a a a a a a	H_2O H_2O H_2O H_2O NH_3 NH_3 $OH/H_2O/NH_3$ OH OH OH	 H_2O rock H_2O rock H_2O rock H_2O rock H_2O twist H_2O wag H_2O wag H_2O wag
1	2	3	C_1 [5+1]	188.5 248.7 267.1 378.4 389.7 471.9 544.8	a a a a a a a	H_2O H_2O H_2O NH_3 NH_3 OH OH	 H_2O rock H_2O rock H_2O rock H_2O twist
1	3	0	C_1	302.1 335.1 439.0 454.5 502.1 566.4	a a a a a a	NH_3 NH_3 OH OH OH OH	
1	3	1	C_1 [4+1]	357.0 370.8 440.6 466.4 490.6	a a a a a	NH_3 NH_3 OH OH OH	
1	3	2	C_1 [4+2]	343.8 444.7 454.6 494.3	a a a a	NH_3 OH OH OH	
1	4	0	C_1 [4+1]	339.0 390.5 412.5 434.2	a a a a	OH OH OH OH	

1	4	1	C_1 [4+2]	370.6 380.3 392.7 418.9 427.1 432.0	a a a a a a	OH OH OH OH OH OH	
2	1	0	C_1	411.6 420.4 441.2 697.0 716.0	a a a a a	NH_3 NH_3 NH_3 OH OH	
2	1	1	C_1	327.6 378.4 394.5 398.0 641.3	a a a a a	H_2O/NH_3 NH_3 NH_3 NH_3 OH	H_2O twist H_2O wag H_2O wag H_2O wag
2	1	2	C_1	230.9 257.6 288.9 371.1 385.2 594.5	a a a a a a	H_2O H_2O H_2O/NH_3 NH_3 H_2O/NH_3 OH	 H_2O wag H_2O rock H_2O rock
2	1	3	fac-C_1	236.5 256.9 291.1 337.9 355.7 367.5 373.5 504.1 522.5	a a a a a a a a a	H_2O H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 NH_3 H_2O/NH_3 NH_3 OH OH	H_2O rock H_2O wag H_2O rock H_2O twist H_2O rock H_2O twist H_2O rock H_2O twist
2	2	0	C_2	274.2 328.6 513.0 584.1 596.7 661.2	a b a b a b	NH_3 NH_3 OH OH OH OH	
2	2	1	C_1 [4+1]	362.7 380.0 477.2 575.1 583.5	a a a a a	NH_3 NH_3 OH OH OH	

2	2	2	C_2 #2	386.5 387.4 411.1 473.8 536.0 564.3	b a a a b b	NH_3 NH_3 NH_3 OH OH OH	
2	3	0	C_1 [4+1]	362.8 443.4 469.7 478.0	a a a a	NH_3 OH/NH_3 OH OH	
2	3	1	C_1 [4+2]	361.8 376.1 441.5 454.2 481.1 501.5	a a a a a a	NH_3 NH_3 OH OH OH OH	
2	4	0	C_2 [4+2]	370.3 376.8 417.9 425.9	b a a b	OH OH OH OH	
3	1	0	C_s	356.3 373.8 384.2 625.7 642.4	a" a' a' a' a'	NH_3 NH_3 NH_3 OH OH	
3	1	1	C_1	235.3 322.6 327.2 365.9 380.8 543.0	a a a a a a	H_2O/NH_3 H_2O/NH_3 NH_3 NH_3 NH_3 OH	 H_2O rock H_2O rock
3	1	2	fac-C_s	223.5 265.7 281.7 343.7 351.9 355.7 470.6	a' a' a" a" a' a' a'	H_2O H_2O NH_3 NH_3 NH_3 NH_3 OH	H_2O wag H_2O twist H_2O rock H_2O twist H_2O wag

3	2	0	C_1	215.0 232.1 250.5 290.0 310.3 337.8 455.0 458.1 511.3	a a a a a a a a a	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3 OH OH OH	
3	2	1	C_1 [5+1]	238.8 265.4 320.1 333.9 451.1 482.3	a a a a a a	NH_3 NH_3 NH_3 NH_3 OH OH	
3	3	0	C_1 [4+2]	358.5 390.7 444.4 467.8 481.5	a a a a a	NH_3 NH_3 OH OH OH	
4	1	0	C_s	262.8 314.3 343.5 365.2 369.3 527.0	a' a" a' a' a" a'	NH_3 NH_3 NH_3 NH_3 NH_3 OH	
4	1	1	cis-C_1	198.8 231.6 251.7 284.1 327.8 329.6 342.9 475.4	a a a a a a a a	H_2O/NH_3 H_2O/NH_3 NH_3 NH_3 NH_3 NH_3 NH_3 OH	H_2O wag H_2O rock H_2O wag H_2O wag H_2O wag H_2O twist H_2O wag
4	2	0	cis-C_2	212.0 212.8 253.9 261.7 277.5 304.4 425.0 437.6 450.4	a b b a b a b a a	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3 OH OH OH	

5	1	0	C_1	232.9 244.1 256.5 268.9 301.4 327.2 461.1 498.7	a a a a a a a a	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3 OH OH	

Table 3A.39: Ni-N and Ni-O vibrational stretching frequencies for optimized geometries of $[Ni(NH_3)_n(OH)_m(H_2O)_l]^{2-m}$, where n=1 – 5, m=1 – (5-n), l=0 – (6-n-m) calculated at B3LYP/6-31+G*.

n	m	l	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	OH/H_2O/NH_3	Mixing
1	1	0	C_s #3	452.2	a'	NH_3	
				786.2	a'	OH	
1	1	1	C_1	340.6	a	H_2O	
				423.5	a	NH_3	
				717.8	a	OH	
1	1	2	C_1	264.1	a	H_2O	H_2O twist
				317.8	a	H_2O	H_2O wag
				378.3	a	H_2O/NH_3	H_2O wag
				407.4	a	NH_3	H_2O wag
				650.2	a	OH	H_2O twist
				692.1	a	OH	H_2O twist
1	1	3	C_1	216.9	a	H_2O	
				238.7	a	H_2O	
				262.2	a	H_2O	H_2O rock
				284.4	a	H_2O/NH_3	H_2O wag
				367.7	a	H_2O/NH_3	H_2O rock
				390.2	a	NH_3	H_2O wag
				616.9	a	OH	H_2O rock
1	1	4	trans-C_1	200.4	a	H_2O	H_2O rock
				209.8	a	H_2O	H_2O twist
				220.6	a	H_2O	H_2O rock
				245.7	a	H_2O/NH_3	H_2O twist
				258.0	a	H_2O	H_2O rock
				265.7	a	H_2O	H_2O rock
				285.5	a	H_2O/NH_3	H_2O rock
				292.2	a	H_2O	H_2O wag
				360.4	a	NH_3	H_2O twist
				470.3	a	OH	H_2O wag
				496.0	a	OH	H_2O twist
				511.9	a	OH	H_2O wag
				538.5	a	OH	H_2O twist
1	2	0	C_1	369.4	a	NH_3	
				573.9	a	OH	
				613.3	a	OH	
				705.9	a	OH	
1	2	1	C_1	177.3	a	H_2O	
				360.0	a	NH_3	
				535.3	a	OH	H_2O twist
				595.4	a	OH	H_2O twist
				639.4	a	OH	H_2O wag

1	2	2	C_1	183.1 190.2 218.6 260.3 355.2 548.1 576.0	a a a a a a a	H_2O H_2O H_2O H_2O NH_3 OH OH	 H_2O wag H_2O rock H_2O rock
1	2	3	C_1 [5+1]	161.7 175.0 242.6 338.3 363.7 391.2 462.4 504.7 534.4	a a a a a a a a a	H_2O H_2O H_2O NH_3 NH_3 NH_3 OH/H_2O OH OH	 H_2O twist H_2O twist H_2O twist H_2O rock H_2O rock H_2O rock
1	3	0	C_1	193.8 224.0 241.7 447.2 477.7 483.5	a a a a a a	NH_3 NH_3 NH_3 OH/NH_3 OH OH	
1	3	1	C_1 [4+1]	346.0 423.3 461.8 479.7	a a a a	NH_3 OH/NH_3 OH OH	
1	3	2	C_1 [4+2]	332.8 426.0 449.2 480.8	a a a a	NH_3 OH OH OH	
1	4	0	C_1 [4+1]	304.6 375.0 407.6 425.2	a a a a	OH OH OH OH	
1	4	1	C_1 [4+2]	355.2 362.8 412.8 420.3	a a a a	OH OH OH OH	
2	1	0	C_1	389.7 402.3 678.5 684.7 712.7	a a a a a	NH_3 NH_3 OH OH OH	

2	1	1	C_1	298.3 344.2 373.8 628.7 657.4 662.0 688.6	a a a a a a a	H_2O NH_3 NH_3 OH OH OH OH	H_2O twist H_2O twist H_2O wag H_2O twist H_2O twist
2	1	2	C_1	212.6 238.2 270.2 355.1 355.8 382.8 588.7 599.5	a a a a a a a a	H_2O H_2O H_2O NH_3 NH_3 NH_3 OH OH	 H_2O rock H_2O rock H_2O wag H_2O rock H_2O wag
2	1	3	fac-C_1	170.7 206.7 224.2 252.3 257.2 260.4 329.0 342.6 350.9 368.7 496.4 508.9	a a a a a a a a a a a a	H_2O H_2O H_2O H_2O H_2O H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 H_2O/NH_3 OH OH	H_2O twist H_2O twist H_2O twist H_2O wag H_2O wag H_2O twist H_2O twist H_2O twist H_2O twist H_2O twist H_2O twist H_2O twist
2	2	0	C_2	255.5 299.6 514.9 572.5 652.5	a b a a b	NH_3 NH_3 OH OH OH	
2	2	1	C_1 [4+1]	309.8 321.1 365.1 469.9 563.2 575.1 588.4	a a a a a a a	NH_3 NH_3 NH_3 OH OH OH OH	
2	2	2	C_2 #2	313.0 370.8 378.6 465.5 527.5	a b a a b	NH_3 NH_3 NH_3 OH OH	

2	3	0	C_1 [4+1]	348.2 426.0 432.4 462.2 469.2	a a a a a	NH_3 OH/NH_3 OH OH OH	
2	3	1	C_1 [4+2]	350.4 372.4 428.1 455.9 480.6 497.6	a a a a a a	NH_3 NH_3 OH/NH_3 OH/NH_3 OH OH	
2	4	0	C_2 [4+2]	344.4 356.9 408.5 415.7	a b b a	OH OH OH OH	
3	1	0	C_1	315.9 348.6 362.2 612.8 619.3 649.3 679.0	a a a a a a a	NH_3 NH_3 NH_3 OH OH OH OH	
3	1	1	C_1	213.1 307.9 310.4 343.2 362.9 519.5	a a a a a a	H_2O H_2O/NH_3 NH_3 NH_3 NH_3 OH	H_2O wag H_2O rock H_2O rock
3	1	2	fac-C_s	233.5 242.5 265.4 325.9 330.5 458.9	a' a' a' a' a" a'	H_2O H_2O OH/NH_3 NH_3 NH_3 OH	 H_2O wag H_2O wag
3	2	0	C_1	207.0 226.8 250.4 265.4 280.4 301.6 443.9 498.8 519.8	a a a a a a a a a	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3 OH OH OH	

3	2	1	fac-C_s	174.8 246.3 290.8 306.7 417.3 438.8	a' a" a' a' a" a'	H_2O NH_3 NH_3 NH_3 OH/NH_3 OH	
3	3	0	C_3 [3+3]	517.0 545.3 545.4	a e e	OH OH OH	
4	1	0	C_s	244.4 297.5 319.9 345.3 347.3 505.9	a' a" a' a' a" a'	NH_3 NH_3 NH_3 NH_3 NH_3 OH/NH_3	
4	1	1	cis-C_1	58.6 238.3 276.0 307.5 313.0 323.9 352.1 470.7	a a a a a a a a	H_2O NH_3 NH_3 NH_3 NH_3 NH_3 H_2O/NH_3 OH/NH_3	H_2O twist H_2O twist H_2O twist H_2O twist H_2O wag H_2O wag H_2O wag H_2O wag
4	2	0	C_1 [5+1]	240.9 268.0 290.4 319.7 439.3 488.4	a a a a a a	NH_3 NH_3 NH_3 NH_3 OH/NH_3 OH	
5	1	0	C_s	220.1 235.1 248.0 270.4 274.8 302.3 445.6 481.3	a' a' a' a" a' a' a' a'	NH_3 NH_3 NH_3 NH_3 NH_3 NH_3 OH OH	

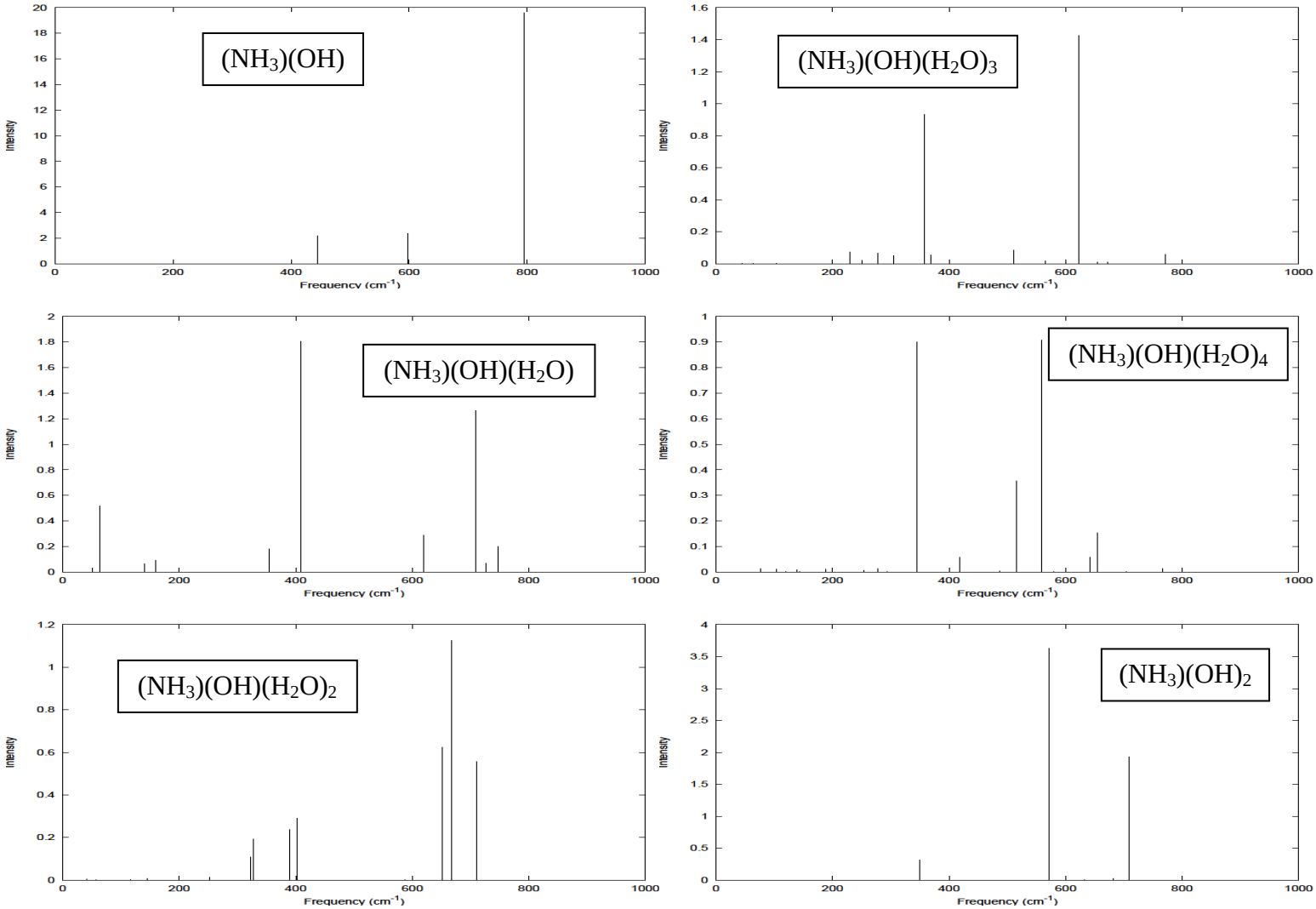


Figure 3A-7: Simulated polarized Raman spectra for $[Ni(NH_3)_n(OH)_m(H_2O)_l]^{2-m}$, where n=1 – 5, m=1 – (5-n) and l=0 – (6-n-m)

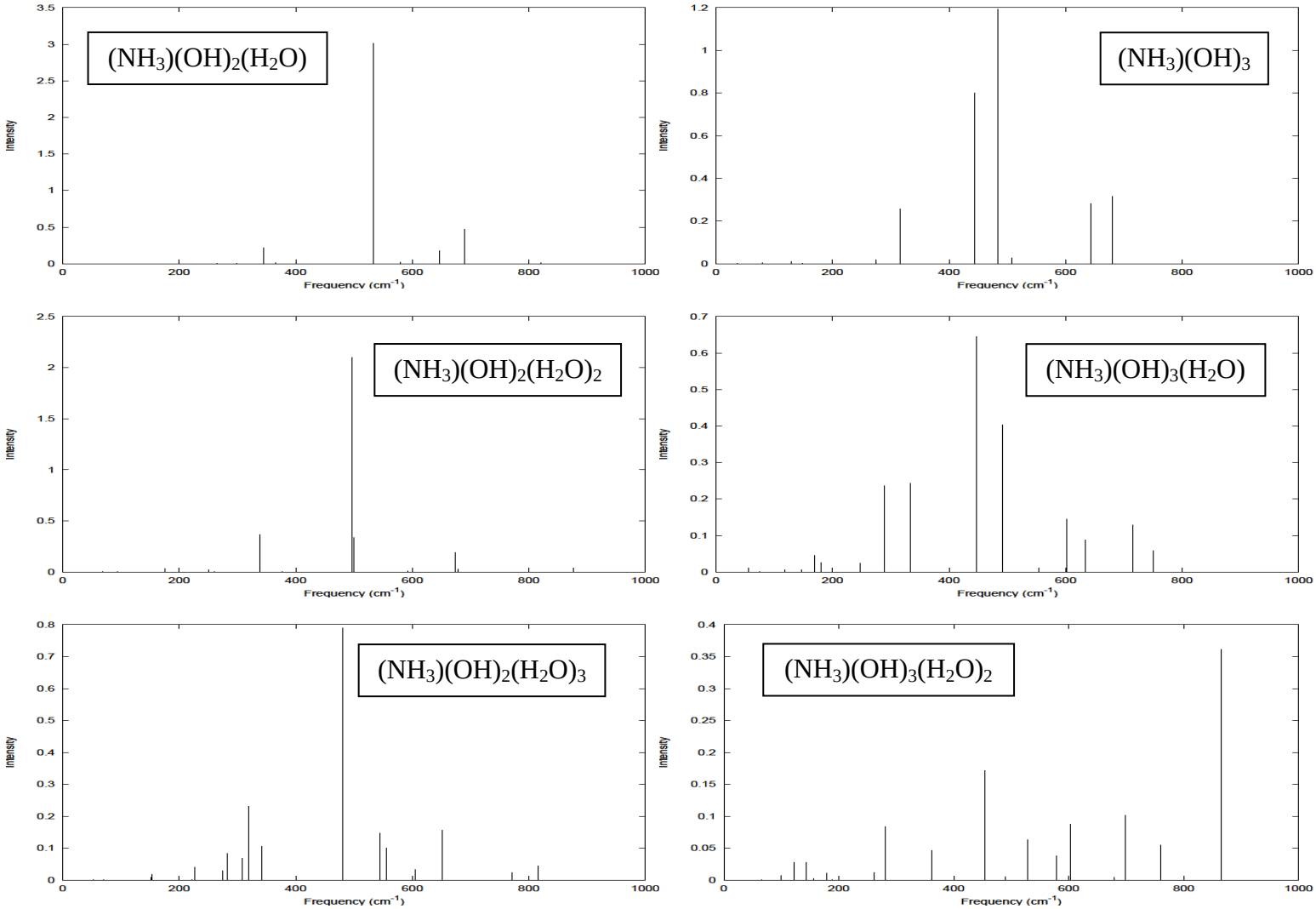


Figure 3A-7: *(continued)*

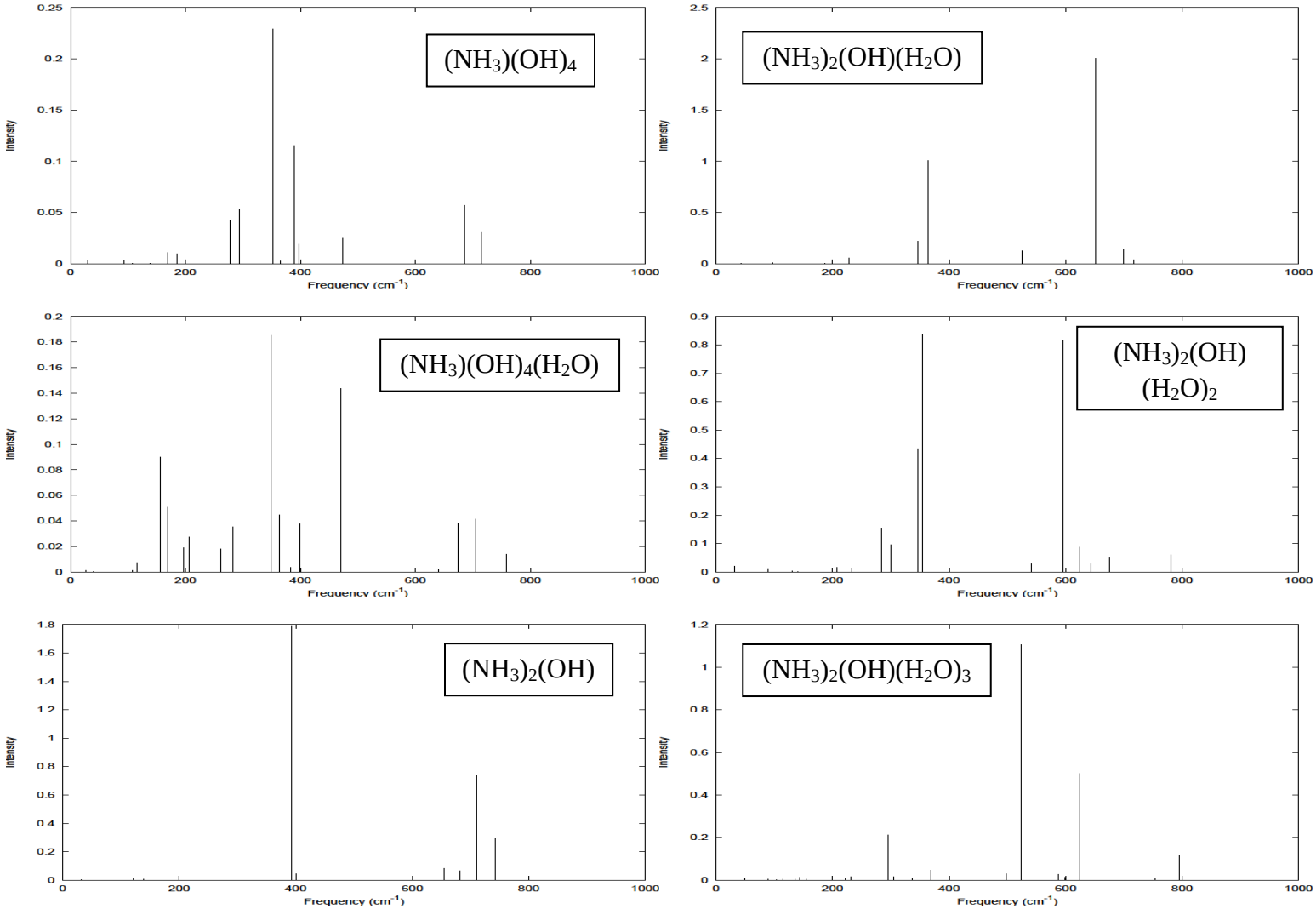


Figure 3A-7: *(continued)*

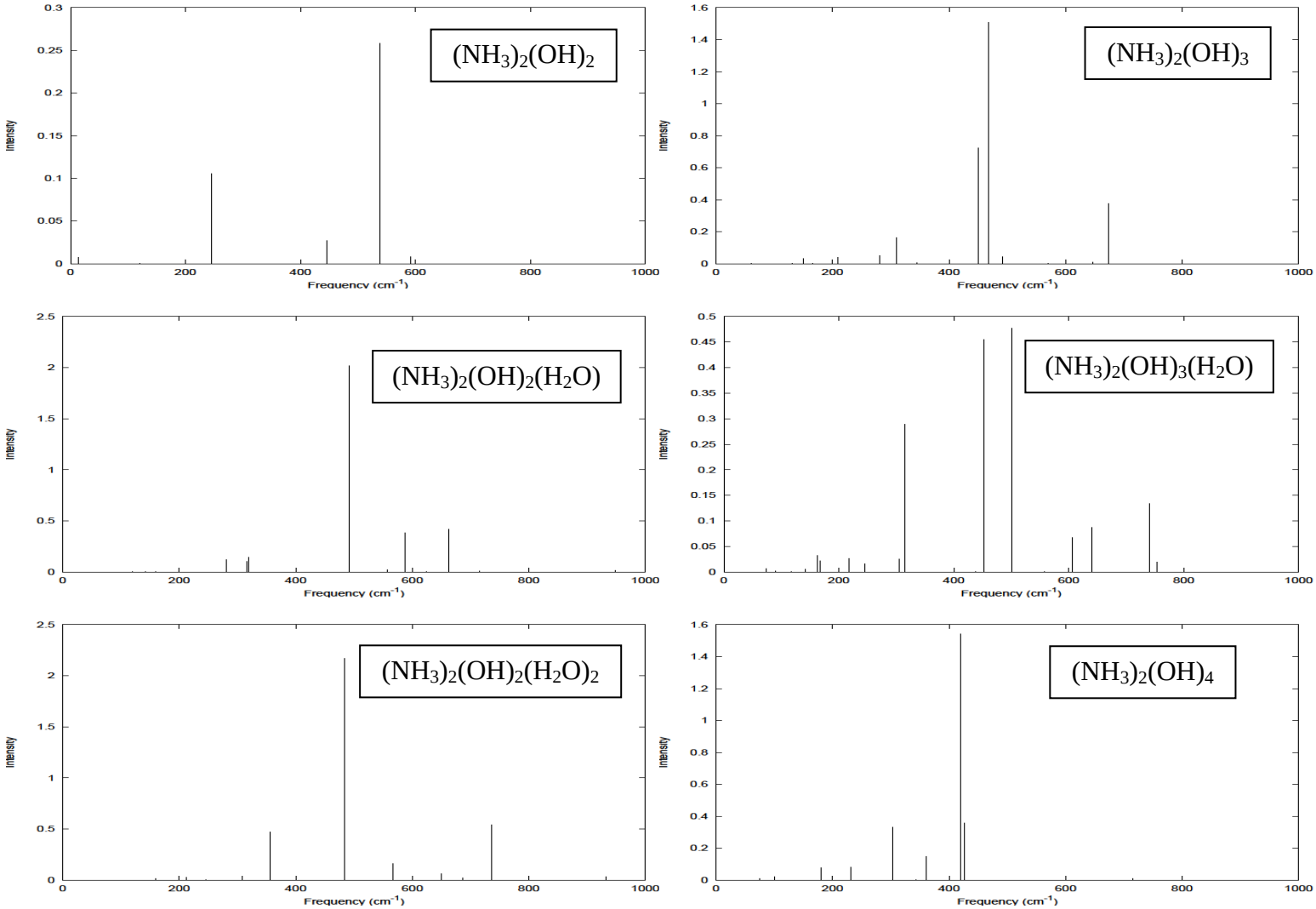


Figure 3A-7: *(continued)*

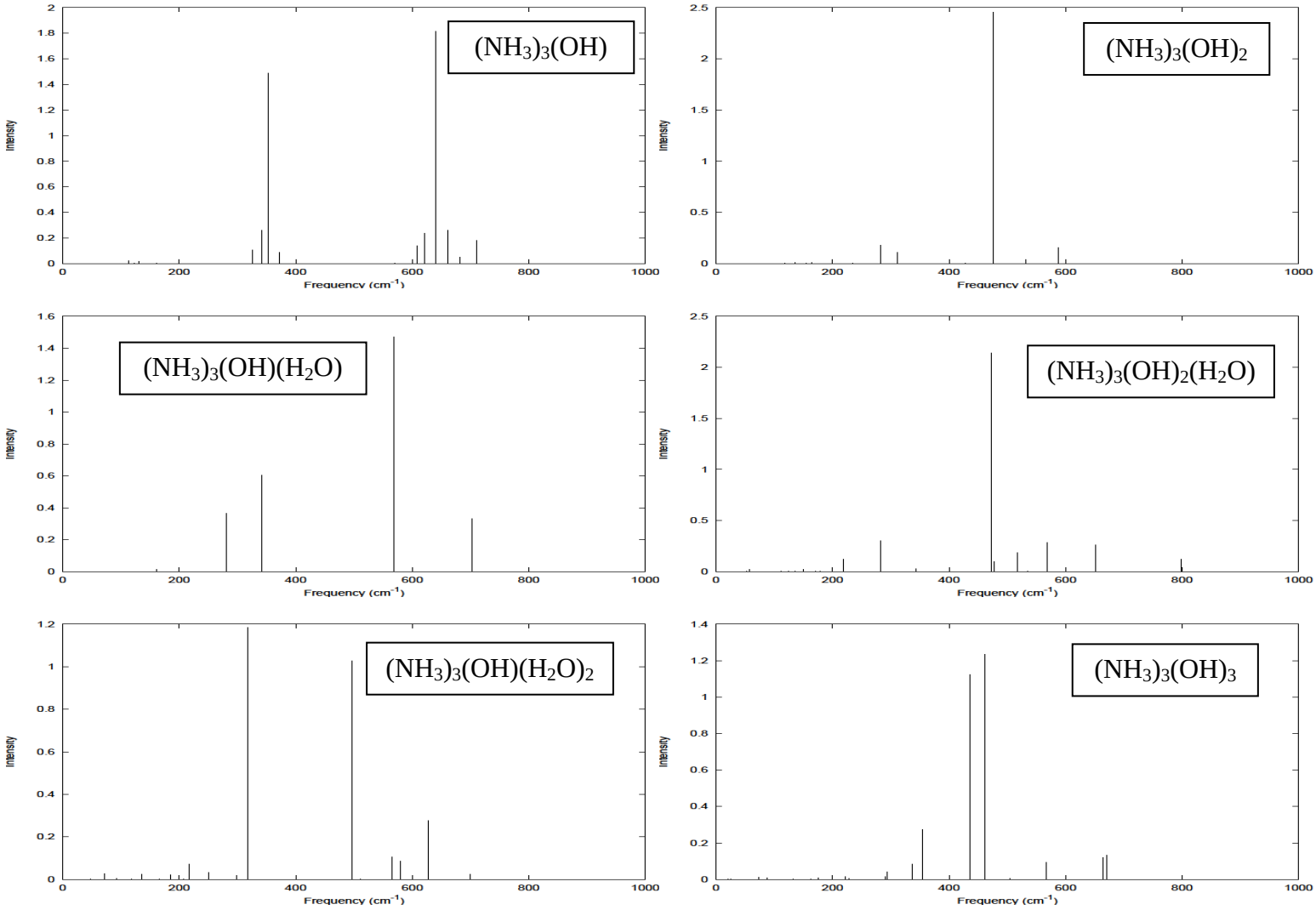


Figure 3A-7: *(continued)*

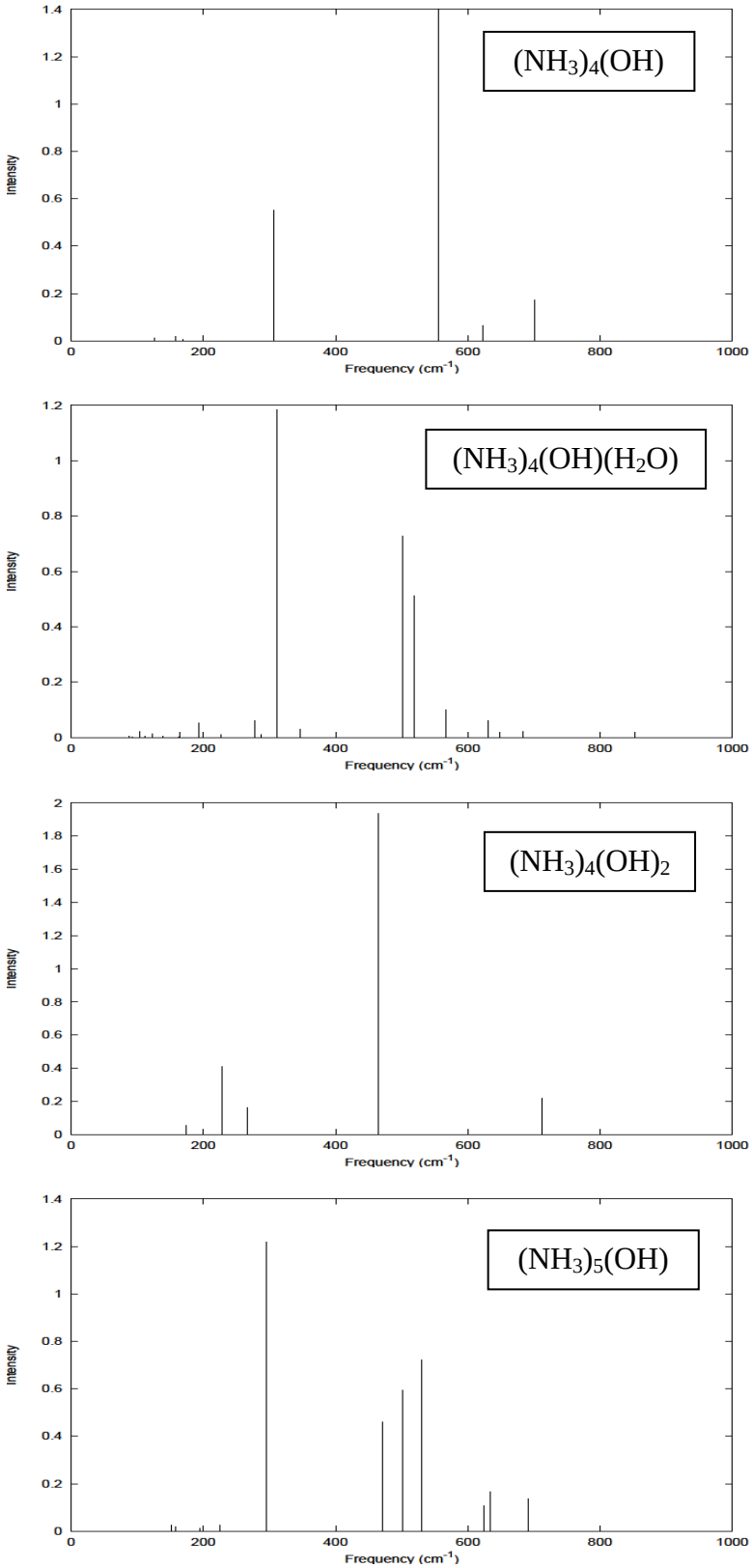


Figure 3A-7: *(continued)*

Table 3A.40: Total energies for all stable geometries of $[NiCl_m(OH)_n(NH_3)_l(H_2O)_k]^{2-m-n}$, where m=1 – 3, n=0 – (4-m), l=0 – (6-n-m), k=0 – (6-m-n-l)

					Optimized Energies (Hartrees)			
m	**n**	**l**	**k**	**Point Group**	**HF**	**MP2**	**B3LYP**	**C-PCM**
1	1	1	0	C_s #1	-2097.8984682	-2098.5388668	-2100.8625140	-2100.892474
				C_s #2	-2097.9019941	-2098.6137560	-2100.8508198	-2100.894441
1	1	1	1	C_1	-2173.9491185	-2174.8612469	-2177.3071303	-2177.330319
1	1	1	2	C_1	-2249.9872851	-2251.0984984	-2253.7513385	-2253.779722
1	1	1	3	mer-C_1	-2326.0225184	-2327.3359178	-2330.1944851	-2330.223985
				fac-C_1	-2326.01966	-2327.331969	-2330.191261	-2330.222185
1	1	2	0	C_1	-2154.1248193	-2155.0212360	-2157.4472270	-2157.477865
1	1	2	1	C_1	-2230.1570685	-2231.2535203	-2233.8920347	-2233.915077
1	1	2	2	C_s	-2306.195543	-2307.494401	-2310.333518	-2310.360297
				C_1 #1 [5+1]	-2306.2028961	-2307.4992239	-2310.3407447	-2310.368487
				C_1 #2 [5+1]	-2306.203406	-2307.497626	-2310.340389	-2310.370309
				C_1 #3	-2306.194825	-2307.491797	-2310.330825	-2310.361186
				C_1 #4	-2306.191886	-2307.488249	-2310.327375	-2310.358122
				C_1 #5	-2306.192607	-2307.489724	-2310.327102	-2310.360359
1	1	3	0	C_1	-2210.3318567	-2211.4117202	-2214.0248236	-2214.05687
1	1	3	1	C_1 [5+1]	-2286.3691018	-2287.6500380	-2290.4701886	-2290.500483
				fac-C_1	-2286.367663	-2287.650462	-2290.469077	-2290.492377
1	1	4	0	trans-C_s #1	-2266.5354987	-2267.7995529	-2270.5950098	--
				trans-C_s #2	-2266.5352952	-2267.7995004	-2270.5952726	-2270.630848
				trans-C_1	-2266.5354985	-2267.7995449	-2270.5952923	-2270.63082
				cis-C_s	-2266.534896	-2267.799598	-2270.597736	-2270.627465
1	2	1	0	C_s	-2173.3936442	-2174.3192795	-2176.7681097	-2176.867711
				C_1	-2173.3967838	-2174.3202679	-2176.7663338	-2176.865202
1	2	1	1	C_s [4+1]	-2249.4455366	-2250.5688308	-2253.2229647	--
				C_1 [4+1]	-2249.4464390	-2250.5705451	-2253.2236988	-2253.313611
1	2	1	2	C_s [5+1]	-2325.4709678	-2326.7884388	-2329.6517312	-2329.742757
				C_1 [5+1]	-2325.4758255	-2326.7976464	-2329.6622890	-2329.747874
1	2	2	0	C_2 [4+1]	-2229.5968442	-2230.6998961	-2233.3500060	-2233.445901
				C_1 [4+1]	-2229.6061514	-2230.7103147	-2233.3500491	-2233.445947
1	2	2	1	C_1 [5+1]	-2305.6421258	-2306.9487756	-2309.7882295	-2309.878751
1	2	3	0	mer-C_s	-2285.7922783	-2287.0858493	-2289.9007494	-2290.003169
				C_1 [4+2]	-2285.8067508	-2287.0898089	-2289.9175125	-2290.009799
1	3	1	0	C_1 [4+1]	--	-2249.8641152	--	--
2	1	1	0	C_1	-2557.5042787	-2558.3605060	-2561.1939057	-2561.288064

2	1	1	1	C_s	-2633.536808	-2634.5941230	-2637.6348453	-2637.722687
				C_1	-2633.5370403	-2634.5941182	-2637.6348519	-2637.722751
2	1	1	2	C_1 [5+1]	-2709.5742442	-2710.8305547	-2714.0797189	-2714.157337
2	1	2	0	C_s	-2613.7085975	-2614.7482600	-2617.7688541	-2617.861955
2	1	2	1	C_1 [5+1]	-2689.7503930	-2690.9893122	-2694.2212681	-2694.31123
2	1	3	0	C_s	-2669.9078460	-2671.1304689	-2674.3363495	--
				C_1 [5+1]	-2669.9184376	-2671.1407828	-2674.3533063	-2674.448303
2	2	1	0	C_s [3+2]	-2632.8680342	-2633.9250347	-2636.9869744	-2637.253409
2	2	1	1	C_1 [4+2]	-2708.9236489	-2710.1727474	-2713.4340753	-2713.692583
2	2	2	0	C_2 [4+2]	-2689.0922393	-2690.3243690	-2693.5669970	-2693.828113
3	1	1	0	C_1 [4+1]	-3016.9669700	-3017.9572953	-3021.3878438	-3021.650009
3	1	1	1	C_1 [4+2]	-3093.0284103	-3094.2111638	-3097.8593914	-3098.109172
3	1	2	0	C_s [4+2]	-3073.1900418	-3074.3617904	-3077.9883992	-3078.249442

NOT Stable

†Total free energy in solution at 25°C, CPCM-B3LYP/6-31+G*//B3LYP/6-31+G*

Table 3A.41: Ni-O bond lengths for stable geometries of $[NiCl_m(OH)_n(NH_3)_l(H_2O)_k]^{2-m-n}$, where m=1 – 3, n=0 – (4-m), l=0 – (6-n-m), k=0 – (6-m-n-l)

					Optimized Ni-O Bond Lengths (Å)					
					HF/6-31+G*		MP2/6-31+G*		B3LYP/6-31+G*	
m	**n**	**l**	**k**	**Point Group**	**OH**	**H_2O**	**OH**	**H_2O**	**OH**	**H_2O**
1	1	1	0	C_s #1	1.819	N/A	1.792	N/A	1.779	N/A
				C_s #2	1.849	N/A	1.841	N/A	1.844	N/A
1	1	1	1	C_1	1.890	2.158	1.898	2.111	1.914	2.149
1	1	1	2	C_1	1.907	2.225 2.198	1.900	2.157 2.145	1.875	2.184 2.170
1	1	1	3	mer-C_1	1.970	2.303 2.214 2.195	1.986	2.218 2.153 2.139	1.988	2.250 2.174 2.162
				fac-C_1	1.963	2.199 2.225 2.291	1.976	2.140 2.161 2.211	1.977	2.170 2.185 2.241
1	1	2	0	C_1	1.891	N/A	1.881	N/A	1.857	N/A
1	1	2	1	C_1	1.939	2.395	1.955	2.281	1.919	[4+1]
1	1	2	2	C_s	1.976	2.218	2.000	2.162	2.007	2.188
				C_1 #1 [5+1]	1.938	2.298	1.934	2.224	1.937	2.247
				C_1 #2 [5+1]	1.932	2.190	1.925	2.140	1.917	2.160
				C_1 #3	1.973	2.395 2.252	1.991	2.273 2.192	1.992	2.331 2.214
				C_1 #4	1.967	2.350 2.280	1.982	2.271 2.204	1.983	2.329 2.271
				C_1 #5	1.975	2.246 2.312	1.991	2.173 2.230	1.994	2.213 2.273
1	1	3	0	C_1	1.923	N/A	1.921	N/A	1.894	N/A
1	1	3	1	C_1 [5+1]	1.968	[5+1]	2.014	2.372	1.980	[5+1]
				fac-C_1	1.977	2.288	1.997	2.231	2.001	2.252
1	1	4	0	trans-C_s #1	1.978	N/A	--	N/A	--	N/A
				trans-C_s #2	--	N/A	--	N/A	2.003	N/A
				trans-C_1	1.978	N/A	1.997	N/A	2.003	N/A
				cis-C_s	1.972	N/A	1.992	N/A	1.996	N/A
1	2	1	0	C_s	--	N/A	1.908	N/A	1.877	N/A
				C_1	1.920 1.937	N/A	1.907 1.922	N/A	1.867 1.915	N/A

1	2	1	1	C_s [4+1]	--	--	1.932	--	--	--
				C_1 [4+1]	1.947 1.937	--	1.938 1.922	--	1.939 1.918	--
1	2	1	2	C_s [5+1]	1.979 1.923	2.316	1.986 1.914	2.261	1.979 1.914	2.303
				C_1 [5+1]	1.926 2.002	2.208 2.200	1.904 2.017	2.152 2.151	1.886 2.023	2.182 2.182
1	2	2	0	C_2 [4+1]	1.912	N/A	--	N/A	1.896	N/A
				C_1 [4+1]	1.925 1.925	N/A	1.909 1.909	N/A	1.896 1.896	N/A
1	2	2	1	C_1 [5+1]	1.962 1.970	--	1.978 1.980	--	1.987 1.970	--
1	2	3	0	mer-C_s	--	N/A	2.036 2.035	N/A	2.044 2.030	N/A
				C_1 [4+2]	1.936 1.929	N/A	1.915 1.919	N/A	1.904 1.909	N/A
1	3	1	0	C_1 [4+1]	--	N/A	1.949 1.979 1.947	N/A	--	N/A
2	1	1	0	C_1	1.908	N/A	1.903	N/A	1.881	N/A
2	1	1	1	C_s	--	--	1.903	2.279	1.885	2.292
				C_1	1.919	2.313	1.903	2.279	1.886	2.287
2	1	1	2	C_1 [5+1]	1.952	2.343	1.959	2.256	1.955	2.297
2	1	2	0	C_s	1.954	N/A	1.972	N/A	1.969	N/A
2	1	2	1	C_1 [5+1]	1.920	2.188	1.914	2.147	1.888	2.178
2	1	3	0	C_s	1.950	N/A	2.004	N/A	--	N/A
				C_1 [5+1]	1.921	N/A	1.917	N/A	1.879	N/A
2	2	1	0	C_s [3+2]	1.858	N/A	1.827	N/A	1.809	N/A
2	2	1	1	C_1 [4+2]	1.914 1.924	2.141	1.903 1.922	2.083	1.883 1.900	2.143
2	2	2	0	C_2 [4+2]	1.928	N/A	1.919	N/A	1.904	N/A
3	1	1	0	C_1 [4+1]	1.931	N/A	1.919	N/A	1.903	N/A
3	1	1	1	C_1 [4+2]	1.894	2.110	1.886	2.059	1.881	2.067
3	1	2	0	C_s [4+2]	1.897	N/A	1.889	N/A	1.873	N/A

Table 3A.42: Ni-N and Ni-Cl bond lengths for stable geometries of $[NiCl_m(OH)_n(NH_3)_l(H_2O)_k]^{2-m-n}$, where m=1 – 3, n=0 – (4-m), l=0 – (6-n-m), k=0 – (6-m-n-l)

					Optimized Ni-N and Ni-Cl Bond Lengths (Å)					
					HF/6-31+G*		**MP2/6-31+G***		**B3LYP/6-31+G***	
m	**n**	**l**	**k**	**Point Group**	**NH_3**	**Cl**	**NH_3**	**Cl**	**NH_3**	**Cl**
1	1	1	0	C_s #1	2.147	2.232	2.065	2.158	2.075	2.169
				C_s #2	2.121	2.232	2.048	2.166	2.058	2.169
1	1	1	1	C_1	2.129	2.268	2.044	2.184	2.045	2.184
1	1	1	2	C_1	2.132	2.356	2.048	2.278	2.061	2.345
1	1	1	3	mer-C_1	2.155	2.418	2.070	2.322	2.083	2.376
				fac-C_1	2.166	2.429	2.080	2.335	2.089	2.389
1	1	2	0	C_1	2.155 2.155	2.290	2.071 2.066	2.218	2.083 2.088	2.265
1	1	2	1	C_1	2.175 2.162	2.353	2.087 2.082	2.266	2.080 2.064	2.251
1	1	2	2	C_s	2.189 2.238	2.453	2.095 2.139	2.344	2.116 2.148	2.398
				C_1 #1 [5+1]	2.169 2.141	2.383	2.082 2.053	2.306	2.090 2.063	2.355
				C_1 #2 [5+1]	2.229 2.158	2.386	2.128 2.069	2.306	2.136 2.080	2.366
				C_1 #3	2.172 2.193	2.431	2.085 2.103	2.336	2.101 2.115	2.390
				C_1 #4	2.179 2.187	2.450	2.086 2.100	2.355	2.088 2.100	2.411
				C_1 #5	2.197 2.177	2.458	2.105 2.091	2.362	2.114 2.095	2.437
1	1	3	0	C_1	2.177 2.245 2.213	2.410	2.080 2.140 2.123	2.329	2.109 2.159 2.135	2.423
1	1	3	1	C_1 [5+1]	2.184 2.196 2.195	2.430	2.102 2.111 2.105	2.353	2.097 2.111 2.122	2.395
				fac-C_1	2.211 2.202 2.270	2.476	2.115 2.106 2.164	2.366	2.143 2.119 2.176	2.252

1	1	4	0	trans-C_s #1	2.265 2.238 2.254	2.512	--	--	--	--	--
				trans-C_s #2	--	--	--	--	2.159 2.172	2.475
				trans-C_1	2.266 2.237 2.237 2.255	2.513	2.155 2.151 2.140 2.137	2.395	2.174 2.159 2.171 2.157	2.476
				cis-C_s	2.232 2.307 2.250	2.513	2.132 2.191 2.158	2.401	2.167 2.211 2.160	2.476
1	2	1	0	C_s	--	--	2.118	2.311	2.164	2.395
				C_1	2.167	2.453	2.071	2.338	2.106	2.442
1	2	1	1	C_s [4+1]	--	--	2.085	2.280	--	--
				C_1 [4+1]	2.162	2.403	2.069	2.296	2.074	2.340
1	2	1	2	C_s [5+1]	2.152	--	2.070	--	2.072	--
				C_1 [5+1]	2.179	--	2.093	--	2.104	--
1	2	2	0	C_2 [4+1]	2.208	--	--	--	2.093	--
				C_1 [4+1]	2.147 2.147	--	2.067 2.067	--	2.093 2.093	--
1	2	2	1	C_1 [5+1]	2.220 2.210	2.672	2.161 2.120	2.398	2.183 2.119	2.467
1	2	3	0	mer-C_s	--	--	2.128 2.138	2.503	2.146 2.144	2.646
				C_1 [4+2]	2.130 2.159	--	2.048 2.075	--	2.069 2.092	--
1	3	1	0	C_1 [4+1]	--	--	--	2.551	--	--
2	1	1	0	C_1	2.153	2.384 2.390	2.063	2.282 2.296	2.062	2.329 2.348
2	1	1	1	C_s	--	--	2.075	2.362	2.075	2.427
				C_1	2.157	2.494 2.458	2.075	2.361 2.364	2.075	2.428 2.429
2	1	1	2	C_1 [5+1]	2.166	2.407 2.482	2.077	2.313 2.364	2.075	2.352 2.421
2	1	2	0	C_s	2.174	2.503 2.530	2.093	2.369 2.384	2.083	2.438 2.459
2	1	2	1	C_1 [5+1]	2.193 2.148	2.485	2.105 2.064	2.367	2.120 2.081	2.455
2	1	3	0	C_s	2.178 2.262	2.432 [5+1]	2.110 2.118	2.500 2.503	--	--
				C_1 [5+1]	2.228 2.154 2.189	2.527	2.139 2.070 2.108	2.399	2.153 2.107 2.121	2.513

2	2	1	0	C_s [3+2]	2.120	--	2.045	--	2.072	--
2	2	1	1	C_1 [4+2]	2.147	--	2.056	--	2.072	--
2	2	2	0	C_2 [4+2]	2.168	--	2.079	--	2.106	--
3	1	1	0	C_1 [4+1]	--	2.474 2.477 2.444	--	2.361 2.350 2.332	--	2.422 2.406 2.355
3	1	1	1	C_1 [4+2]	2.112	2.363	2.034	2.281	2.047	2.321
3	1	2	0	C_s [4+2]	2.138	2.393	2.057	2.299	2.069	2.356

Table 3A.43: Ni-N, Ni-Cl and Ni-O vibrational stretching frequencies for optimized geometries of $[NiCl_m(OH)_n(NH_3)_l(H_2O)_k]^{2-m-n}$, where m=1 – 3, n=0 – (4-m), l=0 – (6-n-m), k=0 – (6-m-n-l) calculated at HF/6-31+G*.

m	n	l	k	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	Cl/OH/H_2O /NH_3	Mixing
1	1	1	0	C_s #2	355.6	a'	Cl/NH_3	
					368.0	a'	Cl/NH_3	
					642.1	a'	OH	
					677.7	a'	OH	
1	1	1	1	C_1	290.7	a	H_2O	
					332.8	a	Cl	H_2O rock
					356.2	a	NH_3	H_2O wag
					585.3	a	OH	H_2O wag
1	1	1	2	C_1	202.4	a	H_2O	
					222.2	a	Cl/H_2O	
					254.5	a	H_2O	H_2O rock
					275.1	a	H_2O	H_2O rock
					286.0	a	Cl/H_2O	H_2O rock
					298.2	a	Cl/H_2O	H_2O rock
					352.2	a	NH_3	H_2O wag
					551.3	a	OH	H_2O wag
1	1	1	3	mer-C_1	163.4	a	H_2O	H_2O wag
					179.1	a	H_2O	H_2O rock
					220.0	a	$Cl/OH/NH_3/H_2O$	H_2O wag
					250.1	a	$Cl/NH_3/H_2O$	H_2O rock
					270.4	a	Cl/H_2O	H_2O rock
					274.1	a	$Cl/NH_3/H_2O$	H_2O wag
					331.4	a	$Cl/NH_3/H_2O$	H_2O wag
					502.3	a	OH	H_2O wag
1	1	2	0	C_1	319.2	a	Cl/NH_3	
					329.1	a	NH_3	
					332.2	a	NH_3	
					579.2	a	OH	
1	1	2	1	C_1	256.6	a	$Cl/OH/NH_3/H_2O$	
					276.4	a	Cl/NH_3	
					306.3	a	Cl/NH_3	H_2O twist
					335.0	a	NH_3	H_2O twist
					524.1	a	OH	

1	1	2	2	C_1 #2 [5+1]	214.1 249.0 282.4 288.9 292.1 334.3 507.0	a a a a a a a	$Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ Cl/NH_3 $Cl/NH_3/H_2O$ OH	 H_2O rock H_2O twist
1	1	3	0	C_1	208.6 211.6 274.7 289.0 313.5 521.8	a a a a a a	Cl/NH_3 Cl/NH_3 Cl/NH_3 NH_3 Cl/NH_3 OH	
1	1	3	1	C_1 [5+1]	209.8 216.8 273.4 286.7 307.6 315.7 473.6	a a a a a a a	Cl/NH_3 Cl/NH_3 Cl/NH_3 Cl/NH_3 Cl/NH_3 Cl/NH_3 OH	
1	1	4	0	trans-C_s #1	183.3 186.7 209.7 261.0 265.3 277.4 289.5 464.4	a' a' a' a'' a' a' a'' a'	NH_3 Cl/NH_3 Cl/NH_3 NH_3 Cl/NH_3 Cl/NH_3 NH_3 OH	
1	2	1	0	C_1	218.7 313.3 491.2 528.1 546.9	a a a a a	Cl NH_3 OH OH OH	
1	2	1	1	C_1 [4+1]	238.6 250.4 259.4 324.8 491.5 508.6	a a a a a a	Cl Cl/NH_3 Cl/NH_3 NH_3 OH OH	
1	2	1	2	C_1 [5+1]	231.1 240.1 321.5 460.1 507.9	a a a a a	H_2O H_2O NH_3/H_2O OH OH	

1	2	2	0	C_1 [4+1]	335.1 355.7 495.7 535.6	a a a a	NH_3 NH_3 OH OH	
1	2	2	1	C_1 [5+1]	248.0 257.4 288.5 298.1 448.2 475.0	a a a a a a	Cl/NH_3 Cl/NH_3 NH_3 NH_3 OH OH	
1	2	3	0	C_1 [4+2]	331.3 338.3 367.1 472.8 501.1 531.4	a a a a a a	NH_3 NH_3 NH_3 OH OH OH	
2	1	1	0	C_1	247.3 263.9 334.7 547.6	a a a a	Cl/NH_3 Cl NH_3 OH	
2	1	1	1	C_1	143.0 216.6 244.5 330.1 524.7	a a a a a	H_2O Cl/H_2O $Cl/NH_3/H_2O$ NH_3 OH	
2	1	1	2	C_1 [5+1]	95.5 101.4 125.7 218.5 245.2 251.8 323.5 480.1 509.3	a a a a a a a a a	H_2O H_2O Cl/H_2O $Cl/NH_3/H_2O$ Cl/H_2O $Cl/NH_3/H_2O$ NH_3 OH OH	 H_2O twist H_2O rock H_2O rock H_2O rock H_2O rock H_2O rock
2	1	2	0	C_s	173.6 205.4 288.0 346.7 494.2	a' a' a' a'' a'	Cl/NH_3 Cl Cl/NH_3 NH_3 OH	
2	1	2	1	C_1 [5+1]	188.7 193.9 261.2 309.6 345.0 531.8	a a a a a a	Cl/H_2O Cl/H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ NH_3/H_2O OH	 H_2O wag

2	1	3	0	C_1 [5+1]	178.8 182.9 269.3 308.3 345.6 531.9	a a a a a a	Cl Cl/NH_3 Cl/NH_3 NH_3 NH_3 OH	
2	2	1	0	C_s [3+2]	375.1 551.7 645.3	a' a' a''	NH_3 OH OH	
2	2	1	1	C_1 [4+2]	315.4 348.9 498.7 559.8	a a a a	H_2O NH_3 OH OH	 H_2O rock H_2O twist
2	2	2	0	C_2 [4+2]	325.6 334.9 490.8 541.2	b a a b	NH_3 NH_3 OH OH	
3	1	1	0	C_1 [4+1]	186.6 202.5 208.0 220.2 515.5	a a a a a	Cl Cl Cl Cl OH	
3	1	1	1	C_1 [4+2]	270.9 344.8 372.8 387.4 562.4	a a a a a	Cl H_2O NH_3 NH_3 OH	H_2O rock H_2O twist H_2O twist H_2O rock
3	1	2	0	C_s [4+2]	255.3 332.9 377.2 559.7	a' a' a' a'	Cl NH_3 NH_3 OH	

Table 3A.44: Ni-N, Ni-Cl and Ni-O vibrational stretching frequencies for optimized geometries of $[NiCl_m(OH)_n(NH_3)_l(H_2O)_k]^{2-m-n}$, where m=1 – 3, n=0 – (4-m), l=0 – (6-n-m), k=0 – (6-m-n-l) calculated at MP2/6-31+G*.

m	n	l	k	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	Cl/OH/H_2O /NH_3	Mixing
1	1	1	0	C_s #2	374.0	a'	Cl/NH_3	
					408.7	a'	Cl/NH_3	
					626.4	a'	Cl/OH	
1	1	1	1	C_1	298.8	a	H_2O	H_2O rock
					309.3	a	H_2O	
					360.6	a	Cl/NH_3/H_2O	H_2O rock
					407.3	a	NH_3	H_2O rock
					562.0	a	OH	
1	1	1	2	C_1	228.6	a	H_2O	H_2O wag
					250.3	a	Cl/H_2O	H_2O rock
					303.9	a	H_2O	H_2O rock
					322.4	a	Cl/H_2O	H_2O rock
					399.5	a	NH_3	H_2O rock
					527.4	a	OH	H_2O twist
					554.5	a	OH	H_2O wag
1	1	1	3	mer-C_1	196.5	a	H_2O	H_2O wag
					220.0	a	H_2O	H_2O rock
					242.4	a	Cl/OH/NH_3/H_2O	
					268.1	a	Cl/NH_3/H_2O	H_2O rock
					298.3	a	Cl/H_2O	H_2O rock
					308.1	a	Cl/NH_3/H_2O	H_2O rock
					373.7	a	NH_3	H_2O twist
					374.5	a	NH_3	H_2O rock
					482.8	a	OH	H_2O rock
					494.2	a	OH	H_2O wag
1	1	2	0	C_1	341.0	a	Cl	
					375.6	a	NH_3	
					377.5	a	NH_3	
					564.6	a	OH	
1	1	2	1	C_1	271.7	a	Cl/NH_3/H_2O	
					310.0	a	Cl/NH_3	
					332.9	a	Cl/NH_3	H_2O twist
					350.9	a	Cl/NH_3	H_2O twist
					383.7	a	NH_3	H_2O wag
					500.5	a	OH	H_2O wag

1	1	2	2	C_1 #1 [5+1]	210.3 305.9 372.3 399.5 477.0 519.1	a a a a a a	Cl/H_2O Cl/H_2O NH_3 NH_3 OH OH	 H_2O twist H_2O wag H_2O twist H_2O twist
1	1	3	0	C_1	246.8 310.3 341.4 362.1 494.0 508.0	a a a a a a	Cl/NH_3 Cl/NH_3 NH_3 NH_3 OH OH	
1	1	3	1	fac-C_1	201.2 230.9 238.6 258.7 300.5 328.6 342.0 464.5	a a a a a a a a	Cl/H_2O $Cl/NH_3/H_2O$ Cl/NH_3 Cl/NH_3 $Cl/NH_3/H_2O$ NH_3/H_2O Cl/NH_3 OH	 H_2O rock
1	1	4	0	cis-C_s	238.2 254.4 287.8 297.4 325.9 459.6	a' a' a' a'' a' a'	Cl/NH_3 Cl/NH_3 Cl/NH_3 NH_3 Cl/NH_3 OH	
1	2	1	0	C_1	259.5 366.1 387.6 476.6 521.5	a a a a a	Cl NH_3 NH_3 OH OH	
1	2	1	1	C_1 [4+1]	268.5 288.3 346.0 380.8 479.3 500.5	a a a a a a	Cl Cl NH_3 NH_3 OH OH	
1	2	1	2	C_1 [5+1]	260.0 283.0 361.2 443.6 503.8	a a a a a	H_2O H_2O NH_3/H_2O OH OH	
1	2	2	0	C_1 [4+1]	376.9 398.4 483.3 526.4	a a a a	NH_3 NH_3 OH OH	

1	2	2	1	C_1 [5+1]	214.4 239.2 245.8 276.4 336.2 423.2 455.0	a a a a a a a	Cl/NH_3 Cl/NH_3 Cl/NH_3 Cl/NH_3 NH_3 OH/NH_3 OH	
1	2	3	0	C_1 [4+2]	372.7 382.0 413.1 475.9 523.1	a a a a a	NH_3 NH_3 NH_3 OH OH	
1	3	1	0	C_1 [4+1]	135.9 421.1 441.0 471.5 478.4	a a a a a	Cl OH OH OH OH	
2	1	1	0	C_1	274.2 307.1 383.3 529.2	a a a a	Cl Cl NH_3 OH	
2	1	1	1	C_s	154.1 255.4 275.5 371.1 506.5	a' a" a' a' a'	H_2O Cl Cl/H_2O NH_3 OH	 H_2O wag
2	1	1	2	C_1 [5+1]	159.7 164.6 251.8 273.1 290.3 371.3 479.3	a a a a a a a	H_2O Cl/H_2O Cl/H_2O $Cl/NH_3/H_2O$ Cl/H_2O NH_3 OH	 H_2O rock H_2O wag H_2O rock H_2O rock
2	1	2	0	C_s	211.2 259.9 316.0 363.3 401.2 459.6	a' a' a' a" a" a'	Cl/NH_3 Cl Cl/NH_3 NH_3 NH_3 OH	

2	1	2	1	C_1 [5+1]	222.7 295.3 354.0 385.4 411.5 512.2	a a a a a a	Cl/H_2O Cl/H_2O $Cl/NH_3/H_2O$ NH_3/H_2O NH_3 OH	 H_2O wag
2	1	3	0	C_1 [5+1]	217.9 308.3 349.1 385.1 497.2 516.3	a a a a a a	Cl Cl/NH_3 NH_3 NH_3 OH OH	
2	2	1	0	C_s [3+2]	414.0 544.9 654.0	a' a' a"	NH_3 OH OH	
2	2	1	1	C_1 [4+2]	355.3 407.0 479.7 538.0	a a a a	H_2O NH_3 OH OH	 H_2O rock
2	2	2	0	C_2 [4+2]	377.6 387.7 472.8 520.9	b a a b	NH_3 NH_3 OH OH	
3	1	1	0	C_1 [4+1]	232.8 252.8 255.1 269.7 500.4	a a a a a	Cl Cl Cl Cl OH	
3	1	1	1	C_1 [4+2]	294.6 382.6 432.0 546.1	a a a a	Cl H_2O NH_3 OH	 H_2O twist H_2O rock
3	1	2	0	C_s [4+2]	283.9 379.5 421.4 537.0	a' a" a' a'	Cl NH_3 NH_3 OH	

Table 3A.45: Ni-N, Ni-Cl and Ni-O vibrational stretching frequencies for optimized geometries of $[NiCl_m(OH)_n(NH_3)_l(H_2O)_k]^{2-m-n}$, where m=1 – 3, n=0 – (4-m), l=0 – (6-n-m), k=0 – (6-m-n-l) calculated at B3LYP/6-31+G*.

m	n	l	k	Point Group Symmetry	Freq. (cm^{-1})	Irr. Rep. Symm.	Cl/OH/H_2O /NH_3	Mixing
1	1	1	0	C_s #1	353.7	a'	Cl/NH_3	
					367.8	a'	Cl/NH_3	
					639.8	a'	Cl/OH	
					700.0	a'	Cl/OH	
1	1	1	1	C_1	244.1	a	H_2O	
					259.5	a	H_2O	
					310.2	a	Cl/H_2O	H_2O rock
					351.8	a	Cl/NH_3/H_2O	H_2O twist
					398.5	a	NH_3	H_2O rock
					537.3	a	OH	
1	1	1	2	C_1	210.4	a	Cl/H_2O	
					271.8	a	Cl/H_2O	H_2O rock
					278.8	a	Cl/H_2O	H_2O rock
					306.2	a	Cl/H_2O	H_2O rock
					380.8	a	NH_3	H_2O rock
					517.9	a	OH	H_2O twist
					553.5	a	OH	H_2O wag
1	1	1	3	mer-C_1	179.3	a	Cl/NH_3/H_2O	H_2O wag
					221.6	a	Cl/H_2O	H_2O rock
					223.6	a	Cl/OH/NH_3/H_2O	
					254.8	a	Cl/NH_3/H_2O	H_2O rock
					277.6	a	Cl/H_2O	H_2O rock
					280.1	a	Cl/NH_3/H_2O	H_2O rock
					356.3	a	NH_3	H_2O rock
					475.1	a	OH/NH_3	H_2O rock
					494.5	a	OH	H_2O rock
1	1	2	0	C_1	300.4	a	Cl/NH_3	
					344.8	a	Cl/NH_3	
					355.3	a	NH_3	
					373.6	a	NH_3	
					559.3	a	OH	
1	1	2	1	C_1 [4+1]	286.6	a	Cl/NH_3	
					297.7	a	Cl/NH_3	
					341.9	a	Cl/NH_3	
					383.7	a	NH_3	
					497.5	a	OH	

1	1	2	2	C_1 #1 [5+1]	181.3 275.1 359.0 385.6 468.6	a a a a a	Cl/H_2O Cl/H_2O NH_3 NH_3 OH	 H_2O rock H_2O wag H_2O twist
1	1	3	0	C_1	209.3 278.4 310.4 334.6 504.5 557.9	a a a a a a	Cl/NH_3 Cl/NH_3 NH_3 NH_3 OH OH	
1	1	3	1	C_1 [5+1]	219.0 291.6 307.9 338.7 345.6 438.8	a a a a a a	Cl/NH_3 Cl/NH_3 Cl/NH_3 NH_3 Cl/NH_3 OH	
1	1	4	0	cis-C_s	191.9 209.4 233.7 265.1 281.8 303.0 447.2	a' a' a' a' a" a' a'	Cl/NH_3 Cl/NH_3 Cl/NH_3 Cl/NH_3 NH_3 Cl/NH_3 OH	
1	2	1	0	C_s	207.2 276.6 487.6 539.9 578.4	a' a' a' a" a"	Cl/NH_3 Cl/NH_3 OH OH OH	
1	2	1	1	C_1 [4+1]	246.1 265.4 356.6 367.9 465.3 493.1	a a a a a a	Cl Cl NH_3 NH_3 OH OH	
1	2	1	2	C_1 [5+1]	236.8 246.9 341.6 432.3 507.6	a a a a a	NH_3/H_2O H_2O NH_3/H_2O OH OH	
1	2	2	0	C_1 [4+1]	329.2 363.8 490.4 518.3	a a a a	NH_3 NH_3 OH OH	

1	2	2	1	C_1 [5+1]	185.0 213.6 249.4 311.8 342.3 406.5 431.2 452.5	a a a a a a a a	Cl/NH_3 Cl/NH_3 Cl/NH_3 NH_3 NH_3 OH/NH_3 OH OH	
1	2	3	0	C_1 [4+2]	342.2 351.9 366.7 388.3 470.5 511.8	a a a a a a	NH_3 NH_3 NH_3 NH_3 OH OH	
2	1	1	0	C_1	238.1 264.5 372.0 530.4	a a a a	Cl Cl NH_3 OH	
2	1	1	1	C_1	141.5 210.4 248.5 363.1 510.4	a a a a a	H_2O Cl Cl/H_2O NH_3 OH	 H_2O wag
2	1	1	2	C_1 [5+1]	128.8 219.8 250.8 267.4 354.9 372.1 477.3	a a a a a a a	H_2O Cl/H_2O Cl $Cl/NH_3/H_2O$ NH_3 NH_3 OH	 H_2O rock H_2O rock H_2O rock
2	1	2	0	C_s	180.1 212.0 316.4 370.3 403.7 454.0	a' a' a' a" a" a'	Cl/NH_3 Cl Cl/NH_3 NH_3 NH_3 OH	
2	1	2	1	C_1 [5+1]	190.3 257.8 263.2 328.2 367.0 521.2	a a a a a a	Cl/H_2O Cl/H_2O $Cl/NH_3/H_2O$ $Cl/NH_3/H_2O$ NH_3 OH	 H_2O wag

2	1	3	0	C_1 [5+1]	164.1 172.5 187.5 292.5 315.3 356.3 527.5	a a a a a a a	Cl Cl Cl Cl/NH_3 NH_3 NH_3 OH	
2	2	1	0	C_s [3+2]	380.9 561.0 662.8	a' a' a"	NH_3 OH OH	
2	2	1	1	C_1 [4+2]	282.1 301.5 376.5 481.5 537.6	a a a a a	H_2O H_2O NH_3 OH OH	 H_2O rock
2	2	2	0	C_2 [4+2]	317.5 348.1 349.4 478.9 507.1	b b a a b	NH_3 NH_3 NH_3 OH OH	
3	1	1	0	C_1 [4+1]	200.4 207.0 240.0 497.9	a a a a	Cl Cl Cl OH	
3	1	1	1	C_1 [4+2]	258.6 365.9 405.7 536.1	a a a a	Cl H_2O NH_3 OH	 H_2O twist H_2O rock
3	1	2	0	C_s [4+2]	218.9 241.8 358.2 403.9 537.2	a' a' a" a' a'	Cl Cl NH_3 NH_3 OH	

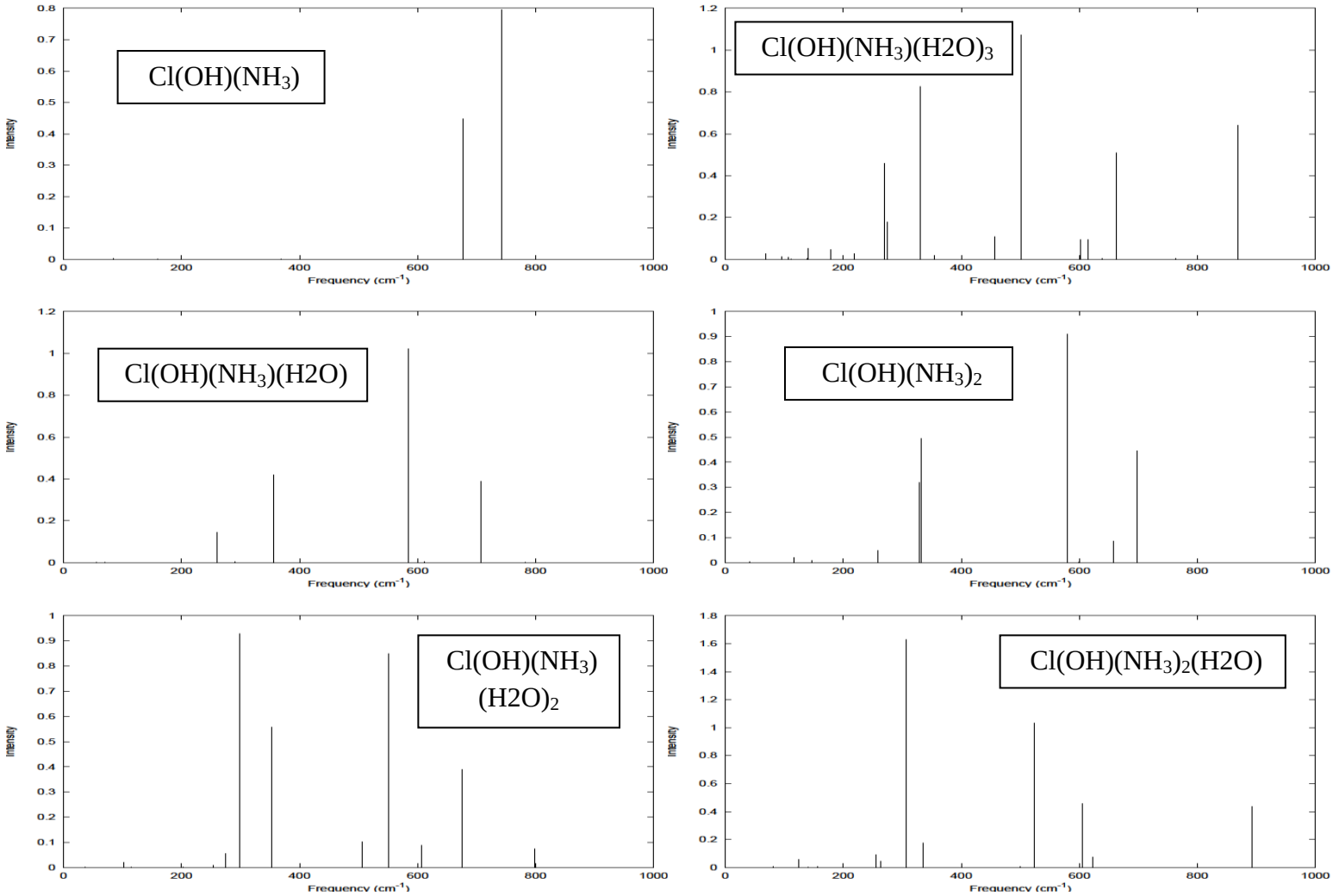


Figure 3A-8: Simulated polarized Raman spectra for $[NiCl_m(OH)_n(NH_3)_l\ (H_2O)_k]^{2-m-n}$, where m=1 – 3, n=0 – (4-m), l=0 – (6-n-m), k=0 – (6-m-n-l)

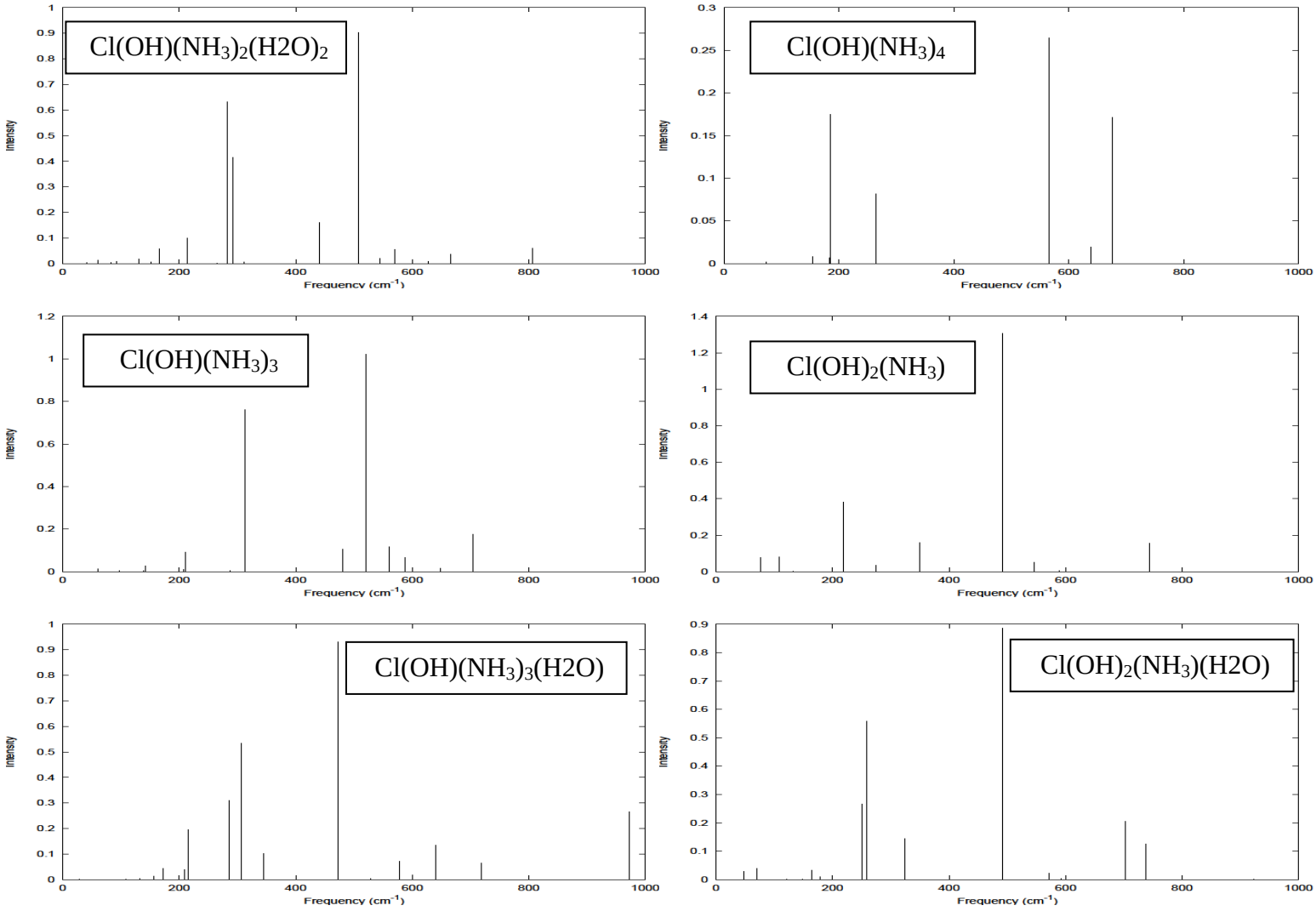


Figure 3A-8: *(continued)*

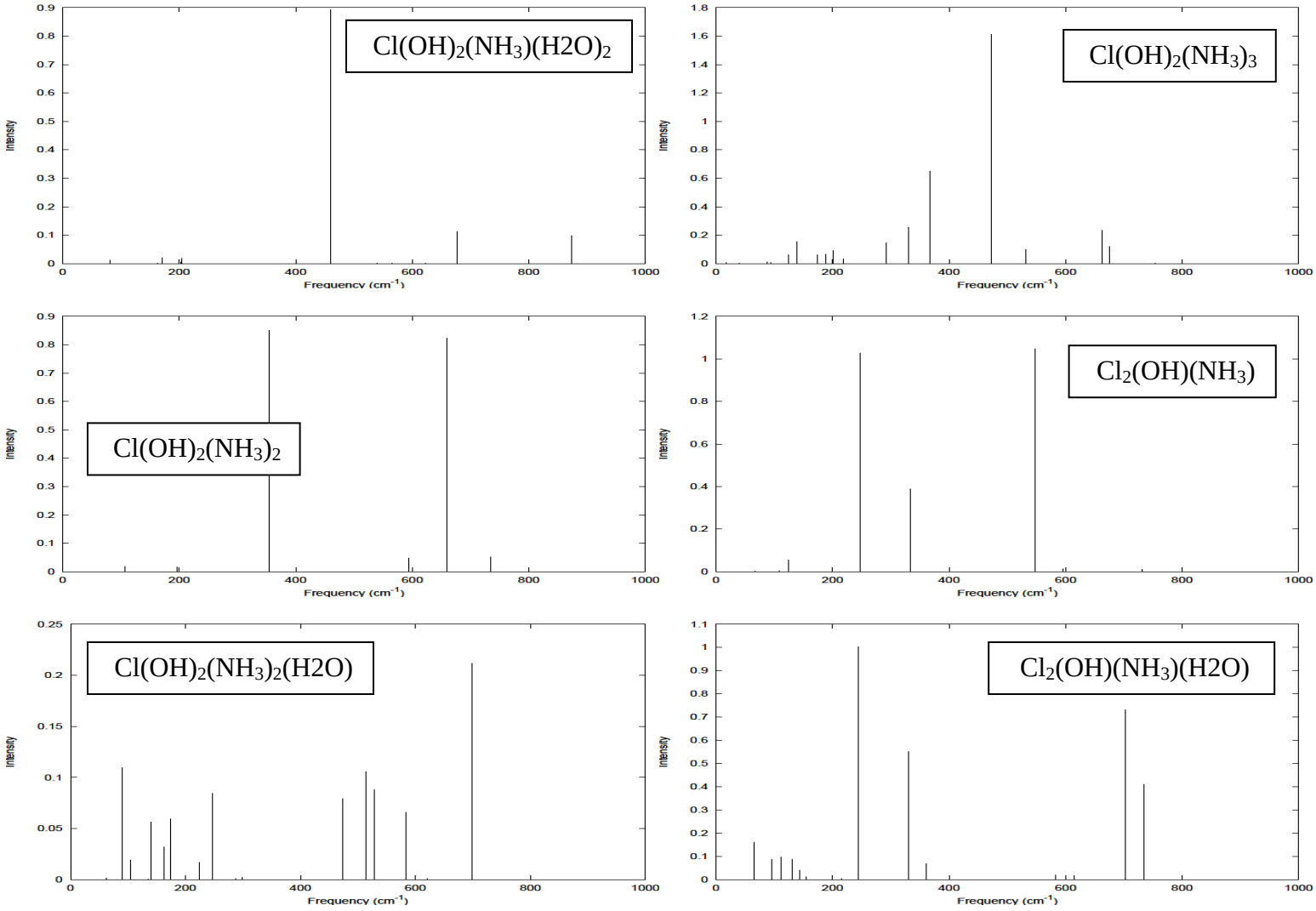


Figure 3A-8: *(continued)*

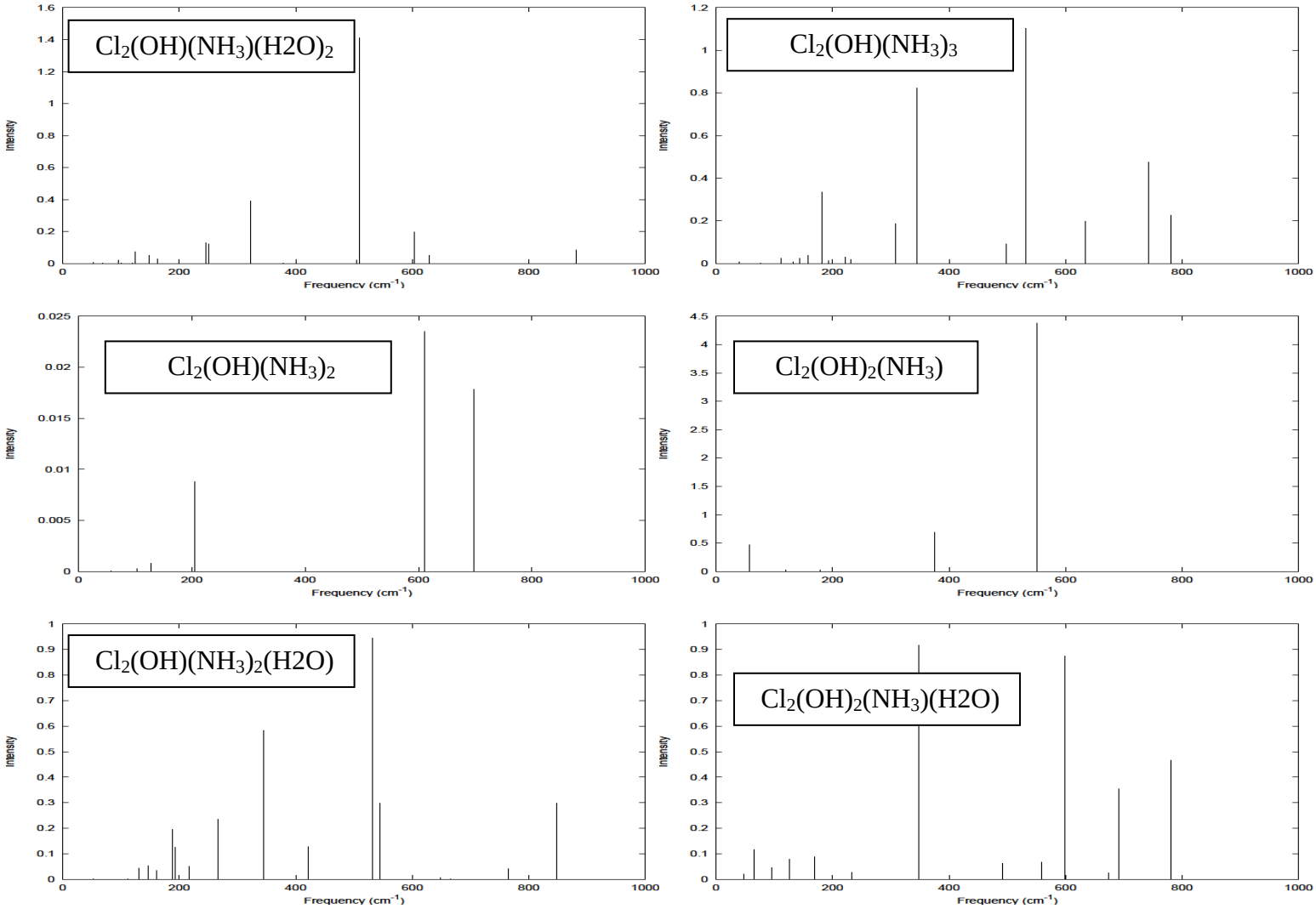


Figure 3A-8: *(continued)*

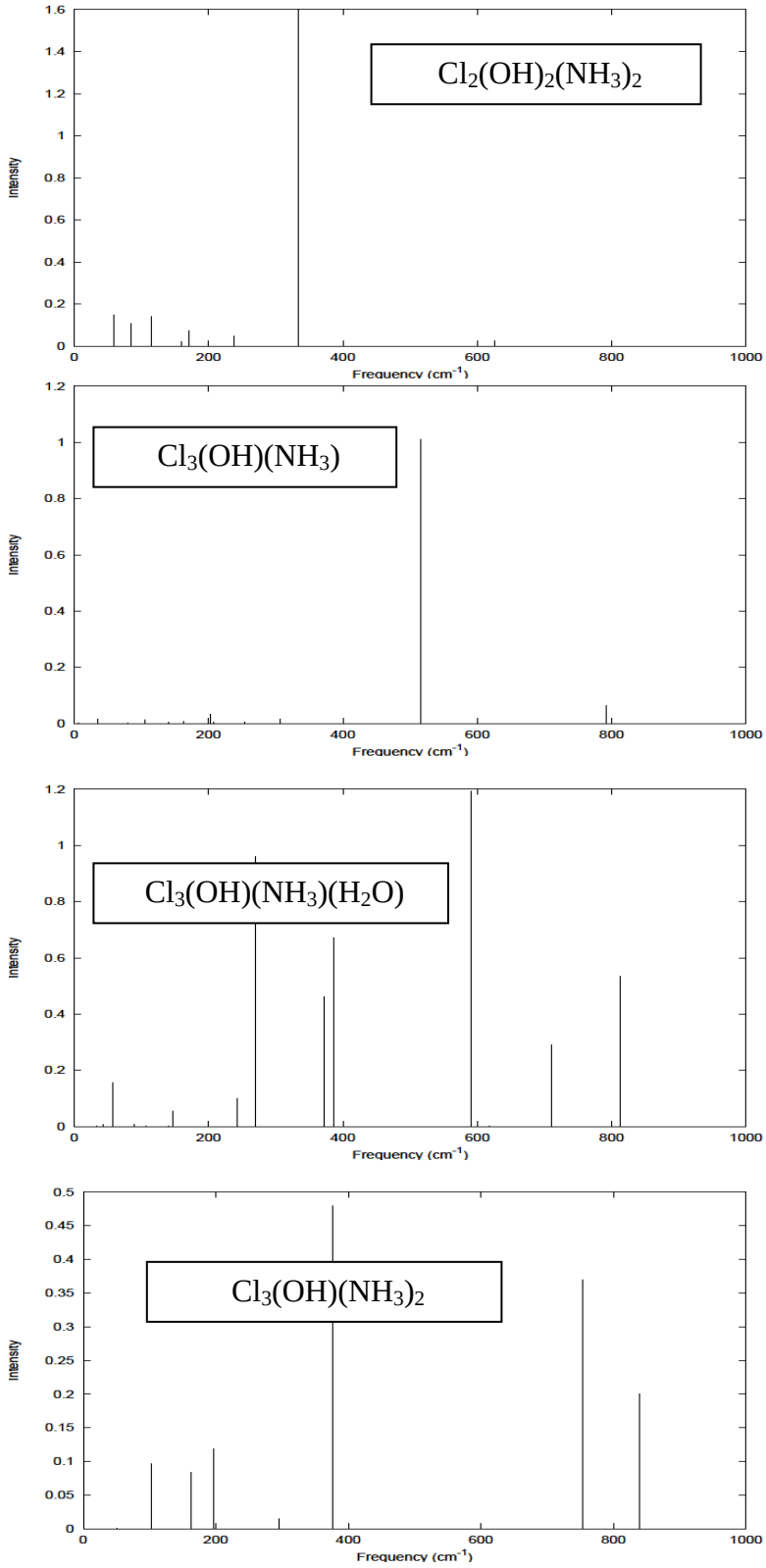


Figure 3A-8: *(continued)*