

Electronic Supplementary Information

Ground and Excited Electronic Structure Analysis of XM_4 ($X = N, P$ and $M = Li, Na$) and their Anions

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849-5312, USA

Current Address: Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, MA, 02139

Isuru R. Ariyaratna

Email: ira0002@auburn.edu

Table S1. CCSD(T)/aug-cc-pVTZ optimized geometries (coordinates in Å) of the $\text{XM}^{+0/-}$ ($\text{X} = \text{N, P and M} = \text{Li, Na}$) species.

N Li_4^+ ($^1\text{A}_1$)				N Li_4 ($^2\text{A}_1$)			
N	0.0000000000	0.0000000000	-0.0000000054	N	0.0000000000	0.0000000000	-0.0000000054
Li	1.4755964246	0.0000000000	1.0434042450	Li	1.4688362650	0.0000000000	1.0386240902
Li	-1.4755964246	0.0000000000	1.0434042450	Li	-1.4688362650	0.0000000000	1.0386240902
Li	0.0000000000	1.4755964362	-1.0434042395	Li	0.0000000000	1.4688362765	-1.0386240848
Li	0.0000000000	-1.4755964362	-1.0434042395	Li	0.0000000000	-1.4688362765	-1.0386240848
N Li_4^- ($^1\text{A}_1$)				N Na_4^+ ($^1\text{A}_1$)			
N	0.0000000000	0.0000000000	-0.0000000054	N	0.0000000000	0.0000000000	-0.0000000087
Li	1.4721602980	0.0000000000	1.0409745365	Na	1.8181380507	0.0000000000	1.2856177511
Li	-1.4721602980	0.0000000000	1.0409745365	Na	-1.8181380507	0.0000000000	1.2856177511
Li	0.0000000000	1.4721603095	-1.0409745310	Na	0.0000000000	1.8181380649	-1.2856177485
Li	0.0000000000	-1.4721603095	-1.0409745310	Na	0.0000000000	-1.8181380649	-1.2856177485
N Na_4 ($^2\text{A}_1$)				N Na_4^- ($^1\text{A}_1$)			
N	0.0000000000	0.0000000000	-0.0000000087	N	0.0000000000	0.0000000000	-0.0000000088
Na	1.8155649446	0.0000000000	1.2837982904	Na	1.8247237676	0.0000000000	1.2902745562
Na	-1.8155649446	0.0000000000	1.2837982904	Na	-1.8247237676	0.0000000000	1.2902745562
Na	0.0000000000	1.8155649588	-1.2837982877	Na	0.0000000000	1.8247237818	-1.2902745535
Na	0.0000000000	-1.8155649588	-1.2837982877	Na	0.0000000000	-1.8247237818	-1.2902745535
P Li_4^+ ($^1\text{A}_1$)				P Li_4 ($^2\text{A}_1$)			
P	0.0000000000	0.0000000000	-0.0000000049	P	-0.2303913665	-0.1152108266	0.0215266188
Li	1.8637297466	0.0000000000	1.3178559527	Li	-2.1709644132	0.1152196107	1.1269069497
Li	-1.8637297466	0.0000000000	1.3178559527	Li	0.8462527716	1.9199158817	0.0463312788
Li	0.0000000000	1.8637297612	-1.3178559419	Li	1.3748690915	-0.7001112523	1.5670134760
Li	0.0000000000	-1.8637297612	-1.3178559419	Li	1.2970701966	-0.7312656227	-1.5583678042
P Li_4^- ($^1\text{A}_1$)				P Na_4^+ ($^1\text{A}_1$)			
P	0.0000000000	0.0000000000	0.4793047493	P	0.0000000000	0.0000000000	-0.0000000089
Li	2.2690653733	0.0000000000	0.1091917777	Na	2.1523197279	0.0000000000	1.5219198839
Li	0.0000000000	1.5116435978	-1.2893821024	Na	-2.1523197279	0.0000000000	1.5219198839
Li	0.0000000000	-1.5116435978	-1.2893821024	Na	0.0000000000	2.1523197448	-1.5219198779
Li	-2.2690653733	0.0000000000	0.1091917777	Na	0.0000000000	-2.1523197448	-1.5219198779
P Na_4 ($^2\text{A}_1$)				P Na_4^- ($^1\text{A}_1$)			
P	0.0000000000	0.0000000000	-0.0000000089	P	0.0000000000	0.0000000000	0.2285255794
Na	2.1496439165	0.0000000000	1.5200277995	Na	2.6401772272	0.0000000000	0.5760411560
Na	-2.1496439165	0.0000000000	1.5200277995	Na	0.0000000000	1.9237548883	-1.6308418957
Na	0.0000000000	2.1496439334	-1.5200277935	Na	0.0000000000	-1.9237548883	-1.6308418957
Na	0.0000000000	-2.1496439334	-1.5200277935	Na	-2.6401772272	0.0000000000	0.5760411560

Table S2. Harmonic vibrational frequencies (cm^{-1}) of studied $\text{XM}^{+/0/-}$ ($\text{X} = \text{N}, \text{P}$ and $\text{M} = \text{Li}, \text{Na}$) species at CCSD(T)/aug-cc-pVTZ

NLi_4^+ ($^1\text{A}_1$)	NLi_4 ($^2\text{A}_1$)	NLi_4^- ($^1\text{A}_1$)	NNa_4^+ ($^1\text{A}_1$)	NNa_4 ($^2\text{A}_1$)	NNa_4^- ($^1\text{A}_1$)	PLi_4^+ ($^1\text{A}_1$)	PLi_4 (^2A)	PLi_4^- ($^1\text{A}_1$)	PNa_4^+ ($^1\text{A}_1$)	PNa_4 ($^2\text{A}_1$)	PNa_4^- ($^1\text{A}_1$)
218.82	187.99	157.14	94.94	81.34	61.06	114.91	32.12	105.98	63.43	8.80	31.96
218.83	191.87	157.30	96.29	83.87	66.25	115.82	49.97	117.20	63.54	8.88	38.17
272.75	194.42	179.34	106.83	115.68	85.85	115.95	97.72	150.63	63.63	26.62	45.41
272.77	201.50	179.40	107.49	116.40	86.78	126.10	134.19	160.59	63.78	26.62	53.61
272.81	204.64	179.49	107.55	129.60	93.83	126.52	142.99	174.48	63.88	38.33	59.06
594.89	595.83	584.74	262.20	260.12	252.97	458.02	457.31	417.46	217.23	212.99	197.43
731.57	744.35	726.98	421.85	440.06	409.80	511.79	464.82	440.71	299.50	297.36	255.05
731.58	746.19	727.01	422.08	440.36	410.81	512.02	474.03	470.62	299.50	297.51	256.13
731.58	746.25	727.02	422.23	441.02	411.87	512.04	548.45	489.36	299.53	297.60	297.55

Table S3. Optimized geometries (coordinates in Å) of the $\text{XM}_3^{0/-}$ ($\text{X} = \text{N}, \text{P}$ and $\text{M} = \text{Li}, \text{Na}$) species.

NLi_3 ($^1\text{A}_1$) (CCSD(T)/aug-cc-pVTZ)				NLi_3^- ($^2\text{A}_1$) (CCSD(T)/aug-cc-pVTZ)			
N	0.0000000000	0.3663042399	0.2590318369	N	-0.0000000000	0.3405854698	0.2408472546
Li	1.5153264502	-0.1376005385	0.9741949150	Li	1.5311327274	-0.1342952209	0.9877061019
Li	-1.5153264502	-0.1376005385	0.9741949150	Li	-1.5311327274	-0.1342952209	0.9877061019
Li	0.0000000000	1.3777331315	-1.1687975640	Li	0.0000000000	1.3968412665	-1.1776353554
PLi_3 ($^1\text{A}_1$) (CCSD(T)/aug-cc-pVTZ)				PLi_3^- ($^2\text{A}_1$) (CCSD(T)/aug-cc-pVTZ)			
P	0.0000000000	-0.3593331496	-0.2540792350	P	0.0000000000	-0.5411628098	-0.3826387034
Li	1.6630127715	0.0550486252	1.2148559304	Li	1.5154390547	0.1648594154	1.1881242167
Li	-1.6630127715	0.0550486252	1.2148559304	Li	-1.5154390547	0.1648594154	1.1881242167
Li	0.0000000000	1.7180721938	-1.1370085230	Li	0.0000000000	1.6802802735	-0.9549856272
NNa_3 ($^1\text{A}_1$) (MN15/aug-cc-pVTZ)				NNa_3^- ($^2\text{A}_1$) (MN15/aug-cc-pVTZ)			
N	0.432461	0.255181	0.000000	N	0.000000	0.000000	0.012656
Na	0.432461	-0.941693	1.786308	Na	0.000000	2.174446	-0.002685
Na	0.432461	-0.941693	-1.786308	Na	-1.883125	-1.087223	-0.002685
Na	-1.140125	1.720999	-0.000000	Na	1.883125	-1.087223	-0.002685
PNa_3 ($^1\text{A}_1$) (CCSD(T)/aug-cc-pVTZ)				PNa_3^- ($^2\text{A}_1$) (CCSD(T)/aug-cc-pVTZ)			
P	-0.0000000000	0.0000000000	0.9360946679	P	0.0000000000	0.0000000000	1.1150000775
Na	2.2629686868	0.0000000000	-0.4203933117	Na	2.1432112932	0.0000000000	-0.5007384308
Na	-1.1314843434	-1.9597883707	-0.4203933117	Na	-1.0716056466	-1.8560754256	-0.5007384308
Na	-1.1314843434	1.9597883707	-0.4203933117	Na	-1.0716056466	1.8560754256	-0.5007384308

Table S4. Harmonic vibrational frequencies (cm^{-1}) of studied $\text{NM}^{+/-}$ species at CCSD(T) (or DFT/MN15)^a at aug-cc-pVTZ.

NLi_3 ($^1\text{A}_1$)	NLi_3^{-a} ($^2\text{A}_1$)	PLi_3 ($^1\text{A}_1$)	PLi_3^{-} ($^2\text{A}_1$)	NNa_3^a ($^1\text{A}_1$)	NNa_3^{-a} ($^2\text{A}_1$)	PNa_3 ($^1\text{A}_1$)	PNa_3^{-} ($^2\text{A}_1$)
74.85	101.8	138.83	154.06	89.5	65.6	72.27	86.50
192.22	167.4	146.01	161.11	91.0	79.3	73.24	96.11
192.36	167.5	146.03	176.16	92.5	79.3	86.97	97.06
651.00	635.7	496.95	468.12	311.0	245.0	262.69	250.88
849.26	837.8	530.16	471.95	502.3	475.0	290.74	251.55
849.28	837.8	530.39	488.84	502.4	475.1	291.09	267.58