

Novel and Polynuclear K- and Na-Based Superalkali Hydroxides as Superbases Better than Li-Related Species and Their Enhanced Properties: From *ab Initio* Exploration

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Table S1. Natural Charges and O-H Stretching Frequencies of the Neutral Superalkali XM_{n+1}OH and $\text{XM}_{n+1}\text{OH}_2^+$ Species Using MP2/6-311++G(d, p) Level of Theory

Species	Natural Charge (Q) (in e)					O-H (stretching) (in cm^{-1})
	M (ring)	Q_{O} of O-H	Q_{H} of O-H	Q_{X}	Q_{M} (terminal)	
KOH	0.985	-1.413	0.428	-	-	3961.4
KOH_2^+	0.998	-0.972	0.486	-	-	sym: 3854.3 asym: 3946.8
FK_2OH	0.976	-1.402	0.423	F(-0.973)	-	3934.4
FK_2OH_2^+	0.988	-0.933	0.468	F (-0.979)	-	sym: 3848.2 asym: 3949.8
OK_3OH	0.955	-1.389	0.416	O (-1.89)	0.952	3934
OK_3OH_2^+	0.958	-0.938	0.471	O (-1.883)	0.963	sym: 3849.6 asym: 3950.9
NK_4OH	0.903	-1.388	0.397	N (-3.675)	0.884	3940
NK_4OH_2^+	0.872	-0.94	0.471	N (-2.424)	0.839	sym: 3833.6 asym: 3939.2
NaOH	0.984	-1.419	0.436	-	-	4012.5
NaOH_2^+	0.993	-0.986	0.496	-	-	sym: 3855.3 asym: 3945.4
FNa_2OH	0.967	-1.403	0.435	F (-0.967)	-	3969.8
$\text{FNa}_2\text{OH}_2^+$	0.969	-0.95	0.478	F (-0.945)	-	sym: 3833 asym: 3927.2
ONa_3OH	0.947	-1.383	0.428	O (-1.903)	0.964	3967
$\text{ONa}_3\text{OH}_2^+$	0.956	-0.941	0.48	O (-1.902)	0.97	sym: 3876.8 asym: 3926.3
NNa_4OH	0.927	-1.369	0.425	N (-2.55)	0.821	3958
$\text{NNa}_4\text{OH}_2^+$	0.901	-0.936	0.479	N (-2.582)	0.879	sym: 3881.7 asym: 3918.2
LiOH	0.96	-1.407	0.445	-	-	4049.8
LiOH_2^+	0.99	(-1.016	0.513	-	-	sym: 3833.3 asym: 3918.4
FLi_2OH	0.91	-1.368	0.459	F (-0.912)	-	4016.8
$\text{FLi}_2\text{OH}_2^+$	0.974	(-0.984	0.497	F (-0.959)	-	sym: 3803.7 asym: 3892.5
OLi_3OH	0.871	-1.34	0.45	O (-1.767)	0.915	4009.2
$\text{OLi}_3\text{OH}_2^+$	0.949	(-0.972	0.495	O (-1.886)	0.969	sym: 3811.1 asym: 3905.7
NLi_4OH	0.817	-1.317	0.448	N (-2.454)	0.845	3996
$\text{NLi}_4\text{OH}_2^+$	0.915	(-0.963	0.493	N (-2.723)	0.935	sym: 3805.1 asym: 3904.9

Table S2. O-M bond lengths and changes therein (non-protonated to protonated SAHs)

O-K distance

KOH (2.244) to KOH_2^+ (2.629) (change in O-K: 0.385)

FK_2OH (2.476) to FK_2OH_2^+ (3.241) (change in O-K: 0.765)

OK_3OH (2.497) to OK_3OH_2^+ (3.008) (change in O-K: 0.511)

NK_4OH (2.446) to NK_4OH_2^+ (3.007) (change in O-K: 0.561)

O-Na distance

NaOH (1.98) to NaOH_2^+ (2.27) (change in O-Na: 0.29)

FNa_2OH (2.165) to $\text{FNa}_2\text{OH}_2^+$ (2.792) (change in O-Na: 0.627)

ONa_3OH (2.181) to $\text{ONa}_3\text{OH}_2^+$ (2.696) (change in O-Na: 0.515)

NNa_4OH (2.167) to $\text{NNa}_4\text{OH}_2^+$ (2.722) (change in O-Na: 0.555)

O-Li distance

LiOH (1.607) to LiOH_2^+ (1.869) (change in O-Na: 0.262)

FLi_2OH (1.796) to $\text{FLi}_2\text{OH}_2^+$ (2.296) (change in O-Na: 0.5)

OLi_3OH (1.81) to $\text{OLi}_3\text{OH}_2^+$ (2.217) (change in O-Na: 0.407)

NLi_4OH (1.812) to $\text{NLi}_4\text{OH}_2^+$ (2.217) (change in O-Na: 0.405)

Cartesian Coordinates at MP2/6-311++G(d, p) Level of Theory

Superalkalis Neutral Species

FK₂

F,0,-2.0764656765,-0.1082196994,0.

K,0,0.2670339483,-0.2561589919,0.

K,0,-2.9981956415,2.0514771305,0.

OK₃

O,0,0.0000090301,-0.0000080754,-0.0000182145

K,0,-0.2022693064,2.3587166159,0.0000093387

K,0,2.1438736777,-1.0041740819,0.0000093383

K,0,-1.9415634015,-1.3545424587,-0.0000214624

NK₄

N,0,0.,0.,0.0000066066

K,0,0.,2.1125288733,1.4937574538

K,0,0.,-2.1125288733,1.4937574538

K,0,-2.1125290231,0.,-1.4937478439

K,0,2.1125290231,0.,-1.4937478439

FNa₂

F,0,-2.2581877248,-0.3653504506,0.

Na,0,-0.1497973055,-0.2140321682,0.

Na,0,-2.8193440199,1.672616918,0.

ONa₃

O,0,-0.0000543243,-0.0002367844,-0.0000237437

Na,0,0.1501268851,2.0900010143,-0.0000056952

Na,0,-1.8854997662,-0.9149636286,-0.0000176159

Na,0,1.7352862054,-1.1748836013,0.0000380548

NNa₄ at MP2/6-31+G(d, p) level

N,0,0.00000646,-0.0000008046,-0.0000133593
Na,0,-0.9276286111,-1.7748495387,-0.8434563834
Na,0,-0.9310330587,1.7736707088,-0.8421809048
Na,0,-0.2625920396,-0.0010263633,2.1570699563
Na,0,2.1212662495,0.0022059979,-0.4714593089

NNa₄ (TS = -693.6 cm⁻¹) Using MP2/6-311++G(d, p) Level of Theory

N,0,0.,0.,-0.0049359312
K,0,0.,1.9270027821,-1.62993159
K,0,0.,-1.9270027821,-1.62993159
K,0,1.9268202371,0.,1.6202183484
K,0,-1.9268202371,0.,1.6202183484

FLi₂

F,0,-2.1941574243,-0.2747496747,0.
Li,0,-2.652535367,1.3666576348,0.
Li,0,-0.4938890901,-0.1589227099,0.

OLi₃

O,0,0.0000062325,0.0001011064,-0.00000231
Li,0,-1.4429352766,0.9101647345,0.0000017698
Li,0,1.5097399588,0.7944542793,0.0000017699
Li,0,-0.0668259147,-1.7046031202,0.0000017703

NLi₄

N,0,-0.000005661,0.0000061737,-0.0000174447
Li,0,0.2813964864,-0.6859791493,1.6015659878
Li,0,-0.3876710919,1.714845645,0.1543628591
Li,0,-1.3465037603,-0.8404122764,-0.7716613204
Li,0,1.4527950267,-0.1884343929,-0.9842210817

Superalkali Hydroxides (SAHs)

KOH

O,0,0.,0.,-1.5063512941

H,0,0.,0.,-2.4637327596

K,0,0.,0.,0.7379280537

FK₂OH

F,0,-0.0000087131,1.645369891,0.0001409423

O,0,0.0000425974,-1.7159024166,0.0002706946

H,0,0.0000049972,-2.675132356,0.0002737398

K,0,1.7625164738,0.0229894062,0.0003984298

K,0,-1.7624863552,0.0229794755,0.0003991935

OK₃OH

O,0,0.796487,0.000499,0.000109

O,0,-2.870855,-0.000854,-0.000113

H,0,-3.830036,0.000801,-0.000196

K,0,-1.014928,-1.670334,0.00003

K,0,-1.015587,1.6704,0.00003

K,0,3.105514,0.000042,-0.000049

NK₄OH

N,0,0.,0.,-0.5806881781

O,0,0.,0.,3.1065767208

H,0,0.,0.,4.066035769

K,0,0.,1.8497691716,1.5055039046

K,0,0.,-1.8497691716,1.5055039046

K,0,-2.1818381595,0.,-2.1560255605

K,0,2.1818381595,0.,-2.1560255605

NaOH

Na,0,0.,0.,0.9373441018

O,0,0.,0.,-1.0427745508

H,0,0.,0.,-1.9969085511

FNa₂OH

F,0,1.6039327037,-0.0000412779,0.0000290978

O,0,-1.570102858,0.0000405166,-0.0000631873

H,0,-2.5271967673,0.0000767766,-0.0001012457

Na,0,0.022617518,1.4670816649,0.0000111675

Na,0,0.0225394037,-1.4670806802,0.0000111677

ONa₃OH

O,0,-0.909175135,0.0046267942,0.0005067097

O,0,2.4559111495,-0.005555908,-0.0005126826

H,0,3.4131885833,-0.0082026155,-0.0007151003

Na,0,0.7676594817,-1.3857767726,0.0001174921

Na,0,0.7758461606,1.3847762515,0.0001076261

Na,0,-2.9656652401,0.0019682504,0.0000449549

NNa₄OH

N,0,0.6671083436,0.0000276355,0.0001009931

O,0,-2.7200579928,-0.0001142913,-0.0001322223

H,0,-3.6781995071,-0.0001926228,-0.0001540436

Na,0,2.0759571631,-1.7546397376,0.0000485271

Na,0,2.0760873293,1.7545672935,0.0000331366

Na,0,-1.1333548772,0.0000950177,-1.4758552496

Na,0,-1.1335814588,0.000109705,1.4758318588

LiOH

O,0,0.,0.,0.3220964877

H,0,0.,0.,1.2740270981

Li,0,0.,0.,-1.2844745858

FLi₂OH

F,0,-1.382927742,0.0001604723,0.0001481302

Li,0,-0.064647964,-1.1460442691,-0.0001068386

Li,0,-0.0644304955,1.1461716565,-0.0001068514

O,0,1.3164022713,-0.0001053427,0.0000544151

H,0,2.2848429302,-0.0000395169,0.0002391448

OLi₃OH

O,0,-1.1680681452,0.0002099513,0.0008669869

Li,0,0.2589991333,-1.0906514032,0.0000943842

Li,0,0.2593322938,1.0907823782,0.0000904251

Li,0,-2.8274047688,-0.0005527675,-0.0007480446

O,0,1.703205989,-0.0002235644,-0.0004117705

H,0,2.6576434978,-0.0003685944,0.0014350188

NLi₄OH

N,0,-1.1193283489,0.0000258879,-0.0001263635

Li,0,-2.1134311162,1.4902136228,-0.0003582347

Li,0,-2.1133805098,-1.4901978005,-0.0001938448

Li,0,0.4437233099,0.000070887,1.1093155499

Li,0,0.44400434,-0.0000482592,-1.109164358

O,0,1.8771834054,-0.0000283195,0.000233442

H,0,2.8324539196,0.0001139815,0.0004368091

Protonated Superalkali Hydroxides (PSAHs)

KOH₂⁺

O,0,0.2215546808,-0.2049669382,-1.4162244599
H,0,-0.458299532,-0.7701757514,-1.7979692695
K,0,0.8194860158,0.1463057342,1.1199391672
H,0,0.6264971247,0.2035300377,-2.1885868689

FK₂OH₂⁺ (Linear)

O,0,-4.0295416725,-0.240958915,0.000001724
H,0,-4.2649261088,-1.1734980617,0.0000130463
H,0,-4.8825596847,0.2033601231,-0.0000105191
F,0,0.7463529001,0.1442117035,0.0000036648
K,0,-1.532000545,0.8206714912,-0.0000186289
K,0,2.9958251109,-0.4791383411,0.0000127128

FK₂OH₂⁺ (Ring)

F,0,0.0000055468,-1.1436325614,0.0000273358
O,0,-0.0000124284,2.0953141987,0.000205727
H,0,-0.0000447699,2.6977699041,-0.7510436559
K,0,-2.1685771604,-0.3137332065,-0.0000705542
K,0,2.1685769411,-0.3137025191,-0.0000573672
H,0,-0.0000071292,2.6972061841,0.7519065145

OK₃OH₂⁺

O,0,0.677736956,0.0000823748,-0.0000963372
O,0,-3.0741296619,-0.0003235093,0.0002499455
H,0,-3.6744885843,-0.0003835258,0.7530945162
K,0,-0.7441436051,-1.9022498208,0.0002299589
K,0,-0.7445436681,1.9021140361,0.0002296487
K,0,3.0437000119,0.0003183752,-0.0003366301
H,0,-3.6744744486,-0.0003839301,-0.7526061019

NK₄OH₂⁺

N,0,0.,0.,-0.5036402793
O,0,0.,0.,3.419026882
H,0,0.,0.7536908691,4.0195521882
K,0,-1.9733733513,0.,1.1507024181
K,0,1.9733733513,0.,1.1507024181
K,0,0.,-2.1020287421,-2.0289119077
K,0,0.,2.1020287421,-2.0289119077
H,0,0.,-0.7536908691,4.0195521882

NaOH₂⁺

Na,0,-0.000010412,-1.1375000114,0.
O,0,0.0000094162,1.132209436,0.
H,0,0.0000584979,1.7245952875,0.7594271047
H,0,0.0000584979,1.7245952875,-0.7594271047

FNa₂OH₂⁺ (Linear)

O,0,-2.0334973875,0.0000217257,0.0000011311
H,0,-2.625867744,-0.7589516467,0.000003457
H,0,-2.6256626806,0.7591558221,0.0000035199
F,0,2.4253358882,0.0000706531,-0.0000004971
Na,0,0.2971871634,-0.0000432207,-0.0000093783
Na,0,4.5021417606,-0.0000466836,0.0000074374

FNa₂OH₂⁺ (Ring)

F,0,0.0000000179,1.3037726124,0.0007272073
O,0,0.0000005344,-1.7650273649,0.0000523458
H,0,0.0000004139,-2.3678756172,0.7530206526
Na,0,1.8353070084,0.3391331114,-0.0004960512
Na,0,-1.8353063885,0.3391319694,-0.0004960512
H,0,0.000000414,-2.3682257112,-0.7526351034

ONa₃OH₂⁺

O,0,0.,0.,0.82847

O,0,0.,0.,-2.648505

H,0,0.756075,0.,-3.248687

Na,0,0.,1.631893,-0.502435

Na,0,0.,-1.631893,-0.502435

Na,0,0.,0.,2.919202

H,0,-0.756075,0.,-3.248687

NNa₄OH₂⁺

N,0,0.6769547143,0.0000717761,-0.0000758719

O,0,-2.9776302433,0.0002457965,0.000009627

H,0,-3.577866873,-0.7566934728,-0.0001244327

Na,0,2.0425504036,1.7785117755,0.0002811556

Na,0,2.0433358348,-1.7777780269,-0.0009078794

Na,0,-0.8271947816,-0.0007840666,1.6702114476

Na,0,-0.8280757521,0.0003098852,-1.6696087856

H,0,-3.5772163027,0.757699333,0.0003807393

LiOH₂⁺

O,0,0.2014078595,-0.2060429207,0.23658102

H,0,-0.4309295619,-0.7457772947,0.7261926928

Li,0,0.4195319535,-0.1064341795,-1.616568104

H,0,0.6908241718,0.2771987543,0.9132142707

FLi₂OH₂⁺ (Linear)

O,0,-1.3398777368,-0.0000171599,0.0000501306

H,0,-1.9260828002,-0.0000227302,-0.7638188766

H,0,-1.9257772624,-0.0000227337,0.7641560217

Li,0,0.5712634618,0.0000020807,0.0001143776

F,0,2.2911250242,0.0000020073,0.0002540727

Li,0,3.9720321734,0.0000019257,0.000342654

FLi₂OH₂⁺ (Ring)

F,0,1.3774892875,-0.0000017106,-0.0000725026
Li,0,0.4383847827,-1.4024845852,-0.0000579538
Li,0,0.4383948644,1.4024875141,-0.0000579539
O,0,-1.3796263113,0.0000006674,0.0000813161
H,0,-1.9812755979,0.0000015571,-0.7567835729
H,0,-1.9811090254,0.0000015572,0.7570786671

OLi₃OH₂⁺

O,0,1.2176748224,0.0000024113,-0.0001032855
Li,0,0.0552213108,-1.2698973576,-0.0000478516
Li,0,0.0553623478,1.2700311067,-0.0000466875
Li,0,2.9200547354,-0.0001124767,-0.0001844617
O,0,-1.7613386472,0.000022435,0.0001150897
H,0,-2.3589229873,0.0000318112,-0.7589281374
H,0,-2.3587885819,0.0000310702,0.7592643339

NLi₄OH₂⁺

N,0,1.1816451508,0.0000492699,-0.0001159297
Li,0,2.2461167866,-1.4645957349,-0.000233468
Li,0,2.2459645428,1.4648054296,-0.0002744248
Li,0,-0.1454464454,-0.0000679855,1.2643068797
Li,0,-0.1457950341,-0.0000345145,-1.2641964804
O,0,-1.9671086859,-0.0000465064,0.0001878888
H,0,-2.5637467002,-0.7599190401,0.0002394227
H,0,-2.5636226147,0.7599230818,0.0002571117

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