

Tautomeric Equilibria of Pyridoxal-5'-Phosphate (Vitamin B₆) and 3-Hydroxypyridine Derivatives: A Theoretical Study of Solvation Effects

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4N	S5	4N···2H ₂ O	S8
4Z	S5	4Z···2H ₂ O	S8
5N	S5	5N···2H ₂ O	S8-S9
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TABLE S1. Calculated B3LYP/6-31G* Vibrational Frequencies^a (cm⁻¹) and Infrared Intensities (km mol⁻¹) of the Neutral Form of 3-Hydroxypyridine (1N)

	frequency				intensity			
	<i>e</i> =1.0		<i>e</i> =2.0 ^b	<i>e</i> =40.0 ^b	<i>e</i> =1.0		<i>e</i> =2.0 ^c	<i>e</i> =40.0 ^c
	calc	expt ^d			calc	expt ^d		
v ₁	224		0	0	0		0	0
v ₂	362		-6	-13	131		9	22
v ₃	381		0	-1	14		3	9
v ₄	409		0	0	2		0	-1
v ₅	502		0	1	0		0	0
v ₆	531	542	0	0	6	7	1	2
v ₇	611	620	0	0	4	4	1	2
v ₈	693	704	0	-1	15	27	1	2
v ₉	787	801	-1	-1	30	43	1	2
v ₁₀	811	830	0	1	7	6	1	4
v ₁₁	862	887	0	0	1	2	0	0
v ₁₂	901	924	-1	-2	1	1	0	0
v ₁₃	944	969	0	-1	1	1	0	0
v ₁₄	993	990	0	0	7	0	1	3
v ₁₅	1028	1022	0	0	1	10	0	2
v ₁₆	1093	1100	0	0	7	12	1	3
v ₁₇	1164	1165	-2	-6	93	54	29	95
v ₁₈	1191	1195	-1	-2	45	55	4	7
v ₁₉	1262	1249	0	0	103	78	19	55
v ₂₀	1288	1277	0	0	3	17	1	3
v ₂₁	1335	1346	-1	-2	28	11	4	11
v ₂₂	1430	1440	-1	-4	109	106	18	53
v ₂₃	1479	1488	0	0	17	15	2	8
v ₂₄	1577	1578	0	-1	22	15	4	12
v ₂₅	1592	1591	0	-1	16	24	3	11
v ₂₆	3010	3001	1	2	41	19	8	23
v ₂₇	3059	3029	-2	-5	13	4	5	15
v ₂₈	3081	3040	0	-1	18	9	4	12
v ₂₉	3096	3061	1	2	7	8	0	0
v ₃₀	3595	3626	1	2	44	89	10	31

^a Scaled by a factor of 0.9613 (Ref. 18).

^b Frequency shift from the gas phase to solution.

^c Intensity change from the gas phase to solution.

^d Taken from Ref 8a.

TABLE S2. Calculated B3LYP/6-31G* Vibrational Frequencies^a (cm⁻¹) and Infrared Intensities (km mol⁻¹) of the Zwitterionic Form of 3-Hydroxypyridine (1Z)

	frequency			intensity		
	<i>e</i> =1.0	<i>e</i> =2.0 ^b	<i>e</i> =40.0 ^b	<i>e</i> =1.0	<i>e</i> =2.0 ^c	<i>e</i> =40.0 ^c
v ₁	166	6	17	2	0	0
v ₂	400	1	2	3	0	-1
v ₃	416	0	1	3	1	2
v ₄	473	4	12	22	0	-1
v ₅	520	1	2	7	3	10
v ₆	582	2	5	0	0	0
v ₇	645	2	5	24	7	10
v ₈	657	22	56	40	3	23
v ₉	759	4	13	53	3	2
v ₁₀	793	2	6	1	0	0
v ₁₁	814	3	9	12	-2	-7
v ₁₂	848	6	19	23	-1	-4
v ₁₃	949	1	3	0	0	0
v ₁₄	966	0	1	16	5	14
v ₁₅	1011	2	5	22	0	-4
v ₁₆	1066	1	3	8	2	8
v ₁₇	1144	3	7	4	2	5
v ₁₈	1214	2	4	5	4	15
v ₁₉	1239	3	8	14	3	9
v ₂₀	1339	-2	-7	42	11	33
v ₂₁	1411	-2	-7	30	0	-1
v ₂₂	1482	-1	-4	1	0	0
v ₂₃	1519	4	10	2	1	5
v ₂₄	1569	0	-2	17	24	158
v ₂₅	1653	-11	-31	412	80	153
v ₂₆	3077	-1	-8	9	1	16
v ₂₇	3093	-2	0	8	4	5
v ₂₈	3125	0	-2	1	1	2
v ₂₉	3142	4	6	0	1	8
v ₃₀	3424	1	-7	40	20	70

^a Scaled by a factor of 0.9614 (Ref. 18).

^b Frequency shift from the gas phase to solution.

^c Intensity change from the gas phase to solution.

TABLE S3. Cartesian coordinates of B3LYP/6-31G* Optimized Geometries

1N				1Z			
HF= -323.5005925 Hartrees				HF= -323.4802263 Hartrees			
No of imaginary frequencies = 0				No of imaginary frequencies = 0			
H	2.1925804	0.0000000	0.6800776	H	2.1783459	0.0000000	0.8539261
C	1.2328462	0.0000000	0.1724909	C	1.2390501	0.0000000	0.3083647
N	-1.2732203	0.0000000	-1.0889114	N	-1.1207952	0.0000000	-1.0563258
C	0.0543246	0.0000000	0.9223783	C	0.0182573	0.0000000	1.1054345
C	1.1273362	0.0000000	-1.2147293	C	1.2263982	0.0000000	-1.0719068
C	-0.1411027	0.0000000	-1.8013192	C	0.0223654	0.0000000	-1.7814862
C	-1.1697621	0.0000000	0.2420076	C	-1.1805717	0.0000000	0.2873477
O	0.1480018	0.0000000	2.2837202	O	-0.0256240	0.0000000	2.3460991
H	2.0181964	0.0000000	-1.8361834	H	2.1557575	0.0000000	-1.6341303
H	-0.2524945	0.0000000	-2.8836098	H	-0.0712662	0.0000000	-2.8582734
H	-2.1056086	0.0000000	0.8055479	H	-2.1644025	0.0000000	0.7403939
H	-0.7459985	0.0000000	2.6618164	H	-2.0008724	0.0000000	-1.5629520

2N				2Z			
HF= -362.8213385 Hartrees				HF= -362.8049327 Hartrees			
No of imaginary frequencies = 0				No of imaginary frequencies = 0			
H	0.6400164	-2.2306909	-1.1844582	H	-2.3372813	0.0000000	1.2449220
C	0.6014943	-1.3912524	-0.4968361	C	-1.2805639	0.0000000	0.9942231
N	0.4455722	0.7989222	1.2312101	N	1.3670377	0.0000000	0.3529982
C	-0.3252566	-0.3726883	-0.7146839	C	-0.9414423	0.0000000	-0.4127991
C	1.4489095	-1.2923534	0.6027617	C	-0.3181183	0.0000000	1.9895095
C	1.3334964	-0.1801756	1.4368870	C	1.0369904	0.0000000	1.6722865
C	-0.3760304	0.7166739	0.1769687	C	0.4950627	0.0000000	-0.6709457
O	-1.1520659	-0.4808126	-1.7983034	O	-1.7536544	0.0000000	-1.3577532
H	2.1851989	-2.0637103	0.8089059	H	-0.6060630	0.0000000	3.0368015
H	1.9783936	-0.0677070	2.3061870	H	1.8507519	0.0000000	2.3835368
C	-1.3664555	1.8391414	-0.0260883	C	0.9922511	0.0000000	-2.0771904
H	-1.2375988	2.5715715	0.7729920	H	2.3550905	0.0000000	0.1163149
H	-1.7408872	0.2885922	-1.8280218	H	0.6027365	0.8743293	-2.6117639
H	-2.4070996	1.4847429	0.0040271	H	0.6027365	-0.8743293	-2.6117639
H	-1.2174468	2.3551731	-0.9857309	H	2.0869224	0.0000000	-2.1375121

3N				3Z			
HF= -476.156386 Hartrees				HF= -476.1334471 Hartrees			
No of imaginary frequencies = 0				No of imaginary frequencies = 0			
C	0.3891666	-0.0000100	-2.2963153	C	-0.6532991	0.0000000	-2.2602132
C	0.5690381	-0.0000062	-0.8479366	C	-0.0087946	0.0000000	-0.9341507
N	0.8892349	0.0000022	1.9270223	N	1.2572732	0.0000000	1.4925367
C	-0.5511136	-0.0000041	0.0097115	C	-0.8371022	0.0000000	0.2599875
C	1.8524616	-0.0000042	-0.2703540	C	1.3856214	0.0000000	-0.8535230
C	1.9607165	-0.0000003	1.1080569	C	2.0327973	0.0000000	0.3639672
C	-0.3382462	0.0000004	1.4135626	C	-0.0802358	0.0000000	1.5164745
O	-1.8137851	-0.0000076	-0.4439419	O	-2.0810401	0.0000000	0.2904314
H	2.7358929	-0.0000057	-0.9043735	H	1.9540918	0.0000000	-1.7787074
H	2.9326643	0.0000013	1.5952506	H	3.1037570	0.0000000	0.5104560
C	-1.5159788	0.0000026	2.3494312	C	-0.8109109	0.0000000	2.8154663
H	-1.7698164	-0.0000140	-1.4328081	H	1.7357273	0.0000000	2.3893119
H	-2.1503285	-0.8790833	2.1845779	O	-0.0351758	0.0000000	-3.3154551
H	-2.1503290	0.8790873	2.1845731	H	-1.7577471	0.0000000	-2.2370707
H	-1.1578630	0.0000056	3.3806254	H	-1.4697633	-0.8741920	2.8709342

O	-0.7081741	0.0000216	-2.8547824	H	-1.4697633	0.8741921	2.8709342
H	1.3145439	0.0000127	-2.9041451	H	-0.1359455	0.0000000	3.6785225

4N

HF= -551.3542521 Hartrees

No of imaginary frequencies = 0

C	-0.1914258	-1.5525363	0.9050035
C	-0.1022594	-0.3816065	0.0249733
N	-0.0104904	1.8284215	-1.7141008
C	-1.0276704	-0.2443737	-1.0360164
C	0.8845528	0.6259620	0.1834864
C	0.8735300	1.6933088	-0.7059351
C	-0.9292477	0.8895495	-1.8731373
O	-1.9944942	-1.1331886	-1.2877889
C	1.9330013	0.5734007	1.2765939
H	1.6121625	2.4875862	-0.6135631
H	-1.6426184	1.0009959	-2.6872307
H	0.8159556	1.2469799	2.7302118
H	-1.9064183	-1.8562159	-0.6136041
O	-1.0315510	-2.4433908	0.7535436
H	0.5217988	-1.6143773	1.7397973
H	2.5667174	-0.3130444	1.1658284
O	1.3852694	0.4735876	2.5896644
H	2.5891566	1.4508317	1.1841037

4Z

HF= -551.3333201 Hartrees

No of imaginary frequencies = 0

C	-0.2398213	0.9216176	-1.6272587
C	-0.3033909	0.0427705	-0.4530038
N	-0.5656477	-1.6619575	1.6861519
C	-1.1640661	-1.1391417	-0.6067738
C	0.3704488	0.3110494	0.7550975
C	0.2270998	-0.5634116	1.8252118
C	-1.2384643	-1.9755425	0.5802021
O	-1.7904242	-1.4461851	-1.6327884
C	1.2493612	1.5408161	0.9723160
H	0.7157123	-0.4373657	2.7815520
H	-1.8427036	-2.8743501	0.5853024
H	-0.6467364	-2.2856235	2.4845358
O	0.5151220	1.8817085	-1.7814462
H	-0.9590231	0.6528505	-2.4175928
H	0.6314331	2.4391767	0.8232541
O	2.4002024	1.5609559	0.1617652
H	1.5929054	1.5485779	2.0125364
H	2.0617421	1.7896557	-0.7276424

5N

HF= -590.6767656 Hartrees

No of imaginary frequencies = 0

C	1.9468589	-0.5760255	-0.0934321
C	0.5292183	-0.2246852	0.0381739
N	-2.1922545	0.4362660	0.1856459
C	-0.2986634	-0.2614748	-1.1045315
C	-0.0541779	0.1491154	1.2783381
C	-1.4035702	0.4670800	1.2784821
C	-1.6737050	0.0828238	-0.9837709
O	0.1505513	-0.6072970	-2.3182455
C	0.7353466	0.2089265	2.5691375
H	-1.8938716	0.7632744	2.2044579
C	-2.5625120	0.0520841	-2.1960054
H	1.1161108	-0.8198820	-2.2195068
H	-2.5867091	-0.9497159	-2.6412145
H	-2.1918845	0.7299195	-2.9742044
H	-3.5739575	0.3465435	-1.9098448
H	0.0590268	0.4979695	3.3867570
O	1.8696354	1.0728428	2.5075835
H	1.1438687	-0.7747495	2.8247833
H	1.5501583	1.9579105	2.2695999
O	2.4597557	-0.9266216	-1.1603455
H	2.5707292	-0.5035927	0.8093616

5Z

HF= -590.6596012 Hartrees

No of imaginary frequencies = 0

C	-0.5834114	1.2120870	1.5819714
C	-0.0899122	0.3462526	0.5076493
N	0.9409659	-1.3483752	-1.3925288
C	0.6455343	-0.8352586	0.9502890
C	-0.2685736	0.6283516	-0.8667839
C	0.2573761	-0.2378983	-1.8072279
C	1.1630048	-1.6879875	-0.1233798
O	0.8558554	-1.1630378	2.1319384
C	-0.9969034	1.8661763	-1.3826718
H	0.1632005	-0.1060260	-2.8764176
C	1.9251210	-2.9225505	0.2136722
H	1.3080874	-1.9653608	-2.1126573
O	-1.3333187	2.1815245	1.4564818
H	-0.2178774	0.9264026	2.5816159
H	2.2663833	-3.4615754	-0.6768065
H	-0.4692179	2.7588320	-1.0136479
O	-2.3646659	1.8977407	-1.0490532
H	-0.9361361	1.8791609	-2.4765410
H	-2.3709648	2.1159603	-0.0947217
H	1.3040144	-3.5879564	0.8242184
H	2.7893692	-2.6656658	0.8366128

6N

HF= -1158.3942462 Hartrees

No of imaginary frequencies = 0

N	2.0791410	2.6165038	0.2702937
C	2.9292237	1.6606048	0.6230380
C	4.2722207	2.0475270	1.1761318

6Z

HF= -1158.3745255 Hartrees

No of imaginary frequencies = 0

N	1.0244880	2.4367324	-0.6790837
C	2.3421990	2.2686735	-0.7980718
C	3.2161845	3.3882111	-1.2471476

C	2.5888073	0.2853779	0.4880776
O	3.5002278	-0.6184429	0.8685607
C	1.3272457	-0.0698806	-0.0359739
H	-0.8987982	0.0300517	-1.8178809
C	0.4390687	0.9758102	-0.4007939
C	0.8711275	2.2799564	-0.2219678
C	-0.9299212	0.7220010	-0.9705536
O	-1.7946227	0.1691301	0.0644691
P	-2.9223760	-0.9052252	-0.3715008
O	-4.1541636	-0.0533790	-0.9575477
O	-3.4946757	-1.3412706	1.0718003
O	-2.4428872	-1.9640762	-1.2812354
H	0.0116065	-1.7464943	-0.6226149
H	4.3532444	3.1357968	1.2005399
H	4.4107498	1.6487367	2.1881369
H	5.0832754	1.6344377	0.5647367
H	3.1028144	-1.5155219	0.7091763
H	-2.9772014	-2.0637618	1.4642095
H	-4.5353369	0.5567096	-0.3038292
C	0.9907969	-1.4891192	-0.1889247
H	0.2209496	3.1116117	-0.4875743
H	-1.3718545	1.6636294	-1.3095469
O	1.7549700	-2.4002128	0.1440656

1N⁺⁺H₂O

HF= -399.9260287 Hartrees

No of imaginary frequencies = 0

H	-1.0276521	2.3698561	0.0002630
C	-1.0834050	1.2852431	0.0001410
N	-1.1740969	-1.5161729	-0.0001610
C	0.0985380	0.5365691	-0.0002040
C	-2.2985180	0.6075370	0.0003100
C	-2.2977599	-0.7892580	0.0001470
C	-0.0078629	-0.8644439	-0.0003350
O	1.2864740	1.1903712	-0.0004350
H	-3.2370950	1.1551630	0.0005770
H	-3.2330619	-1.3458970	0.0002690
H	0.8960581	-1.4737878	-0.0005550
H	2.0274900	0.5432772	-0.0003610
O	3.4914661	-0.5181847	0.0004360
H	4.0518751	-0.3332057	0.7698770
H	4.0515891	-0.3335717	-0.7693040

1N⁺⁺2H₂O

HF= -476.3489835 Hartrees

No of imaginary frequencies = 0

H	-2.7667420	-1.1846333	0.0317542
C	-1.9089562	-0.5280118	0.1426316
N	0.3276077	1.1214530	0.4046204
C	-0.6497839	-0.9701731	-0.2811034
C	-2.0207898	0.7447629	0.6921466
C	-0.8797018	1.5403845	0.8057440
C	0.4413133	-0.1005309	-0.1252949
O	-0.5399672	-2.2080342	-0.8184238
H	-2.9832773	1.1192616	1.0286505
H	-0.9134490	2.5430256	1.2234845

C	2.9299420	0.9662323	-0.4819519
O	4.1604275	0.8128082	-0.5850689
C	1.9770974	-0.0577690	-0.0690104
H	-0.4354121	-1.6411757	-0.2744589
C	0.5969673	0.2210638	0.0326303
C	0.1292107	1.4858395	-0.2774617
C	-0.3938406	-0.8369087	0.4654034
O	-1.7018707	-0.2263937	0.6176532
P	-3.0147940	-1.1018727	0.3045799
O	-4.1602837	-0.0772688	0.7814507
O	-2.9279871	-2.2348846	1.4646637
O	-3.2122746	-1.6252149	-1.0582907
H	0.6488963	3.3528755	-0.9094934
H	3.7736692	3.0872301	-2.1413990
H	2.6513499	4.3017574	-1.4626158
H	3.9712689	3.6011907	-0.4816912
H	-3.2920022	-3.0745648	1.1376008
H	-0.1081537	-1.2850344	1.4179805
H	-4.0415289	0.2055818	1.7034533
C	2.5301130	-1.3845450	0.2248680
H	-0.9078600	1.7771561	-0.2310503
O	1.8665454	-2.3627857	0.5558886
H	3.6265731	-1.4489223	0.1206395

1Z⁺⁺H₂O

HF= -399.9116452 Hartrees

No of imaginary frequencies = 0

H	1.0857621	2.4021331	0.0169191
C	1.0503661	1.3167961	0.0109691
N	0.9498810	-1.4039869	-0.0063109
C	-0.2585889	0.7013061	-0.0069239
C	2.2156431	0.5711041	0.0160271
C	2.1731890	-0.8221219	0.0059411
C	-0.2197020	-0.7421819	-0.0100119
O	-1.3386839	1.3428752	-0.0192189
H	3.1848801	1.0604541	0.0266641
H	3.0348710	-1.4747949	0.0065041
H	-1.1408870	-1.3168498	-0.0184429
H	0.9071350	-2.4184219	-0.0155739
H	-2.7355309	0.1923442	-0.1393669
O	-3.2945070	-0.6206578	-0.0731299
H	-3.6853140	-0.5441108	0.8102551

1Z⁺⁺2H₂O

HF= -476.3390909 Hartrees

No of imaginary frequencies = 0

H	2.4975411	-0.6571960	-1.8669394
C	1.5474215	-0.7507212	-1.3489543
N	-0.8394097	-0.9817465	-0.0489778
C	1.1561869	0.3381156	-0.4826780
C	0.7522052	-1.8702529	-1.5268269
C	-0.4708873	-1.9923462	-0.8669016
C	-0.1113636	0.1237039	0.1666415
O	1.8377014	1.3813084	-0.2990525
H	1.0695266	-2.6715700	-2.1876811
H	-1.1479940	-2.8304773	-0.9588503

H	1.4355762	-0.4113757	-0.4424198
H	1.4027886	2.7166256	0.7827359
H	0.3921526	-2.3819415	-1.0828167
O	1.5918847	3.5863975	1.1951696
H	1.8783920	3.3457714	2.0884789
O	2.0590689	-2.7795337	-1.6279960
H	2.3761548	-3.6214061	-1.2660373
H	2.1047694	-2.8847249	-2.5909144

H	-0.5099523	0.8644401	0.8511376
H	-1.7352097	-1.0129154	0.4544393
H	0.9229537	2.5069908	0.7720194
O	0.3277816	2.8848650	1.4691547
H	0.8930259	2.8780216	2.2561539
O	-3.0753815	-0.2487902	1.5478773
H	-2.7530880	-0.0534361	2.4417004
H	-3.3231251	0.6183072	1.1893441

2N⁺⁺2H₂O

HF= -515.6687307 Hartrees

No of imaginary frequencies = 0

H	0.2556417	1.2984319	2.8936156
C	-0.0323363	0.5584241	2.1529846
H	-1.1727238	-2.5049765	-1.2675569
C	0.1973576	0.8346144	0.8020407
C	-0.6123958	-0.6544051	2.5098193
C	-0.9482617	-1.5535903	1.5007787
C	-0.1928395	-0.1214220	-0.1620787
O	0.7632754	2.0271635	0.4952422
H	-0.7964429	-0.9000782	3.5515059
H	-1.3965472	-2.5173735	1.7303676
C	-0.0100736	0.1279298	-1.6389001
H	-0.4689624	-0.6860793	-2.2049044
H	1.1030393	2.0694744	-0.4247254
H	1.0535424	0.1695857	-1.9094725
H	-0.4607704	1.0813667	-1.9435930
O	2.3166721	2.6023179	-1.7302426
H	2.5824158	1.9830839	-2.4264580
H	3.1422050	2.8484725	-1.2847714
N	-0.7473586	-1.2882671	0.2040937
O	-1.4125856	-2.9119824	-2.1300286
H	-2.3574868	-2.7133347	-2.2102995

2Z⁺⁺2H₂O

HF= -515.6593171 Hartrees

No of imaginary frequencies = 0

H	2.6336157	0.0883031	1.8450228
C	1.5854833	0.0535692	1.5626505
N	-1.0348519	-0.0200974	0.8317472
C	1.2791808	0.2729047	0.1743334
C	0.6028006	-0.1968520	2.5089640
C	-0.7345007	-0.2390505	2.1367510
C	-0.1378589	0.2297444	-0.1399177
O	2.1467516	0.4960616	-0.7119008
H	0.8652104	-0.3647286	3.5493356
H	-1.5649755	-0.4311550	2.8022170
C	-0.6200765	0.4763242	-1.5330532
H	-2.0264696	-0.0483454	0.5611020
H	-0.1172948	-0.1964591	-2.2390609
H	-0.3492377	1.4920511	-1.8491715
H	-1.7059906	0.3594595	-1.6114176
O	-3.8352713	-0.1465741	0.0796423
H	-4.0455114	-0.8467919	-0.5574481
H	-4.2070938	0.6608124	-0.3077855
H	2.0421004	-0.1304914	-2.4100426
O	1.8855101	-0.6630520	-3.2251675
H	2.2935157	-1.5132965	-3.0039412

3N⁺⁺2H₂O

HF= -628.9957693 Hartrees

No of imaginary frequencies = 0

C	2.8748642	0.4055726	0.6650369
C	1.4223028	0.3916732	0.8360346
H	-3.3521870	0.3911754	1.2016225
C	0.5755995	0.2027322	-0.2743156
C	0.8377985	0.5664035	2.1031624
C	-0.5403835	0.5425511	2.2046494
C	-0.8307299	0.2043919	-0.0847901
H	-4.4735794	-0.6456889	1.1388689
H	1.4633766	0.7160168	2.9792234
H	-1.0393346	0.6707432	3.1611771
C	-1.7629529	0.0313559	-1.2508099
H	3.4760672	0.5568525	1.5811335
O	1.0600099	0.0234815	-1.5208744
H	-1.5597052	-0.9037056	-1.7867530
H	-1.6203252	0.8415967	-1.9769068
H	-2.7961024	0.0488930	-0.8977378
O	3.4381200	0.2606304	-0.4193870
N	-1.3440568	0.3663576	1.1369077
O	-4.3119906	0.3031363	1.0285123

3Z⁺⁺2H₂O

HF= -628.9874022 Hartrees

No of imaginary frequencies = 0

C	0.8016714	0.7246108	-2.7797363
C	0.5955429	0.6978149	-1.3193560
N	0.2441656	0.7180142	1.3932835
C	0.1016308	-0.5071138	-0.6922109
C	0.8775612	1.8458547	-0.5703589
C	0.6971889	1.8593851	0.7941053
C	-0.0486461	-0.4226873	0.7588043
O	-0.1797871	-1.5675949	-1.3054203
H	1.2400802	2.7260001	-1.0923061
H	0.8861341	2.7016488	1.4456177
C	-0.5158971	-1.6030360	1.5442307
H	0.1179306	0.7373981	2.4149433
O	1.2078923	1.7037562	-3.3892121
H	0.5595435	-0.2193509	-3.2997578
H	0.1918490	-2.4330187	1.4234715
H	-1.4717041	-1.9715256	1.1498898
H	-0.6112712	-1.3671240	2.6085052
O	-0.1217517	0.8386458	4.2482232
H	0.4190117	0.2681795	4.8157052

H	0.3942054	-1.5166030	-2.7430508
H	2.0495064	0.0827419	-1.4615817
O	-0.0401602	-2.3206932	-3.0753362
H	0.2396488	-3.0070477	-2.4514723

H	-1.0251270	0.7486096	4.5885846
H	-1.5964564	-2.6750557	-0.8934858
O	-2.4526043	-3.0421087	-0.5792698
H	-3.1034564	-2.5724172	-1.1215897

4N⁺⁺2H₂O

HF= -704.1946109 Hartrees

No of imaginary frequencies = 0

C	2.4357527	0.1468094	0.3244364
C	0.9700277	0.0835329	0.2406327
H	-3.7202824	-0.4431228	0.5331669
C	0.3355715	0.3985389	-0.9814963
C	0.1525608	-0.2757781	1.3426802
C	-1.2224818	-0.3068614	1.1498933
C	-1.0711059	0.3311868	-1.0619184
H	-0.1026758	-0.8656870	3.3856301
C	0.7239495	-0.6214832	2.7041039
H	-1.9013079	-0.5820367	1.9534744
H	-1.5561356	0.5606943	-2.0088039
H	1.2523277	-2.4663363	2.3368311
O	1.0209119	0.7627284	-2.0812668
O	3.1451119	0.4841119	-0.6272328
H	2.9032656	-0.1350514	1.2782015
H	1.2499781	0.2383128	3.1330043
O	1.6926773	-1.6665283	2.6663421
H	-1.0014330	2.1562344	-4.2568914
H	1.9870558	0.7522569	-1.8402162
O	-0.9325968	1.1897780	-4.2469453
H	-0.0990870	1.0244697	-3.7735149
N	-1.8197586	-0.0114958	-0.0224463
O	-4.3596071	-0.6356944	1.2477349
H	-4.7510209	0.2298997	1.4371956

4Z⁺⁺2H₂O

HF= -704.1917904 Hartrees

No of imaginary frequencies = 0

C	-2.4923392	-0.2757533	-0.2060086
C	-1.0249977	-0.2331060	-0.1703784
N	1.7128903	0.0083488	-0.1042287
C	-0.4445862	1.0177073	0.3047641
C	-0.2037204	-1.3007717	-0.6005474
C	1.1752513	-1.1542340	-0.5590118
C	1.0007521	1.0496026	0.3118590
O	-1.1079685	2.0137482	0.6892455
C	-0.7543701	-2.6168622	-1.1414086
H	1.8726891	-1.9216673	-0.8674925
H	1.5263094	1.9336409	0.6598876
H	2.7364890	0.1299397	-0.0723517
O	-3.1894705	-1.2640817	-0.4341647
H	-2.9678749	0.6974339	-0.0036809
H	-1.3694157	-2.4003890	-2.0281276
O	-1.4685880	-3.3660062	-0.1855066
H	0.0851856	-3.2392632	-1.4694695
H	-2.3173206	-2.8878228	-0.0943650
O	4.3531144	0.9738398	0.1640036
H	4.5832273	1.1896484	1.0809962
H	4.4230234	1.8162736	-0.3119337
H	0.6874707	4.0351113	2.3193800
O	0.8131646	3.9241724	1.3650051
H	0.0120286	3.4157775	1.0924845

5N⁺⁺2H₂O

HF= -743.5161202 Hartrees

No of imaginary frequencies = 0

C	-2.4730730	-0.2478194	0.4473501
C	-1.0043215	-0.2140350	0.4161666
N	1.7820818	-0.1669805	0.2550611
C	-0.3348153	-0.4681240	-0.7987537
C	-0.2263878	0.0617354	1.5709004
C	1.1510947	0.0771314	1.4216018
C	1.0846323	-0.4400115	-0.8439686
H	4.6527071	-0.5285015	1.8025658
C	-0.8412177	0.3332910	2.9289182
H	1.8102535	0.2932154	2.2591818
C	1.8161512	-0.7214837	-2.1255875
H	3.6587420	0.1896030	0.8904059
H	-1.4115931	-0.5339505	3.2786943
O	-1.7745016	1.4117978	2.9266526
H	-0.0353368	0.5026562	3.6566129
H	1.4656141	-0.0773301	-2.9403634
H	1.6435413	-1.7555969	-2.4502357
H	2.8869512	-0.5728058	-1.9727703
O	-0.9995547	-0.7437211	-1.9394640
H	-1.2943708	2.2165410	2.6736785

5Z⁺⁺2H₂O

HF= -743.5134685 Hartrees

No of imaginary frequencies = 0

C	-2.5276854	-0.3261395	0.5060497
C	-1.0695255	-0.3343831	0.3505453
N	1.6615471	-0.1860939	0.1176588
C	-0.4494250	0.9723305	0.2154010
C	-0.2920811	-1.5194894	0.3585727
C	1.0786285	-1.4150905	0.2345842
C	1.0068826	0.9745656	0.1082378
O	-1.0799105	2.0587085	0.1918187
C	-0.8857609	-2.9142118	0.5218060
H	1.7526392	-2.2613737	0.2214929
C	1.7644820	2.2547687	-0.0034006
H	2.6875122	-0.1570481	0.0275383
O	-3.2710280	-1.3081743	0.4923088
H	-2.9526565	0.6805202	0.6482408
H	2.8382869	2.0769263	-0.1154552
H	1.5934267	2.8668847	0.8911919
H	1.3873521	2.8502822	-0.8449149
H	-0.0666600	-3.6407057	0.5605499
O	-1.7248057	-3.3017703	-0.5424929
H	-1.4119138	-2.9604981	1.4875299

O	-3.1603325	-0.5169843	-0.5418850	H	5.0873592	0.2481054	0.4773779
H	-2.9645298	-0.0048826	1.3996499	H	-2.5409888	-2.7804670	-0.4016654
O	4.2964229	0.3523760	1.6142793	O	4.5171165	-0.1752782	-0.1822583
H	-0.6019569	0.1880220	-3.7287207	H	4.8854542	0.0847547	-1.0404925
H	-1.9703968	-0.7530105	-1.7112438	H	-0.6738676	3.5082478	-0.8904704
O	-0.2297765	0.7549108	-4.4262009	O	-0.3348997	4.0840008	-1.6102939
H	-0.4046369	1.6537650	-4.1097013	H	-0.8216453	3.7730335	-2.3879700

6N⁺⁺2H₂O

HF= -1311.2345787 Hartrees

No of imaginary frequencies = 0

N	2.6210302	0.6221548	-0.3311197
C	2.6102335	-0.7080707	-0.3674243
C	3.9146630	-1.4511697	-0.4048728
C	1.3753048	-1.4127349	-0.3696057
H	2.4287398	-3.5930916	-1.9797123
C	0.1585985	-0.7033595	-0.3237745
H	-1.7134961	1.3313884	-1.0428296
C	0.2132029	0.7135664	-0.2787999
C	1.4634752	1.3085839	-0.2853871
C	-1.0170824	1.5792376	-0.2349363
O	-1.6831952	1.4070037	1.0475534
P	-3.2946716	1.4912214	1.0740881
O	-3.6467963	3.0522347	0.8735333
O	-3.5479719	1.2213821	2.6434445
O	-4.0004555	0.6132477	0.1194954
H	-2.0505541	-0.8820490	-0.3144962
H	4.7419408	-0.7388628	-0.3798623
H	3.9942203	-2.1271245	0.4557278
H	3.9758391	-2.0735687	-1.3062716
H	0.4733790	-3.0762882	-0.3887401
H	-4.1644412	0.4792906	2.7605557
H	-3.3251608	3.6080289	1.6035847
C	-1.1085590	-1.4503110	-0.3307965
H	1.5574861	2.3916491	-0.2508259
H	-0.7365208	2.6317112	-0.3347448
O	-1.1537451	-2.6834281	-0.3538344
H	4.4558395	1.4380819	-0.2768883
O	5.4163539	1.6216825	-0.3280326
H	5.5823795	1.6781482	-1.2809014
O	1.4197369	-2.7586341	-0.4142900
O	3.0216061	-3.7918174	-2.7254007
H	3.5899302	-4.4985407	-2.3842475

6Z⁺⁺2H₂O

HF= -1311.2268489 Hartrees

No of imaginary frequencies = 0

N	-1.0592896	1.3893032	0.5757805
C	-1.7563597	0.8465742	1.5749324
C	-2.6246056	1.7069947	2.4303730
C	-1.6485375	-0.5863208	1.8205279
O	-2.3112785	-1.1209999	2.7448738
C	-0.7367234	-1.3029142	0.9493955
H	1.7699178	-1.7693371	-0.4622859
C	-0.0390148	-0.6411220	-0.0886064
C	-0.2209665	0.7174068	-0.2644948
C	0.9047243	-1.3879558	-1.0086392
O	1.3512539	-0.5336578	-2.0967410
P	2.8412645	0.0580984	-2.1416880
O	2.4873768	1.6448838	-2.2470511
O	3.3524383	-0.3516088	-3.6168366
O	3.7889473	-0.3082057	-1.0746957
H	-1.1567564	2.4035548	0.4250439
H	-2.2831818	1.6586619	3.4720401
H	-2.6115108	2.7489127	2.0967452
H	-3.6531840	1.3237501	2.4394210
H	2.6421068	-0.3062447	-4.2785794
H	0.4088247	-2.2390465	-1.4744152
H	3.2772887	2.1704139	-2.0350872
C	-0.5832629	-2.7421403	1.1976115
H	0.2668962	1.3047465	-1.0271870
O	0.1507127	-3.4883756	0.5573715
H	-1.1949781	-3.1251984	2.0318825
O	-1.3186572	4.2230426	0.1396449
H	-2.1774186	4.5736185	-0.1422980
H	-1.0149559	4.8271542	0.8343619
H	-4.0469819	-0.6656418	3.2023558
O	-4.9750829	-0.3432498	3.1914277
H	-5.4072116	-0.9397082	2.5623108

6N⁺⁺4H₂O

HF= -1464.1086505 hartrees

No of imaginary frequencies = 0

H	2.2356922	1.4153257	-4.6181790
C	-0.1306573	0.7501880	-3.2081749
C	-0.6264555	0.7461683	-4.6263129
C	-1.0134743	0.4761562	-2.1299344
H	-2.7001469	-1.4284943	1.7041138
C	-0.5371211	0.5255065	-0.8054166
H	1.0746814	1.5703038	1.4076903

6Z⁺⁺4H₂O

HF= -1464.1052058 hartrees

No of imaginary frequencies = 0

N	-0.5756476	-2.6512039	0.4182656
C	-1.6188576	-2.6486303	1.2448911
C	-2.1683471	-3.9374025	1.7544272
C	-2.2043480	-1.3683894	1.6501874
O	-3.1937673	-1.3464491	2.4202296
C	-1.5578072	-0.1849789	1.1115215
H	-0.5308037	1.5056826	-0.8968481

C	0.8443613	0.7693733	-0.5900432	C	-0.4469462	-0.2983382	0.2376236
C	1.6315590	0.9852905	-1.7077322	C	0.0302419	-1.5426930	-0.1032745
C	1.4623750	0.7544899	0.7872855	C	0.2036891	0.9337899	-0.3239312
O	1.1738214	-0.5119451	1.4216486	O	1.3079491	0.5936548	-1.1731238
P	0.8084612	-0.5404317	3.0021707	P	2.1746170	1.8380882	-1.7616495
O	2.2000589	-0.6065156	3.7629695	O	2.7717922	2.5665409	-0.4550785
O	0.1742627	-1.9803391	3.1756976	O	1.1148874	2.8663640	-2.3458103
O	-0.0559740	0.6232348	3.3946119	O	3.2001998	1.3485065	-2.7188057
H	-1.1057268	0.5346473	1.3219435	H	-0.1772523	-3.5602598	0.1385704
H	0.1961089	0.9920162	-5.3011585	H	-3.2446397	-4.0015213	1.5481955
H	-1.0437117	-0.2355435	-4.8825719	H	-1.6472956	-4.7981099	1.3249943
H	-1.4311801	1.4808169	-4.7546453	H	-2.0770275	-3.9705226	2.8475288
H	-2.7554385	-0.0135379	-1.5629690	H	0.6582229	3.4143107	-1.6377780
H	-0.7728149	-2.0302153	2.8537149	H	0.5531682	1.5664392	0.4962445
H	2.1529108	-0.0177302	4.5746957	H	3.7731428	2.5058926	-0.4866136
C	-1.4582747	0.3078247	0.3078043	C	-2.1129775	1.1034246	1.5180506
H	2.7001951	1.1579777	-1.6045451	H	0.8678264	-1.7059564	-0.7643439
H	2.5478434	0.8655949	0.7090291	O	-1.7100730	2.2165864	1.1664753
O	-2.6171687	-0.1126895	0.1573972	H	-2.9699130	1.0239358	2.2057468
O	-2.3371024	-2.1857875	2.2033025	O	0.6500166	-5.0576445	-0.4855443
H	-2.3542568	-2.9233013	1.5739900	H	0.5734381	-5.3036137	-1.4199228
H	1.0724763	0.7376993	6.4131432	H	1.5662993	-5.2586516	-0.2418931
O	-2.6213347	-2.0503921	-4.3768513	H	-4.6210588	-2.5534231	2.4037762
H	-3.2324925	-1.7817286	-5.0790633	O	-5.2884285	-3.2198787	2.1341604
O	-2.3008523	0.1934427	-2.4206249	H	-5.8175893	-2.7492317	1.4732599
H	0.7374885	1.2843464	5.0040797	H	-0.6675663	3.5729910	0.2050915
O	1.4806008	1.1495436	5.6356979	H	4.8482931	1.7023872	-1.9042619
H	-2.6591263	-1.3145850	-3.7418075	O	-0.0213473	4.1362931	-0.2689770
N	1.1555103	0.9954518	-2.9685271	H	0.7315220	4.2174460	0.3380827
O	2.5575405	1.5218478	-5.5365259	O	5.3139365	2.1561799	-1.1615708
H	2.8573158	0.6315374	-5.7737687	H	5.6823034	2.9573913	-1.5655575