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

Supplementary Information

UV/Vis absorption spectra of related parent and aminonaphthol compounds

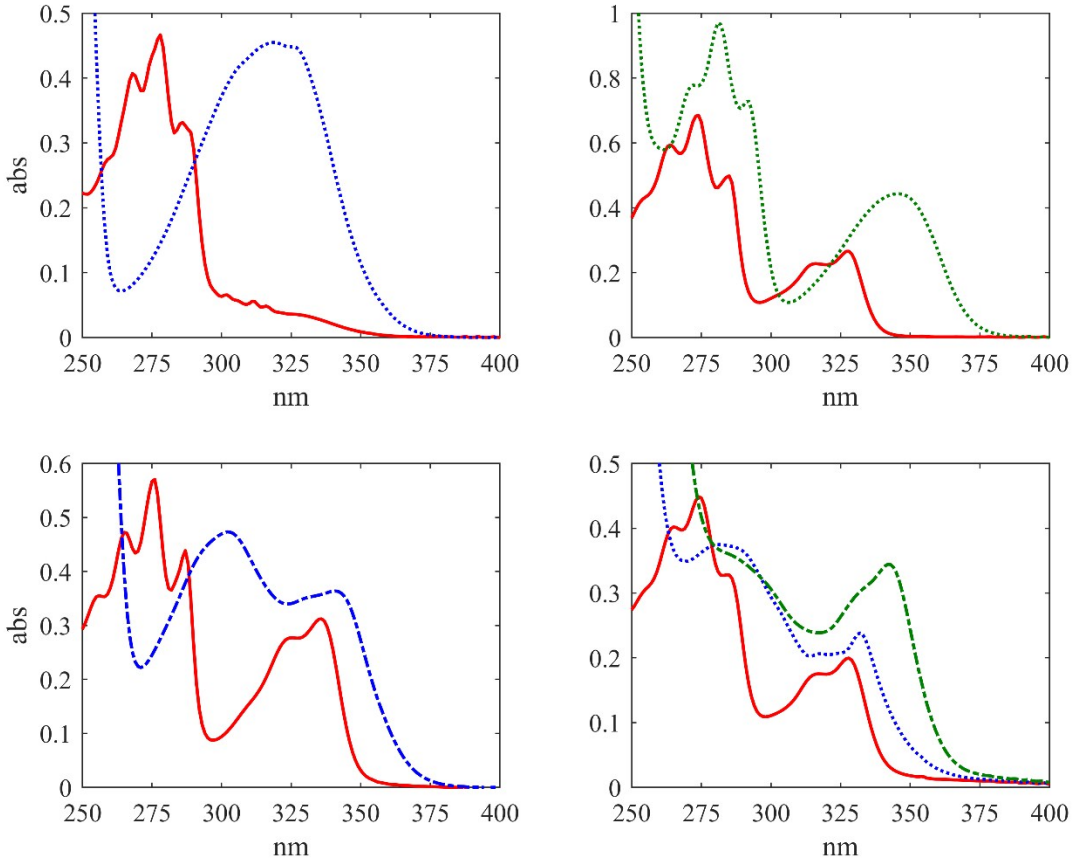

Fig. SI_1. In clockwise order, from the upper left, the UV/Vis absorption spectra of 1NH in methanol, 2OH in water, 7N2OH in water, and 8N2OH in methanol. (8N2OH is stable in water; however, the spectra are shown in methanol for comparison to 1N2OH). The different protonation states of 1NH, 7N2OH, and 8N2OH are shown as: cation (red, solid line), neutral (blue, dotted line), and anion (green, dashed line). For 2OH, the protonated and deprotonated forms are shown in red (solid line) and green (dashed line), respectively.

3N2OH in water and the two-state ESPT model

The two-state ESPT model, or excited state acid-base equilibrium model, has been well-established.[1, 2] In the simplest version, concentrations of the excited acid (A^*) and base (B^*) can be expressed analytically as:[3]

$$[A^*] = \alpha_1 e^{-\frac{t}{\tau_1}} + \alpha_2 e^{-\frac{t}{\tau_2}} \quad \text{(eqn. SI_1)}$$

$$[B^*] = \beta_1 e^{-\frac{t}{\tau_1}} + \beta_2 e^{-\frac{t}{\tau_2}} \quad \text{(eqn. SI_2)}$$

$$\tau_1^{-1}, \tau_2^{-1} = [\frac{1}{2}\{(X+Y)^{\frac{1}{2}} \pm [(Y-X)^2 + 4k_d k_r [H^+]]^{\frac{1}{2}}\}] \quad \text{(eqn. SI_3)}$$

$$\text{with } X = k_A + k_d, Y = k_B + k_r[H^+]$$

where τ_1, τ_2 and α, β are the lifetimes and relative amplitudes of the acid and base species, k_A, k_B are the rates of excited state acid and base relaxation, and k_d, k_r are the rates of excited state proton dissociation and recombination, respectively. The values of τ_1, τ_2 and α, β are $[H^+]$-dependent and can be determined from global-fitting of emission data at different pH. The kinetic parameters {k_A, k_B, k_d, k_r} are then determined from fitting the τ_1, τ_2 parameters at various pH in Matlab using eqn. SI_3. The photoacidity of the acid is thus calculated as:

$$pK_a^* = -log(\frac{k_d}{k_r}) \quad \text{(eqn. SI_4)}$$

The lifetimes collected at various pH for 3N2OH in water have been summarized in Table SI_1. The low pH data, i.e. excited cation-zwitterion equilibrium (highlighted in gray), were fit in Matlab (Fig. SI_2): $k_{cation} = k_A = 2.05 \pm 0.1 \times 10^8$ s^{-1}, $k_{zwitterion} = k_B = 8.9 \pm 0.2 \times 10^7$ s^{-1}, $k_d = 2.3 \pm 0.3 \times 10^9$ s^{-1}, and $k_r = 9.5 \pm 0.7 \times 10^9$ s^{-1}, with pK_a^* = 0.62 ± 0.20. At high pH, the observed lifetimes do not change over the pH range, although their amplitudes change corresponding to the ground state neutral-anion equilibrium. Thus, the relevant kinetic parameters were determined to be: $k_{neutral}$ = 1.7 × 10^8 s^{-1} and k_{anion} = 6.0 × 10^8 s^{-1} with pK_a^* ~ pK_a = 9.1 ± 0.2. (Note three lifetimes were reported in pH regions where the excited cation-zwitterion and excited neutral relaxation kinetics overlap).

Table SI_1. Sample data set of lifetime parameters (τ) of 3N2OH in water determined at each pH from global fitting of TCSPC emission collected at select wavelengths in the 350-450 nm region. The shaded region of the table was used for the excited cation-zwitterion equilibrium state model. For pH 2.0 and 2.2 data, the third component had to be fixed, as the contributions were very minor due to little neutral being present in the ground state.

pH	τ_1 (s)	τ_2 (s)	τ_3 (s)	τ_4 (s)
0.3	1.64e-10	5.87e-9		
0.7	2.31e-10	7.14e-9		
1.0	2.95e-10	8.36e-9		
1.4	3.49e-10	9.56e-9		
1.6	3.68e-10	9.99e-9		
1.9	3.74e-10	1.04e-8		
2.0	3.79e-10	1.06e-8	5.78e-9 (fixed)	
2.2	3.81e-10	1.08e-8	5.78e-9 (fixed)	
3.1	3.91e-10	1.11e-8	5.79e-9	
3.5	3.94e-10	1.12e-8	5.82e-9	
7.2			5.77e-9	
8.0			5.77e-9	1.68e-9
9.6			5.77e-9	1.68e-9
10.4			5.77e-9	1.68e-9
12.1				1.68e-9

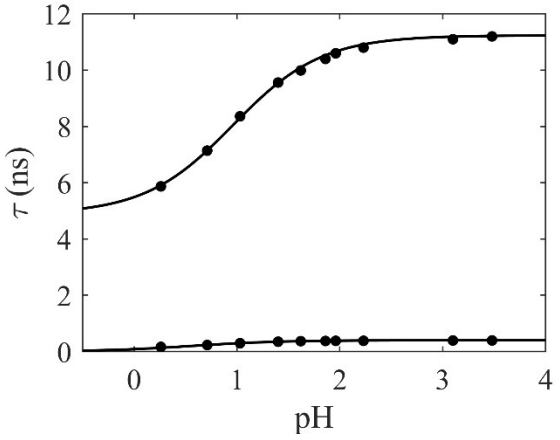

Fig. SI_2. Lifetime vs. pH curves generated from fitting lifetime parameters (τ_1, τ_2) of 3N2OH from Table SI_1 to equation SI_3. The following kinetic parameters were obtained: k_A = 2.05e8 s^{-1}, k_B = 8.9e7 s^{-1}, k_d = 2.3e9 s^{-1}, and k_r = 9.5e9 M^{-1} s^{-1} (pK_a^*(OH) = 0.62).

3N2OH in methanol

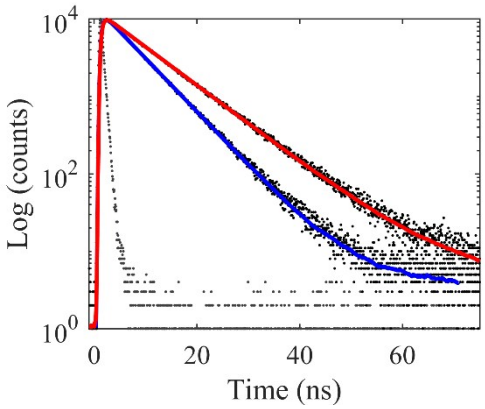

Fig. SI_3. TCSPC emission decays at 350 and 375 nm of 3N2OH cation (red) and neutral (blue) in methanol; the signals were fit to monoexponential decays at τ = 8.7 and 6.3 ns, respectively. (The gray markers = prompt, black markers = emission, and solid line = fit = convolution of exponential function and instrument prompt).

1N2OH in water

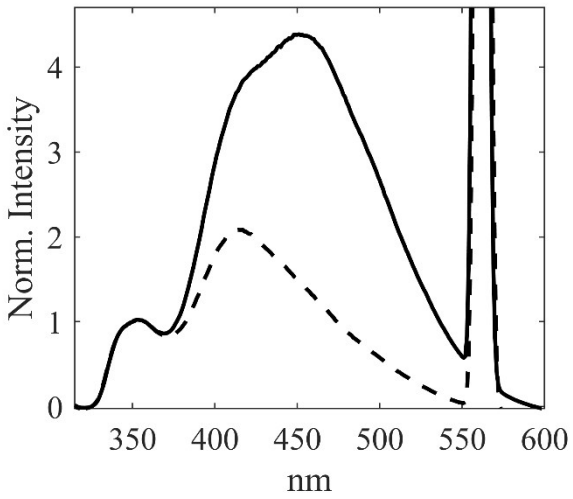

Fig. SI_4. Steady-state emission spectra collected for 1N2OH in water at pH = 2.1 (solid line) and pH = 1.3 (dotted line). The spectra were normalized at the cation peak at 350 nm. The large spike

at 560 nm is scatter from the 280-nm excitation. The corresponding time-resolved emission decays are shown in Fig. 4 and Fig SI_5.

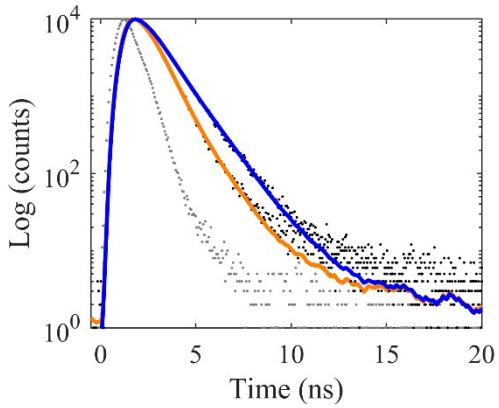

Fig. SI_5. Select TCSPC emission decays at 425 nm and 450 nm of 1N2OH in water at pH = 1.3 with gray markers = prompt, black markers = emission, and solid line = fit = convolution of exponential function and instrument prompt. (The corresponding SS emission spectrum is shown in Fig. SI_4). The emission data collected at 425-500 nm were globally fit to a biexponential function (τ_1 = 610 ps, τ_2 = 1.3 ns), with the 425-nm signal (zwitterion, orange) dominated by the 610-ps decay and the 450-nm signal (zwitterion + remaining neutral, blue) fit to both the 610-ps and 1.3-ns decay.

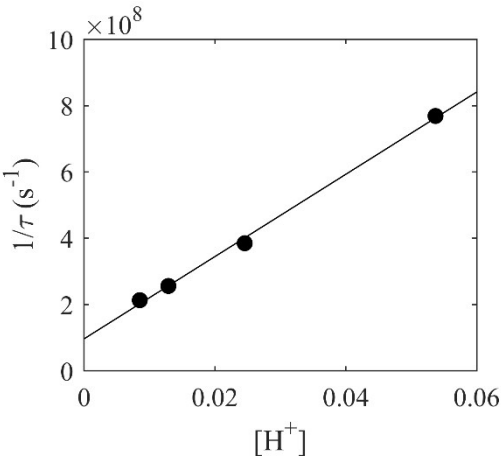

Fig. SI_6. Stern-Volmer plot of τ_2^{-1} vs. $[H^+]$ collected from pH 1.3 to 2.1 for 1N2OH in water. The data were fit to: $\tau^{-1} = 1.24 \times 10^{10}\,[H^+] + 9.64 \times 10^7$ (R^2= 0.998).

1N2OH and 1NH in methanol

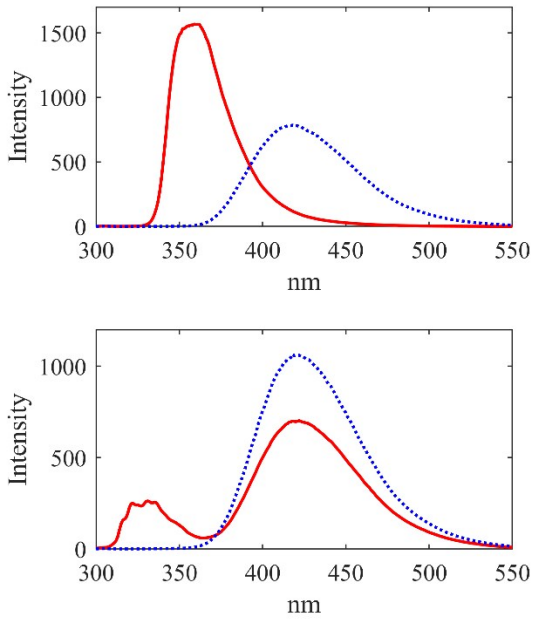

Fig. SI_7. SS emission spectra collected from excitation of 8N2OH cation (top solid red) and neutral (top dotted blue) and 1NH cation (bottom solid red) and neutral (bottom dotted blue) in methanol.

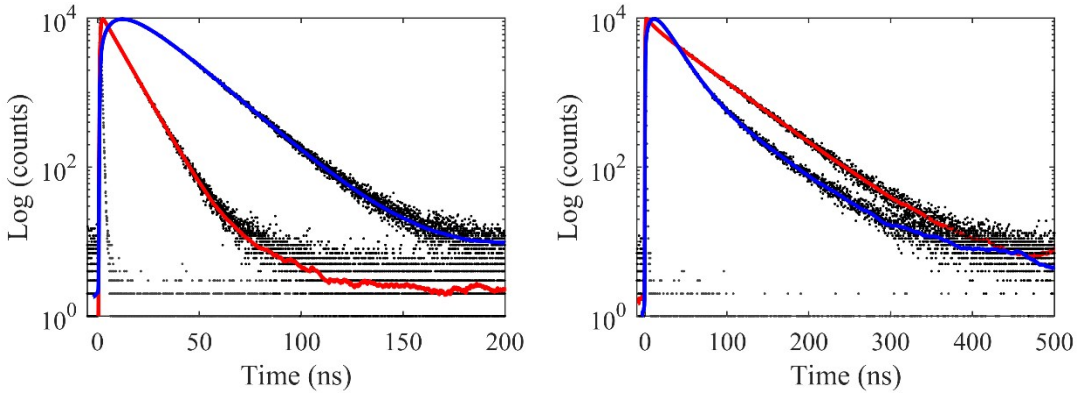

Fig. SI_8. TCSPC emission decays at 330 and 420 nm from excitation of 1NH cation and cation-18C6 complex in methanol with gray markers = prompt, black markers = emission, and solid line = fit = convolution of exponential function and instrument prompt. On the left is the free 1NH cation: the signals were fit simultaneously to a biexponential function (τ_1 = 9.0 ns, τ_N = 18 ns), with the 330-nm signal (cation, red) dominated by the 9.0-ns decay, and the 420-nm signal (neutral, blue) fit to a 9.0-ns rise and 18-ns decay of equal but opposite magnitude. On the right, upon addition of 18C6, a longer lifetime component (τ_2 = 53 ns) for the cation-18C6 complex was included for the 330-nm fit, but the fit of the 420-nm signal remained approximately the same. Note the difference in the timescale of the two plots.

Table SI_2. Tables of the relative amplitudes of the different lifetime components obtained from fitting the 350/330 nm (cation) and 450/420 nm (neutral) signals collected upon titration of 1N2OH (top table) and 1NH (bottom table) in methanol with crown ether and KCl. The data correspond to the SS emission spectra shown in Fig. 5. Each set of 350/330 nm and 450/420 nm signals were globally fit across the titration measurement. The lifetimes reported here are shorter than those reported in the main text as the titration experiments were done in air vs. argon.

	350 nm (cation) signal		**450 nm (neutral) signal**		
1N2OH cation Titration expt.	τ_1 = 1.4 ns component	τ_2 = 5.5 ns component	τ_1 = 1.4 ns component	τ_1 = 8.9 ns component	τ_1 = 3.4 ns component
Free cation	1	0	-0.44	0.44	0.12
Addition of 18C6 #1	0.88	0.12	-0.44	0.44	0.12
Addition of 18C6 #2	0.72	0.28	-0.43	0.45	0.12
Addition of 18C6 #3	0.56	0.44	-0.42	0.47	0.11
Addition of 18C6 #4	0.36	0.64	-0.39	0.51	0.10
Addition of KCl	1	0	-0.42	0.50	0.08

	330 nm (cation) signal		**420 nm (neutral) signal**	
1N cation Titration expt.	τ_1 = 6.5 ns component	τ_2 = 19 ns component	τ_1 = 6.5 ns component	τ_1 = 9.3 ns component
Free cation	1	0	-0.48	0.52
Addition of 18C6 #1	0.38	0.62	-0.48	0.51
Addition of 18C6 #2	0.26	0.74	-0.48	0.51
Addition of KCl	1	0	-0.48	0.52

Optimized S_0 and S_1 structures from the TD-DFT calculations in water

1N2OH cation in water

	Ground State Cation S_0				Excited State Cation S_1		
	x	y	z		x	y	z
C	3.145	-0.219	0.000	C	3.162	-0.227	0.000
C	2.213	-1.236	0.000	C	2.176	-1.263	0.000
C	0.822	-0.949	0.000	C	0.796	-0.979	0.000
C	0.393	0.419	0.000	C	0.403	0.415	0.000
C	1.374	1.448	0.000	C	1.400	1.428	0.000
C	2.717	1.131	0.000	C	2.786	1.104	0.000
H	0.180	-3.018	0.000	H	0.125	-3.033	0.000
H	4.205	-0.448	0.000	H	4.211	-0.504	0.000
H	2.530	-2.275	0.000	H	2.501	-2.299	0.000
C	-0.155	-1.985	0.000	C	-0.194	-1.996	0.000
C	-1.006	0.658	0.000	C	-0.981	0.672	0.000
H	1.080	2.493	0.000	H	1.117	2.476	0.000
H	3.455	1.927	0.000	H	3.524	1.897	0.000
C	-1.938	-0.360	0.000	C	-1.969	-0.376	0.000
C	-1.501	-1.708	0.000	C	-1.585	-1.702	0.000
H	-2.236	-2.507	0.000	H	-2.326	-2.493	0.000
O	-3.251	0.000	0.000	O	-3.242	0.075	0.000
H	-3.838	-0.770	0.000	H	-3.888	-0.649	0.000
N	-1.529	2.036	0.000	N	-1.485	2.048	0.000
H	-1.242	2.570	-0.829	H	-1.190	2.585	-0.829
H	-2.557	2.007	0.000	H	-2.513	2.035	0.000
H	-1.243	2.570	0.829	H	-1.190	2.585	0.829

1N2OH zwitterion in water

	Ground State Zwitterion S_0				Excited State Zwitterion S_1		
	x	y	z		x	y	z
C	-3.125	-0.178	0.000	C	-3.112	-0.209	0.000
C	-2.196	-1.204	0.000	C	-2.162	-1.251	0.000
C	-0.805	-0.937	0.000	C	-0.766	-0.971	0.000
C	-0.353	0.429	0.000	C	-0.371	0.428	0.000
C	-1.330	1.466	0.000	C	-1.344	1.456	0.000
C	-2.680	1.165	0.000	C	-2.727	1.134	0.000
H	-0.184	-3.013	0.000	H	-0.115	-3.022	0.000
H	-4.188	-0.399	0.000	H	-4.169	-0.463	0.000
H	-2.525	-2.241	0.000	H	-2.493	-2.286	0.000
C	0.170	-1.984	0.000	C	0.231	-1.990	0.000
C	1.042	0.636	0.001	C	1.019	0.651	0.000
H	-1.019	2.507	0.000	H	-1.038	2.498	0.000
H	-3.407	1.972	0.000	H	-3.471	1.924	0.000
C	2.026	-0.378	0.000	C	2.047	-0.380	0.000
C	1.518	-1.731	0.000	C	1.610	-1.737	0.000
H	2.238	-2.545	0.000	H	2.346	-2.532	0.000
N	1.661	1.970	0.000	N	1.578	2.000	0.000
H	1.458	2.536	0.829	H	1.321	2.554	0.828
H	2.681	1.715	-0.001	H	2.608	1.845	-0.001
H	1.457	2.535	-0.829	H	1.321	2.554	-0.828
O	3.281	-0.069	0.000	O	3.263	0.017	0.000

1N2OH neutral in water

	Ground State Neutral S_0				Excited State Neutral S_1		
	x	y	z		x	y	z
C	3.119	-0.205	0.000	C	3.139	-0.257	0.003
C	2.187	-1.222	0.000	C	2.159	-1.280	-0.051
C	0.793	-0.940	0.000	C	0.768	-0.939	-0.026
C	0.357	0.430	0.000	C	0.393	0.440	0.034
C	1.344	1.456	0.000	C	1.386	1.445	0.098
C	2.690	1.145	0.000	C	2.775	1.076	0.081
H	0.154	-3.012	0.000	H	0.060	-2.977	-0.089
H	4.181	-0.435	0.000	H	4.192	-0.529	-0.019
H	2.506	-2.261	0.000	H	2.449	-2.324	-0.126
C	-0.182	-1.978	0.000	C	-0.247	-1.935	-0.061
C	-1.043	0.707	0.000	C	-1.019	0.741	-0.031
H	1.031	2.495	0.000	H	1.127	2.493	0.203
H	3.427	1.943	0.000	H	3.532	1.853	0.126
C	-1.954	-0.342	0.000	C	-2.004	-0.308	0.043
C	-1.527	-1.693	0.000	C	-1.620	-1.642	-0.013
H	-2.273	-2.481	0.000	H	-2.371	-2.421	0.032
O	-3.290	-0.076	0.000	O	-3.333	-0.015	0.099
H	-3.346	0.905	0.000	H	-3.507	0.809	0.578
N	-1.621	2.024	0.000	N	-1.439	2.026	-0.160
H	-1.356	2.565	-0.821	H	-2.373	2.235	-0.489
H	-1.356	2.565	0.821	H	-0.757	2.751	-0.343

3N2OH cation in water

	Ground State Cation S_0				Excited State Cation S_1		
	x	y	z		x	y	z
C	-1.661	0.777	0.000	C	-1.682	0.763	0.000
C	-0.456	1.444	0.000	C	-0.431	1.445	0.000
C	0.768	0.721	0.000	C	0.782	0.714	0.000
C	0.745	-0.714	0.000	C	0.729	-0.731	0.000
C	-0.510	-1.378	0.000	C	-0.531	-1.389	0.000
C	-1.666	-0.642	0.000	C	-1.728	-0.629	0.000
H	2.051	2.468	0.000	H	2.071	2.447	0.000
H	-0.437	2.530	0.000	H	-0.422	2.531	0.000
C	2.028	1.383	0.000	C	2.044	1.361	0.000
C	1.973	-1.432	0.000	C	1.950	-1.431	0.000
H	-0.546	-2.464	0.000	H	-0.573	-2.474	0.000
C	3.176	-0.761	0.000	C	3.208	-0.753	0.000
C	3.201	0.658	0.000	C	3.261	0.629	0.000
H	1.946	-2.518	0.000	H	1.939	-2.517	0.000
H	4.109	-1.315	0.000	H	4.119	-1.342	0.000
H	4.156	1.176	0.000	H	4.210	1.154	0.000
O	-2.893	1.365	0.000	O	-2.857	1.422	0.000
H	-2.829	2.331	0.000	H	-2.737	2.385	0.000
N	-2.988	-1.300	0.000	N	-3.032	-1.295	0.000
H	-3.129	-1.890	-0.828	H	-3.171	-1.893	-0.826
H	-3.130	-1.888	0.828	H	-3.171	-1.892	0.826
H	-3.726	-0.586	-0.001	H	-3.787	-0.599	0.000

3N2OH zwitterion in water

	Ground State Zwitterion S_0				Excited State Zwitterion S_1		
	x	y	z		x	y	z
C	-1.731	0.834	0.000	C	-1.731	0.839	0.042
C	-0.478	1.468	0.000	C	-0.446	1.473	0.004
C	0.732	0.729	0.000	C	0.768	0.730	0.004
C	0.712	-0.713	0.000	C	0.689	-0.721	0.011
C	-0.550	-1.372	0.000	C	-0.593	-1.356	0.038
C	-1.687	-0.615	0.000	C	-1.762	-0.600	0.147
H	2.043	2.459	0.000	H	2.077	2.443	-0.017
H	-0.439	2.555	0.000	H	-0.426	2.559	0.012
C	2.009	1.372	0.000	C	2.033	1.356	-0.010
C	1.936	-1.434	0.000	C	1.900	-1.451	0.001
H	-0.594	-2.458	0.000	H	-0.635	-2.443	0.033
C	3.150	-0.777	0.000	C	3.152	-0.793	-0.020
C	3.179	0.643	0.000	C	3.229	0.599	-0.026
H	1.900	-2.521	0.000	H	1.864	-2.537	0.008
H	4.079	-1.339	0.000	H	4.061	-1.388	-0.027
H	4.136	1.159	0.000	H	4.192	1.099	-0.036
O	-2.903	1.393	0.000	O	-2.826	1.495	-0.023
N	-3.051	-1.160	0.000	N	-3.091	-1.180	-0.076
H	-3.279	-1.714	-0.830	H	-3.200	-1.652	-0.992
H	-3.280	-1.714	0.829	H	-3.371	-1.854	0.642
H	-3.609	-0.259	0.000	H	-3.747	-0.383	-0.049

3N2OH neutral in water

	Ground State Neutral S_0				Excited State Neutral S_1		
	x	Y	z		x	y	z
C	1.742	0.714	-0.007	C	1.753	0.696	-0.011
C	0.538	1.399	-0.002	C	0.499	1.404	-0.021
C	-0.710	0.719	-0.001	C	-0.731	0.722	-0.005
C	-0.724	-0.715	-0.001	C	-0.706	-0.733	-0.002
C	0.521	-1.407	0.000	C	0.553	-1.409	-0.028
C	1.710	-0.719	-0.005	C	1.767	-0.710	-0.032
H	-1.945	2.500	-0.001	H	-1.983	2.492	-0.002
H	0.546	2.486	-0.001	H	0.523	2.491	-0.041
C	-1.953	1.413	0.000	C	-1.982	1.405	0.001
C	-1.972	-1.395	0.002	C	-1.945	-1.416	0.007
H	0.525	-2.495	0.005	H	0.563	-2.496	-0.053
C	-3.162	-0.693	0.004	C	-3.174	-0.705	0.014
C	-3.151	0.725	0.003	C	-3.202	0.689	0.011
H	-1.976	-2.482	0.003	H	-1.952	-2.503	0.007
H	-4.108	-1.225	0.005	H	-4.105	-1.266	0.020
H	-4.090	1.271	0.004	H	-4.147	1.222	0.015
O	2.944	-1.324	-0.003	O	3.012	-1.320	-0.035
H	2.848	-2.287	0.031	H	2.959	-2.180	0.409
N	2.979	1.352	-0.073	N	2.908	1.402	0.026
H	3.759	0.812	0.280	H	3.796	0.921	0.066
H	2.992	2.310	0.252	H	2.908	2.411	0.063

3N2OH anion in water

	Ground State Anion S_0				Excited State Anion S_1		
	x	y	z		x	y	z
C	-3.145	0.660	-0.006	C	-3.189	0.626	-0.011
C	-1.960	1.378	-0.001	C	-1.990	1.382	-0.007
C	-0.692	0.728	0.004	C	-0.719	0.727	0.002
C	-0.673	-0.712	0.002	C	-0.647	-0.721	0.005
C	-1.902	-1.420	-0.002	C	-1.882	-1.453	-0.001
C	-3.120	-0.756	-0.006	C	-3.120	-0.773	-0.008
H	0.516	2.529	-0.007	H	0.502	2.524	0.014
H	-4.097	1.184	-0.009	H	-4.154	1.126	-0.016
H	-1.986	2.467	-0.001	H	-2.019	2.469	-0.010
C	0.538	1.440	0.004	C	0.499	1.436	0.011
C	0.594	-1.372	0.009	C	0.628	-1.355	0.024
H	-1.876	-2.508	-0.002	H	-1.856	-2.539	0.002
H	-4.050	-1.318	-0.009	H	-4.040	-1.355	-0.011
C	1.777	-0.665	0.015	C	1.837	-0.650	0.022
C	1.793	0.807	0.005	C	1.798	0.790	0.007
H	0.616	-2.461	0.014	H	0.654	-2.445	0.040
N	3.033	-1.275	0.076	N	3.098	-1.290	0.075
H	3.106	-2.188	-0.356	H	3.157	-2.122	-0.507
H	3.767	-0.632	-0.208	H	3.839	-0.640	-0.173
O	2.938	1.416	-0.012	O	2.870	1.495	-0.016

References:

1. T. Z. Förster, *Elektrochem.*, 1950, **54**, 42-46.
2. A. Weller, *Prog. React. Kinet.*, 1961, **1**, 187.
3. W. R. Laws and L. Brand, *J. Phys. Chem.*, 1979, **83**, 795-802.