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Accessory Publication

The Na_2X superalkali species (X=SH, SCH_3, OCH_3, CN, N_3) as building blocks in the Na_2XY salts (Y=$MgCl_3$, Cl, NO_2). An ab initio study of the electric properties of the Na_2XY salts.

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Table S1. The MP2 geometrical parameters (bond lengths in Å, angles in degrees) and partial atomic charges (in a.u.) fitted to the electrostatic potential according to the Merz-Singh-Kollman scheme for the Na_2X and Na_2X^+ (X=SH, CN, N_3, OCH_3, and SCH_3) species. See Figures 1 and 3 for atom numbering.

Geometrical parameters	Partial atomic charges
Na_2SH (C_s)	
r(NaS)=2.643; r(SH)=1.339; r(Na−Na)=3.318; ∠(NaSNa)=77.74; ∠(NaSH)=100.10; ∠(NaSNaH)=98.54	q^{Na}=0.189; q^{S}=-0.479; q^{H}=0.101
Na_2SH^+ (C_{2v})	
r(NaS)=2.589; r(SH)=1.336; r(Na−Na)=5.112; ∠(NaSNa)=161.55	q^{Na}=0.932; q^{S}=-1.047; q^{H}=0.183
Na_2CN (C_s)	
r(Na_1N)=2.315; r(Na_2C)=2.473; r(NC)=1.193; r(Na_1−Na_2)=3.296; ∠(Na_1NNa_2)=85.88; ∠(Na_2NC)=74.10; ∠(Na_1NCNa_2)=0.00	$q^{Na(1)}$= 0.142; $q^{Na(2)}$= 0.243; q^{C}=-0.344; q^{N}=-0.041
Na_2CN^+ (C_{2v})	
r(NaN)=2.404; r(NaC)=2.552; r(NC)=1.194; r(Na−Na)=4.773; ∠(NaNNa)=166.17	q^{Na}=0.970; q^{C}=-0.378; q^{N}=-0.561
Na_2N_3 (C_{2v})	
r(NaN_1)=2.296; r(N_1N_2)=1.220; r(N_2N_3)=1.187; r(Na−Na)=3.185; ∠(NaN_1Na)=87.84	q^{Na}=0.210; $q^{N(1)}$=-0.605; $q^{N(2)}$=0.867; $q^{N(3)}$= -0.683
$Na_2N_3^+$ (C_{2v})	
r(NaN_1)=2.302; r(N_1N_2)=1.223; r(N_2N_3)=1.185; r(Na−Na)=4.459; ∠(NaN_1Na)=150.96	q^{Na}=0.963; $q^{N(1)}$=-1.100; $q^{N(2)}$=0.586; $q^{N(3)}$= -0.412
Na_2OCH_3 (C_s)	
r(NaO)=2.156; r(OC)=1.398; r(CH_1)=1.104; r(CH_2)=1.105; r(Na−Na)=3.110; ∠(NaONa)=92.33; ∠(OCH_1)=112.72; ∠(OCH_2)=112.51; ∠(NaONaC)=180.00; ∠(NaOCH_2)=180.00; ∠($H_1CH_1H_2$)=112.60	q^{Na}=0.147; q^{O}=-0.636; q^{C}=1.460; $q^{H(1)}$= -0.391; $q^{H(2)}$= -0.336
$Na_2OCH_3^+$ (C_s)	
r(NaO)=2.151; r(OC)=1.414; r(CH_1)=1.101; r(CH_2)=1.108;	q^{Na}=0.960; q^{O}=-1.157; q^{C}=0.305;

r(Na−Na)=4.073; ∠(NaONa)=143.10; ∠(NaOC)=104.30; ∠(NaOC)=112.60; ∠(OCH_1)=113.06; ∠(OCH_2)=112.67; ∠(NaONaC)=180.00; ∠(NaOCH_1)=180.00; ∠(H_1C$H_1$$H_2$)=113.25	$q^{H(1)}$= -0.012; $q^{H(2)}$= -0.045
Na_2SCH_3 (C_s)	
r(NaS)=2.643; r(SC)=1.830; r(CH_1)=1.092; r(CH_2)=1.094; r(Na−Na)=3.317; ∠(NaSNa)=77.74; ∠(NaSC)=110.91; ∠(SCH_1)=110.09; ∠(SCH_2)=112.63; ∠(NaSNaC)=107.94; ∠(NaSCH_1)=78.48; ∠(H_1C$H_1$$H_2$)=116.54	q^{Na}=0.169; q^{S}=-0.575; q^{C}=0.947; $q^{H(1)}$= -0.256; $q^{H(2)}$= -0.199
$Na_2SCH_3^+$ (C_s)	
r(NaS)=2.587; r(SC)=1.836; r(CH_1)=1.092; r(CH_2)=1.091; r(Na−Na)=4.971; ∠(NaSNa)=147.73; ∠(NaSC)=104.86; ∠(SCH_1)=110.72; ∠(SCH_2)=111.42; ∠(NaSNaC)=156.54; ∠(NaSCH_1)=83.65; ∠(H_1C$H_1$$H_2$)=116.89	q^{Na}=0.924 q^{S}=-1.065 q^{C}=0.056 $q^{H(1)}$= 0.070 $q^{H(2)}$= 0.020

Table S2: The MP2 harmonic vibrational frequencies (in cm^{-1}) for the Na_2X and Na_2X^+ (X=SH, CN, N_3, OCH_3, and SCH_3) species.

Species	Vibrational frequencies
Na_2SH	v_1=100 (*a*'); v_2=155 (*a*''); v_3=209 (*a*'); v_4=273 (*a*''); v_5=275 (*a*'); v_6=2769 (*a*')
Na_2SH^+	v_1=33 (b_1); v_2=71 (a_1); v_3=222 (a_1); v_4=316 (b_2); v_5=515 (b_2); v_6=2792 (a_1)
Na_2CN	v_1=97 (*a*''); v_2=125 (*a*'); v_3=137 (*a*'); v_4=243 (*a*'); v_5=303 (*a*'); v_6=2004 (*a*')
Na_2CN^+	v_1=53 (b_2); v_2=62 (b_1); v_3=69 (a_1); v_4=213 (a_1); v_5=327 (b_2); v_6=1983 (a_1)
Na_2N_3	v_1=55 (b_2); v_2=63 (b_1); v_3=126 (a_1); v_4=265 (b_2); v_5=269 (a_1); v_6=549 (b_1); v_7=587 (b_2); v_8=1283 (a_1); v_9=2183 (a_1)
$Na_2N_3^+$	v_1=37 (b_2); v_2=76 (a_1); v_3=104 (b_1); v_4=234 (a_1); v_5=370 (b_2); v_6=519 (b_1); v_7=625 (b_2); v_8=1216 (a_1); v_9=2121 (a_1)
Na_2OCH_3	v_1=13 (*a*''); v_2=109 (*a*'); v_3=124 (*a*''); v_4=137 (*a*'); v_5=338 (*a*'); v_6=341 (*a*'); v_7=1125 (*a*'); v_8=1189 (*a*''); v_9=1200 (*a*'); v_{10}=1501 (*a*'); v_{11}=1517 (*a*''); v_{12}=1524 (*a*'); v_{13}=2953 (*a*'); v_{14}=2998 (*a*'); v_{15}=3006 (*a*'')
$Na_2OCH_3^+$	v_1=54 (*a*''); v_2=100 (*a*'); v_3=108 (*a*'); v_4=149 (*a*''); v_5=293 (*a*'); v_6=468 (*a*'); v_7=1068 (*a*'); v_8=1182 (*a*''); v_9=1211 (*a*'); v_{10}=1508 (*a*''); v_{11}=1514 (*a*'); v_{12}=1542 (*a*'); v_{13}=2943 (*a*'); v_{14}=3015 (*a*'); v_{15}=3050 (*a*'')
Na_2SCH_3	v_1=51 (*a*'); v_2=83 (*a*''); v_3=91 (*a*''); v_4=110 (*a*'); v_5=222 (*a*''); v_6=267 (*a*'); v_7=737 (*a*'); v_8=983 (*a*'); v_9=987 (*a*''); v_{10}=1393 (*a*'); v_{11}=1484 (*a*''); v_{12}=1491 (*a*'); v_{13}=3067 (*a*'); v_{14}=3148 (*a*'); v_{15}=3163 (*a*'')
$Na_2SCH_3^+$	v_1=43 (*a*'); v_2=47 (*a*''); v_3=75 (*a*'); v_4=110 (*a*''); v_5=229 (*a*'); v_6=325 (*a*''); v_7=730 (*a*'); v_8=988 (*a*'); v_9=999 (*a*''); v_{10}=1410 (*a*'); v_{11}=1479 (*a*'); v_{12}=1497 (*a*''); v_{13}=3086 (*a*'); v_{14}=3171 (*a*''); v_{15}=3181 (*a*')

Table S3. The MP2 geometrical parameters (bond lengths in Å, angles in degrees) and partial atomic charges (in a.u.) fitted to the electrostatic potential according to the Merz-Singh-Kollman scheme for the Na_2XMgCl_3 (X=SH, CN, N_3, OCH_3, and SCH_3) species. See Figure 4 for atom numbering.

Geometrical parameters	Partial atomic charges
$Na_2SHMgCl_3$ (C_s)	
r(NaS)=2.612; r(SH)=1.336; r(Na−Na)=3.933; r($NaCl_1$)=2.566; r($MgCl_1$)=2.314; r($MgCl_2$)=2.211; ∠(NaSNa)=97.67; ∠(NaSH)=105.79; ∠(Cl_1MgCl_1)=112.68; ∠(Cl_1MgCl_2)=123.66; ∠(NaSNaH)=108.87; ∠($Cl_2MgCl_1Cl_1$)=179.75	q^{Na}=0.747; q^{S}=-0.820; q^{H}=0.123; q^{Mg}=0.930; $q^{Cl(1)}$=-0.597; $q^{Cl(2)}$=-0.532
$Na_2CNMgCl_3$ (C_s)	
r(NaN)=2.362; r(NC)=1.195; r(Na−Na)=3.877; r($NaCl_1$)=2.558; r($MgCl_1$)=2.315; r($MgCl_2$)=2.211; ∠(NaNNa)=110.34; ∠(NaNC)=89.32; ∠(Cl_1MgCl_1)=112.44; ∠(Cl_1MgCl_2)=123.78; ∠(NaNNaC)=89.03; ∠($Cl_2MgCl_1Cl_1$)=179.70	q^{Na}=0.832; q^{N}=-0.474; q^{C}=-0.342; q^{Mg}=0.987; $q^{Cl(1)}$=-0.651; $q^{Cl(2)}$=-0.533
$Na_2N_3MgCl_3$ (C_1)	
r(Na_1N_1)=2.305; r(Na_2N_1)=2.261; r(N_1N_2)=1.221; r(N_2N_3)=1.185; r(Na_1−Na_2)=3.477; r($MgCl_1$)=2.359; r($MgCl_2$)=2.287; r($MgCl_3$)=2.203; r(Na_1Cl_2)=2.612; r(Na_2Cl_1)=2.621; ∠($Na_1N_1Na_2$)=99.20; ∠(Cl_1MgCl_2)=100.37; ∠(Cl_1MgCl_3)=136.23; ∠($MgNa_1N_1Na_2$)=-21.17 ∠($Cl_3MgN_1N_2$)=116.95	$q^{Na(1)}$=0.843; $q^{Na(2)}$=0.891; $q^{N(1)}$=-1.222; $q^{N(2)}$=0.852; $q^{N(3)}$=-0.560; q^{Mg}=0.970; $q^{Cl(1)}$=-0.640; $q^{Cl(2)}$=-0.582; $q^{Cl(3)}$=-0.553
$Na_2OCH_3MgCl_3$ (C_1)	
r(NaO)=2.151; r(OC)=1.401; r(CH_1)=1.103; r(CH_2)=1.104; r(CH_3)=1.105; r(Na−Na)=3.461; r($MgCl_1$)=2.313; r($MgCl_2$)=2.211; r($NaCl_1$)=2.569; ∠(NaONa)=107.11; ∠(NaOC)=127.37; ∠(OCH_1)=112.48; ∠(Cl_1MgCl_1)=111.27; ∠(Cl_1MgCl_2)=124.36; ∠(NaONaC)=179.69; ∠($H_1CH_2H_3$)=112.48; ∠(Cl_2MgOC)=-74.01	q^{Na}=0.896; q^{O}=-1.277; q^{C}=0.774; $q^{H(1)}$=-0.141; $q^{H(2)}$=-0.143; $q^{H(3)}$=-0.144; q^{Mg}=1.014; $q^{Cl(1)}$=-0.659; $q^{Cl(2)}$=-0.555
$Na_2SCH_3MgCl_3$ (C_s)	
r(NaS)=2.607; r(SC)=1.829; r(CH_1)=1.109; r(CH_2)=1.109; r(Na−Na)=3.937; r($MgCl_1$)=2.314; r($MgCl_2$)=2.212; r($NaCl_1$)=2.568; ∠(NaSNa)=98.07; ∠(NaSC)=113.60; ∠(SCH_1)=112.48; ∠(Cl_1MgCl_1)=112.82; ∠(NaSNaC)=120.21; ∠(Cl_1MgCl_2)=123.59; ∠($H_1CH_1H_2$)=116.98	q^{Na}=0.787; q^{S}=-0.922; q^{C}=0.104; $q^{H(1)}$=0.058; $q^{H(2)}$=-0.054; q^{Mg}=0.942; $q^{Cl(1)}$=-0.613; $q^{Cl(2)}$=-0.535

Table S4: The MP2 vibrational frequencies (in cm^{-1}) for the Na_2XMgCl_3 (X=SH, CN, N_3, OCH_3, and SCH_3) species.

Species	Vibrational frequencies
$Na_2SHMgCl_3$	v_1=6 (*a*'); v_2= 26 (*a*''); v_3= 33 (*a*''); v_4= 62 (*a*'); v_5= 76 (*a*'); v_6= 80 (*a*'); v_7=118 (*a*'); v_8= 154 (*a*'); v_9= 189 (*a*'); v_{10}= 207 (*a*''); v_{11}= 270 (*a*'); v_{12}= 287 (*a*'); v_{13}=294 (*a*''); v_{14}= 316 (*a*'); v_{15}= 351 (*a*''); v_{16}= 411 (*a*''); v_{17}= 515 (*a*'); v_{18}= 2795 (*a*')
$Na_2CNMgCl_3$	v_1=6 (*a*'); v_2= 22 (*a*''); v_3= 29 (*a*''); v_4= 69 (*a*''); v_5= 73 (*a*'); v_6= 77 (*a*'); v_7=81 (*a*''); v_8= 98 (*a*'); v_9= 119 (*a*'); v_{10}= 154 (*a*'); v_{11}= 199 (*a*'); v_{12}= 230 (*a*''); v_{13}=273 (*a*'); v_{14}= 316 (*a*'); v_{15}= 318 (*a*''); v_{16}= 410 (*a*''); v_{17}= 515 (*a*'); v_{18}= 1981 (*a*')
$Na_2N_3MgCl_3$	v_1=15 (*a*); v_2= 38 (*a*); v_3= 44 (*a*); v_4= 62 (*a*); v_5= 77 (*a*); v_6= 110 (*a*); v_7=114 (*a*); v_8= 129 (*a*); v_9= 131 (*a*); v_{10}= 159 (*a*); v_{11}= 192 (*a*); v_{12}= 210 (*a*); v_{13}=288 (*a*); v_{14}= 296 (*a*); v_{15}= 328 (*a*); v_{16}= 382 (*a*); v_{17}= 544 (*a*); v_{18}= 607 (*a*); v_{19}= 619 (*a*); v_{20}= 1256 (*a*); v_{21}= 2171 (*a*)
$Na_2OCH_3MgCl_3$	v_1=10 (*a*); v_2= 14 (*a*); v_3= 18 (*a*); v_4= 31 (*a*); v_5= 49 (*a*); v_6= 70 (*a*); v_7=91 (*a*); v_8= 96 (*a*); v_9= 138 (*a*); v_{10}= 142 (*a*); v_{11}= 159 (*a*); v_{12}= 199 (*a*); v_{13}=236 (*a*); v_{14}= 283 (*a*); v_{15}= 356 (*a*); v_{16}= 404 (*a*); v_{17}= 417 (*a*); v_{18}= 517 (*a*); v_{19}= 1119 (*a*); v_{20}= 1190 (*a*); v_{21}= 1204 (*a*); v_{22}= 1506 (*a*); v_{23}= 1518 (*a*); v_{24}= 1526 (*a*); v_{25}= 2956 (*a*); v_{26}= 3001 (*a*); v_{27}= 3015 (*a*)
$Na_2SCH_3MgCl_3$	v_1=5 (*a*'); v_2= 21 (*a*''); v_3= 33 (*a*'); v_4= 34 (*a*''); v_5= 73 (*a*'); v_6= 74 (*a*''); v_7=82 (*a*''); v_8= 96 (*a*''); v_9= 100 (*a*'); v_{10}= 119 (*a*'); v_{11}= 154 (*a*'); v_{12}= 187 (*a*'); v_{13}=214 (*a*''); v_{14}= 269 (*a*'); v_{15}= 302 (*a*''); v_{16}= 313 (*a*'); v_{17}= 411 (*a*''); v_{18}= 513 (*a*'); v_{19}= 743 (*a*'); v_{20}= 989 (*a*'); v_{21}= 997 (*a*''); v_{22}= 1398 (*a*'); v_{23}= 1491 (*a*''); v_{24}= 1495 (*a*'); v_{25}= 3077 (*a*'); v_{26}= 3163 (*a*'); v_{27}= 3170(*a*'')

Table S5. The MP2 geometrical parameters (bond lengths in Å, angles in degrees) and partial atomic charges (in a.u.) fitted to the electrostatic potential according to the Merz-Singh-Kollman scheme for the Na_2XCl (X=SH, CN, N_3, OCH_3, and SCH_3) species. See Figure 5 for atom numbering.

Geometrical parameters	Partial atomic charges
Na_2SHCl (C_s)	
r(NaS)=2.654; r(SH)=1.336; r(Na−Na)=3.268; r(NaCl)=2.543; ∠(NaSNa)=76.01; ∠(NaSH)=107.07; ∠(ClNaS)=101.86; ∠(NaSNaH)=103.89; ∠(NaSNaCl)=4.13	q^{Na}=0.735; q^{S}=-0.817; q^{H}=0.090; q^{Cl}=-0.743
Na_2CNCl (C_1)	
r(Na_1N)=2.333; r(Na_2C)=2.421; r(CN)=1.190; r(Na_1−Na_2)=3.441; r(Na_1Cl)=2.536; r(Na_2Cl)=2.535; ∠(Na_1NC)=94.05; ∠(Na_2CN)=144.20; ∠(ClNa_1N)=117.85; ∠(Na_1ClNa_2C)=0.00	$q^{Na(1)}$=0.767; $q^{Na(2)}$=0.757; q^{N}=-0.419; q^{C}=-0.357; q^{Cl}=-0.750
Na_2N_3Cl (C_{2v})	
r(NaN_1)=2.299; r(N_1N_2)=1.219; r(N_2N_3)=1.186; r(NaCl)=2.530; r(Na−Na)=3.212; ∠(NaN_1Na)=88.62; ∠(ClNaN_1)=96.27	q^{Na}=0.874; $q^{N(1)}$=-1.252; $q^{N(2)}$=0.898; $q^{N(3)}$=-0.597; q^{Cl}=-0.796
Na_2OCH_3Cl (C_1)	
r(NaO)=2.166; r(OC)=1.395; r(CH_1)=1.106; r(CH_2)=1.105; r(CH_3)=1.105; r(Na−Na)=3.043; r(NaCl)=2.546; ∠(NaONa)=89.28; ∠(NaOC)=135.40; ∠(OCH_1)=112.82; ∠(ClNaO)=98.62; ∠(NaONaC)=179.79; ∠(NaONaCl)=0.00; ∠($H_1CH_2H_3$)=112.37	q^{Na}=0.846; q^{O}=-1.164; q^{C}=0.688; $q^{H(1)}$=-0.130; $q^{H(2)}$=-0.137; $q^{H(3)}$=-0.137; q^{Cl}=-0.811
Na_2SCH_3Cl (C_s)	
r(NaS)=2.646; r(SC)=1.827; r(CH_1)=1.092; r(CH_2)=1.093; r_5(Na−Na)=3.283; r(NaCl)=2.542; ∠(NaSNa)=76.68; ∠(NaSC)=117.19; ∠(SCH_1)=112.48; ∠(ClNaS)=101.25; ∠(NaSNaC)=113.97; ∠($H_1CH_1H_2$)=116.60; ∠(NaSNaCl)=4.70	q^{Na}=0.779; q^{S}=-0.907; q^{C}=0.011; $q^{H(1)}$=0.073; $q^{H(2)}$=-0.027; q^{Cl}=-0.781

Table S6: The MP2 vibrational frequencies (in cm^{-1}) for the Na_2XCl (X=SH, CN, N_3, OCH_3, and SCH_3) species.

Species	Vibrational frequencies
Na_2SHCl	v_1=73 (*a'*); v_2= 123 (*a'*); v_3= 221 (*a''*); v_4= 245 (*a''*); v_5= 251 (*a'*); v_6= 265 (*a'*); v_7=290 (*a'*); v_8= 299 (*a''*); v_9= 2792 (*a'*)
Na_2CNCl	v_1=88 (*a*); v_2= 121 (*a*); v_3= 142 (*a*); v_4= 174 (*a*); v_5= 250 (*a*); v_6= 273 (*a*); v_7=299 (*a*); v_8= 319 (*a*); v_9= 2012 (*a*)
Na_2N_3Cl	v_1=60 (b_2); v_2= 66 (b_1); v_3= 122 (a_1); v_4= 139 (b_2); v_5= 254 (b_2); v_6= 267 (a_1); v_7=288 (b_2); v_8= 293 (a_1); v_9= 601 (b_1); v_{10}=606 (b_2); v_{11}= 1258 (a_1); v_{12}= 2178 (a_1)
Na_2OCH_3Cl	v_1=22 (*a*); v_2= 72 (*a*); v_3= 111 (*a*); v_4= 151 (*a*); v_5= 159 (*a*); v_6= 241 (*a*); v_7=287 (*a*); v_8= 338 (*a*); v_9= 347 (*a*); v_{10}= 1138 (*a*); v_{11}= 1193 (*a*); v_{12}= 1204 (*a*); v_{13}= 1504 (*a*); v_{14}= 1517 (*a*); v_{15}= 1523 (*a*); v_{16}= 2945 (*a*); v_{17}=2987 (*a*); v_{18}=2993 (*a*)
Na_2SCH_3Cl	v_1=27 (*a'*); v_2= 83 (*a''*);v_3= 85 (*a''*); v_4= 108 (*a'*); v_5= 123 (*a'*); v_6= 231 (*a''*); v_7=246 (*a''*); v_8= 258 (*a'*); v_9= 285 (*a'*); v_{10}= 747 (*a'*); v_{11}= 986 (*a'*); v_{12}= 993 (*a''*); v_{13}=1395 (*a'*); v_{14}= 1488 (*a''*); v_{15}= 1494 (*a'*); v_{16}= 3069 (*a'*); v_{17}= 3151 (*a'*); v_{18}= 3161(*a''*)

Table S7. The MP2 geometrical parameters (bond lengths in Å, angles in degrees) and partial atomic charges (in a.u.) fitted to the electrostatic potential according to the Merz-Singh-Kollman scheme for the Na_2XNO_2 (X=SH, CN, N_3, OCH_3, and SCH_3) species. See Figure 6 for atom numbering.

Geometrical parameters	**Partial atomic charges**
Na_2SHNO_2 (C_s)	
r(NaS)=2.642; r(SH)=1.336; r(Na−Na)=3.560; r(NaO)=2.322; r(NO)=1.281; ∠(NaSNa)=84.69; ∠(NaSH)=106.31; ∠(ONO)=115.37; ∠(SNaO)=120.02; ∠(NaSNaH)=105.46; ∠(NaSNaN)=3.81	q^{Na}=0.781; q^{S}=-0.824; q^{H}=0.102; q^{N}=0.098; q^{O}=-0.469
Na_2CNNO_2 (C_1)	
r(Na_2N_1)=2.353; r(Na_1C)=2.424; r(CN_1)=1.192; r(Na_1−Na_2)=3.540; r(Na_1O_1)=2.247; r(Na_2O_1)=2.560; r(Na_2O_2)=2.641; r(N_2O_1)=1.309; r(N_2O_2)=1.272; ∠(Na_2N_1C)=161.28; ∠(Na_1CN_1)=83.15; ∠($Na_1O_1Na_2$)=94.66 ∠($O_1N_2O_2$)=113.93; ∠($Na_1Na_2CN_1$)=0.05; ∠($Na_1O_1N_2O_2$)=144.00	$q^{Na(1)}$=0.800; $q^{Na(2)}$=0.779; $q^{N(1)}$=-0.402; q^{C}=-0.372; $q^{N(2)}$=0.072; $q^{O(1)}$=-0.491; $q^{O(2)}$=-0.385
$Na_2N_3NO_2$ (C_1)	
r(Na_1N_1)=2.280; r(Na_2N_1)=2.357; r(N_1N_2)=1.218; r(N_2N_3)=1.188; r(Na_1O_1)=2.236; r(Na_2O_1)=2.560; r(Na_2O_2)=2.636; r(Na_1−Na_2)=3.352; r(N_4O_1)=1.310; r(N_4O_2)=1.273; ∠($Na_1N_1Na_2$)=92.58; ∠($Na_1O_1Na_2$)=88.40 ∠($O_1N_4O_2$)=113.95; ∠($Na_1N_1Na_2O_1$)=0.32; ∠($Na_1N_1Na_2N_2$)=179.32; ∠($Na_1O_1N_4O_2$)=123.80	$q^{Na(1)}$=0.881; $q^{Na(2)}$=0.891; $q^{N(1)}$=-1.113; $q^{N(2)}$=0.750; $q^{N(3)}$=-0.552; $q^{N(4)}$=0.112; $q^{O(1)}$=-0.562; $q^{O(2)}$=-0.408
$Na_2OCH_3NO_2$ (C_1)	
r(Na_1O_3)=2.139; r(Na_2O_3)=2.176; r(O_3C)=1.398; r(CH_1)=1.104; r(CH_2)=1.105; r(NO_1)=1.279; r(NO_2)=1.213; r(Na_2O_2)=2.186; r(Na_1O_2)=2.402; r(Na_1−Na_2)=3.076; ∠($Na_1O_3Na_2$)=90.88; ∠(O_1NO_2)=113.73; ∠(O_3CH_2)=112.78; ∠($Na_1O_3Na_2C$)=179.92; ∠($H_1CH_1H_2$)=112.51; ∠($Na_1O_1NO_2$)=0.00	$q^{Na(1)}$=0.875; $q^{Na(2)}$=0.862; $q^{O(3)}$=-1.102; q^{C}=0.305; $q^{H(1)}$=-0.053; $q^{H(2)}$=-0.048; $q^{N(4)}$=0.112; $q^{O(1)}$=-0.397; $q^{O(2)}$=-0.587
$Na_2SCH_3NO_2$ (C_1)	
r(Na_1S)=2.605; r(Na_2S)=2.640; r(SC)=1.825; r(CH_1)=1.092; r(CH_2)=1.092; r(NO_1)=1.285; r(NO_2)=1.203; r(Na_1O_1)=2.189; r(Na_2O_2)=2.410; r(Na_2O_1)=2.378; r(Na_1−Na_2)=3.369; ∠(Na_1SNa_2)=79.94; ∠(O_1NO_2)=113.50; ∠(SCH_2)=109.90; ∠(Na_1SNa_2C)=121.64; ∠($H_1CH_1H_2$)=117.10; ∠($Na_1O_1NO_2$)=128.54	$q^{Na(1)}$=0.773; $q^{Na(2)}$=0.796; q^{S}=-0.919; q^{C}=0.020; $q^{H(1)}$=0.064; $q^{H(2)}$=-0.011; q^{N}=0.017; $q^{O(1)}$=-0.466; $q^{O(2)}$=-0.338

Table S8: The MP2 vibrational frequencies (in cm^{-1}) for the Na_2XNO_2 (X=SH, CN, N_3, OCH_3, and SCH_3) species.

Species	Vibrational frequencies
Na_2SHNO_2	v_1=12 (*a*''); v_2= 55 (*a*''); v_3= 55 (*a*'); v_4= 99 (*a*'); v_5= 143 (*a*'); v_6= 247 (*a*''); v_7=255 (*a*'); v_8= 261 (*a*'); v_9= 291 (*a*''); v_{10}= 311 (*a*''); v_{11}= 336 (*a*'); v_{12}= 821 (*a*'); v_{13}=1537 (*a*''); v_{14}= 1816 (*a*'); v_{15}= 2793 (*a*')
Na_2CNNO_2	v_1=19 (*a*); v_2= 73 (*a*); v_3= 90 (*a*); v_4= 99 (*a*); v_5= 104 (*a*); v_6= 147 (*a*); v_7=165 (*a*); v_8= 242 (*a*); v_9= 289 (*a*); v_{10}= 295 (*a*); v_{11}= 323 (*a*); v_{12}= 853 (*a*); v_{13}= 1492 (*a*); v_{14}= 2005 (*a*); v_{15}= 2135 (*a*)
$Na_2N_3NO_2$	v_1=19 (*a*); v_2= 47 (*a*); v_3= 64 (*a*); v_4= 96 (*a*); v_5= 107 (*a*); v_6= 120 (*a*); v_7=168 (*a*); v_8= 235 (*a*); v_9= 254 (*a*); v_{10}= 319 (*a*); v_{11}= 338 (*a*); v_{12}= 576 (*a*); v_{13}= 601 (*a*); v_{14}= 851 (*a*); v_{15}= 1255 (*a*); v_{16}= 1492 (*a*); v_{17}= 2053 (*a*); v_{18}= 2269 (*a*)
$Na_2OCH_3NO_2$	v_1=11 (*a*); v_2= 14 (*a*); v_3= 80 (*a*); v_4= 110 (*a*); v_5= 152 (*a*); v_6= 159 (*a*); v_7=174 (*a*); v_8= 195 (*a*); v_9= 232 (*a*); v_{10}= 302 (*a*); v_{11}= 352 (*a*); v_{12}= 397 (*a*); v_{13}=884 (*a*); v_{14}= 1131 (*a*); v_{15}= 1168 (*a*); v_{16}= 1193 (*a*); v_{17}= 1205 (*a*); v_{18}= 1504 (*a*); v_{19}= 1518 (*a*); v_{20}= 1525 (*a*); v_{21}= 2322 (*a*); v_{22}= 2956 (*a*); v_{23}= 3000 (*a*); v_{24}= 3005 (*a*)
$Na_2SCH_3NO_2$	v_1=29 (*a*); v_2= 47 (*a*); v_3= 82 (*a*); v_4= 91 (*a*); v_5= 109 (*a*); v_6= 129 (*a*); v_7=161 (*a*); v_8= 196 (*a*); v_9= 237 (*a*); v_{10}= 272 (*a*); v_{11}= 275 (*a*); v_{12}= 310 (*a*); v_{13}=751 (*a*); v_{14}= 879 (*a*); v_{15}= 989 (*a*); v_{16}= 997 (*a*); v_{17}= 1139 (*a*); v_{18}= 1394 (*a*); v_{19}= 1490 (*a*); v_{20}= 1496 (*a*); v_{21}= 2614 (*a*); v_{22}= 3077 (*a*); v_{23}= 3162 (*a*); v_{24}= 3169 (*a*)