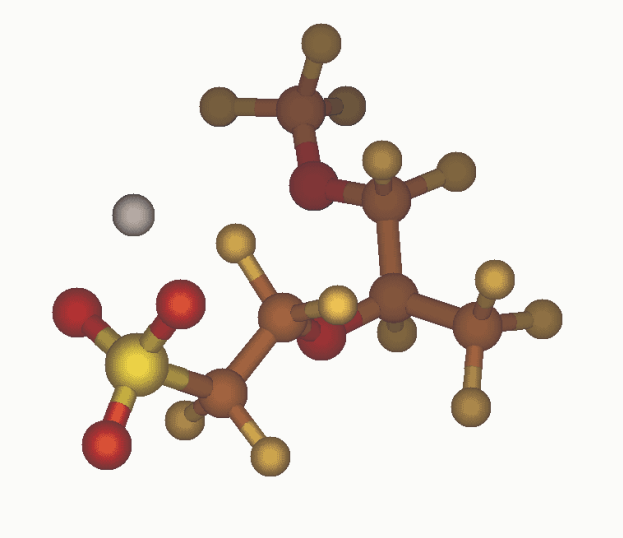
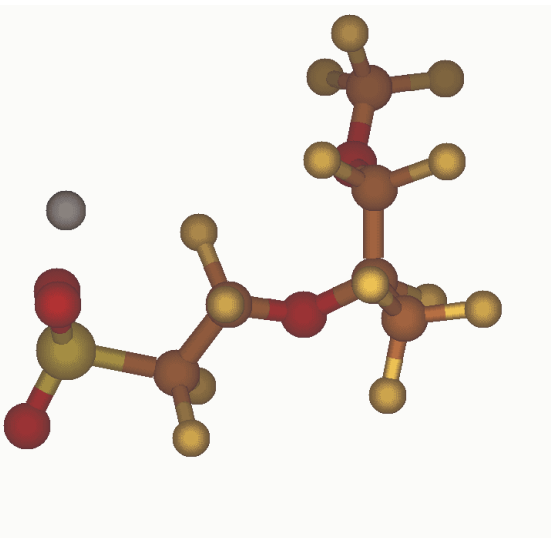
Some points on Na^+ and Li^+ complexes with nafion sidechain:

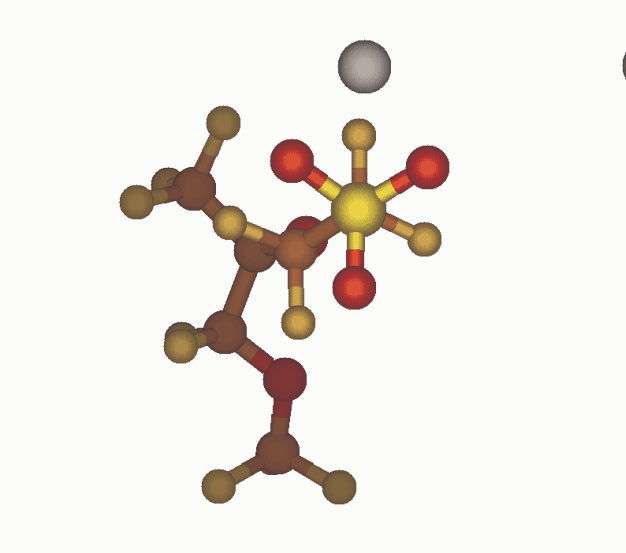
1) Both full and partial optimizations (with only the cation moving relative to fixed chain) suggest 2 coordinated complexes. In case of full optimization and Li^+ the distance with the nearest F (~2.2 Å) indicates some interaction, while that of Na^+ (~3.4 Å) does not (also indicated by the shape of 2-coord dihedral scans) (also notice that solvent may change situation).
2) Larger basis set provides lower total energy while well shape is very similar (3-coord complexes). The 3-coordinated well shapes between Li^+ and Na^+ differ considerably.



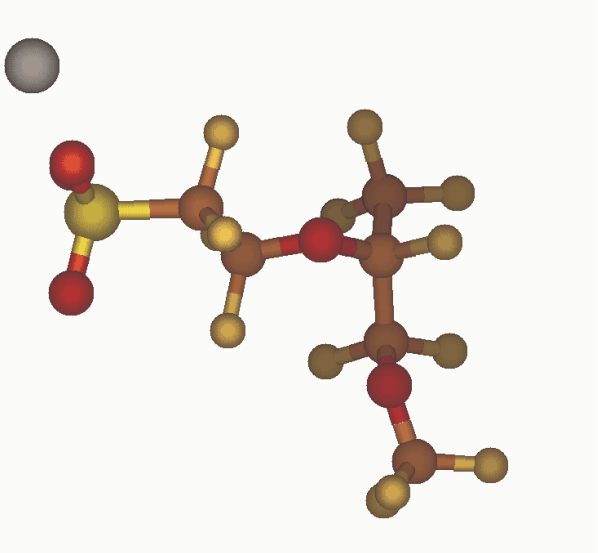
Li^+ - nafion, diagonal;



Li^+ - nafion, side view

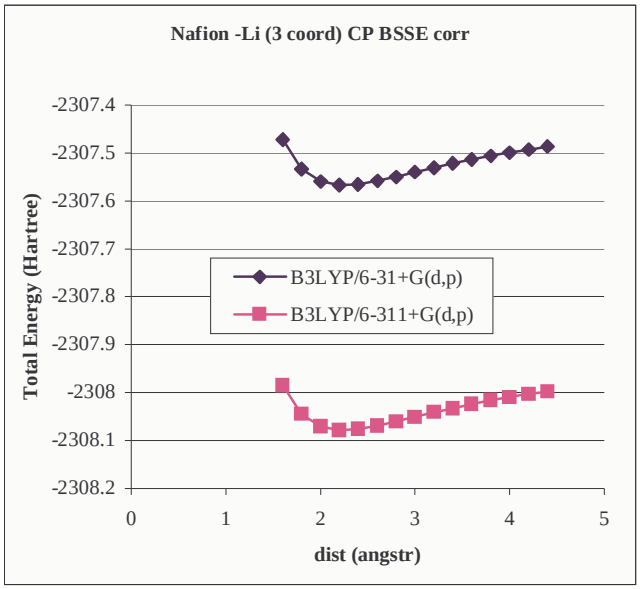


Na^+ - nafion, front;

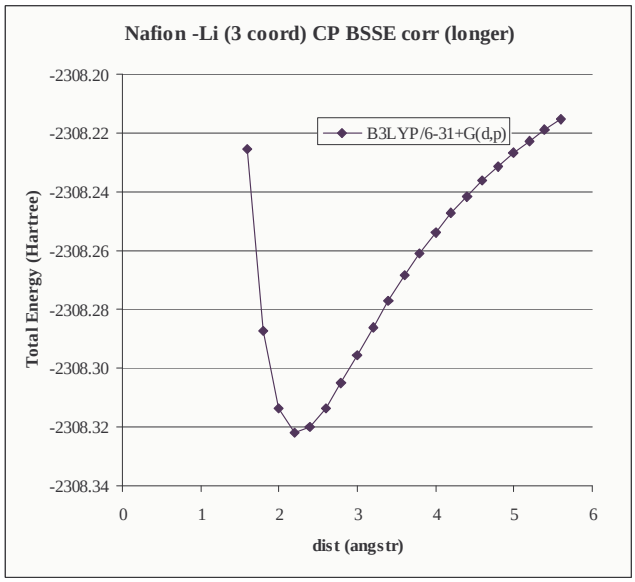


Na^+ - nafion, side view

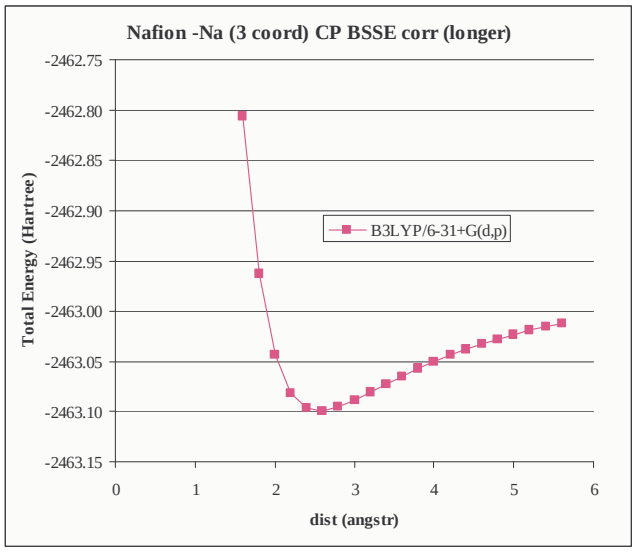
Basis set dependance of energy well shape of 3-coordinated Li^+ and nafion sidechain. Pregiven geometry of sidechain. BSSE corrected by Counterpoise method.



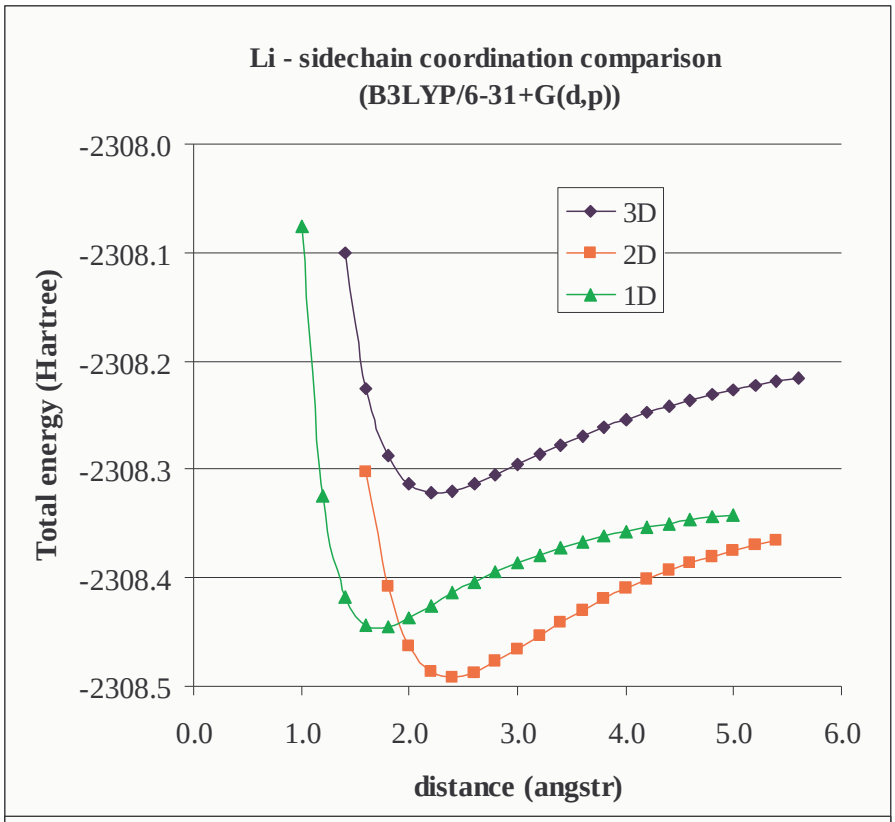
Energy well shape of Li^+ 3-coordinated to nafion sidechain. Pregiven geometry. BSSE corrected by Counterpoise method. Distance given as Li - S



Energy well shape of Na^+ 3-coordinated to nafion sidechain. Pregiven geometry. BSSE corrected by Counterpoise method. Disance as Li - S



Comparison of energy *vs* distance plots of 3-, 2- and 1-coordinated nafion sidechain – Li^+ complexes. Slight surprise to find 3-coordinated complexes to be most unstable.
All energies with Counterpoise BSSE correction. Note that 1-coord distance is given as Li-O, others as Li-S, hence shift of well location.



Comparison of energy *vs* distance plots of 3-, 2- and 1-coordinated nafion sidechain –Na^+ complexes. Same surprise to find 3-coordinated complexes to be most unstable.
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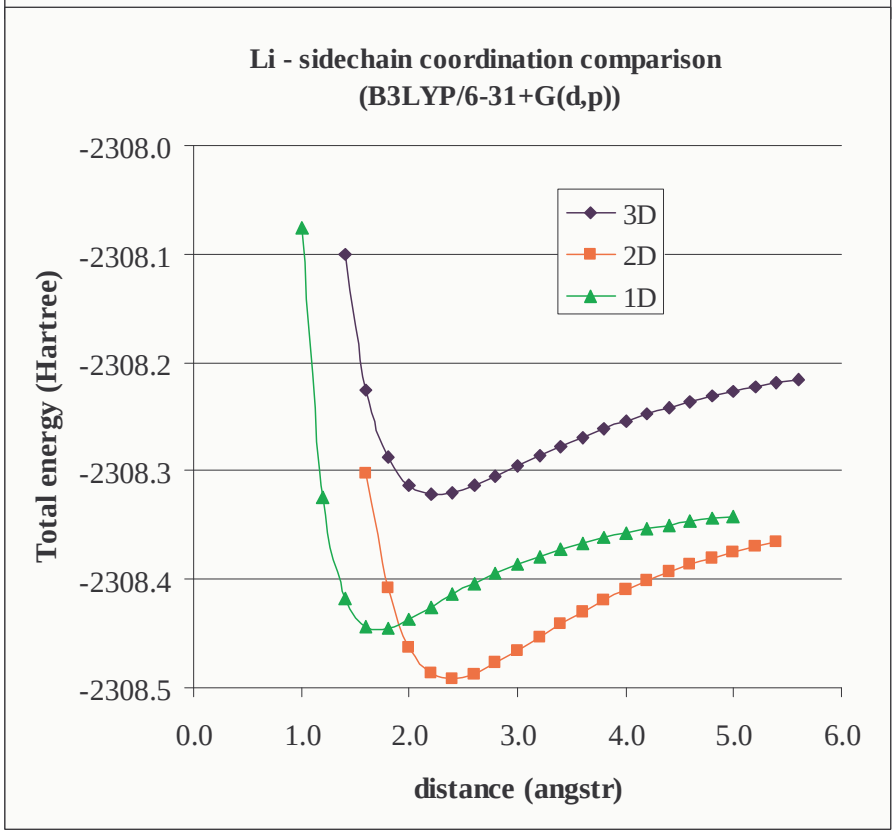
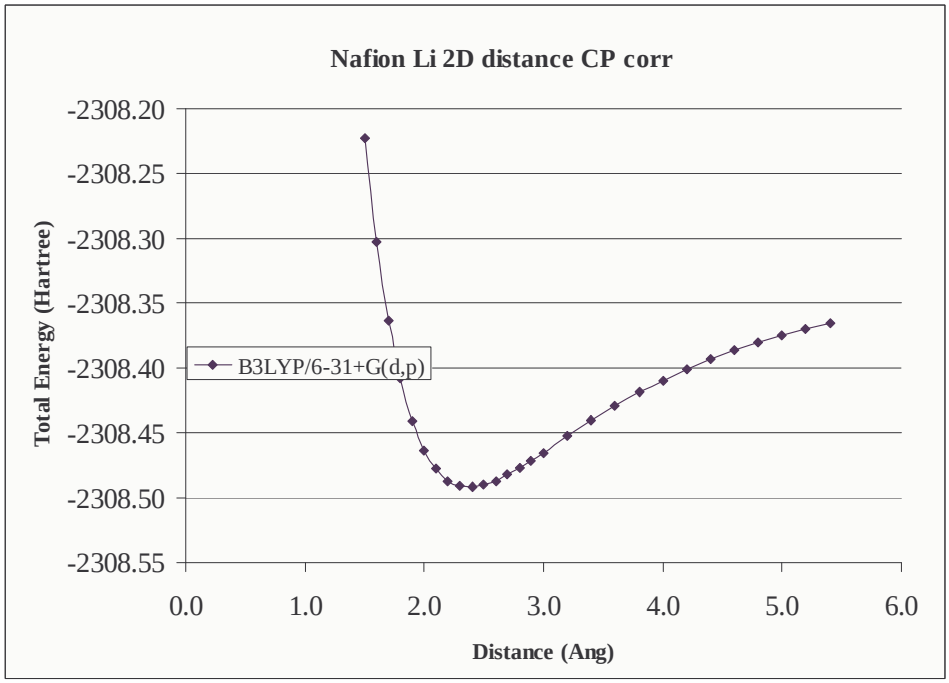
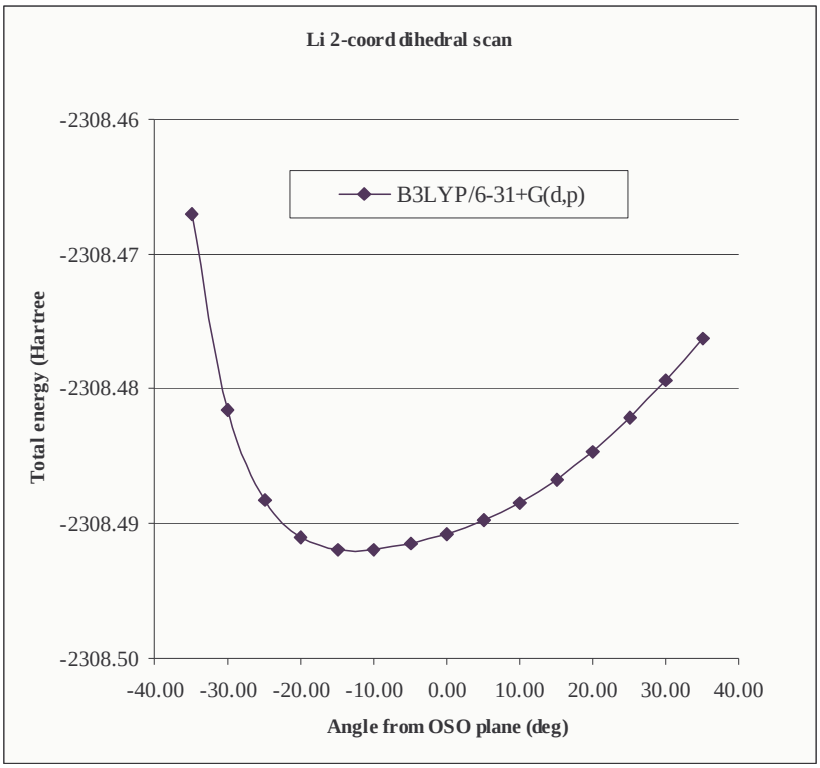


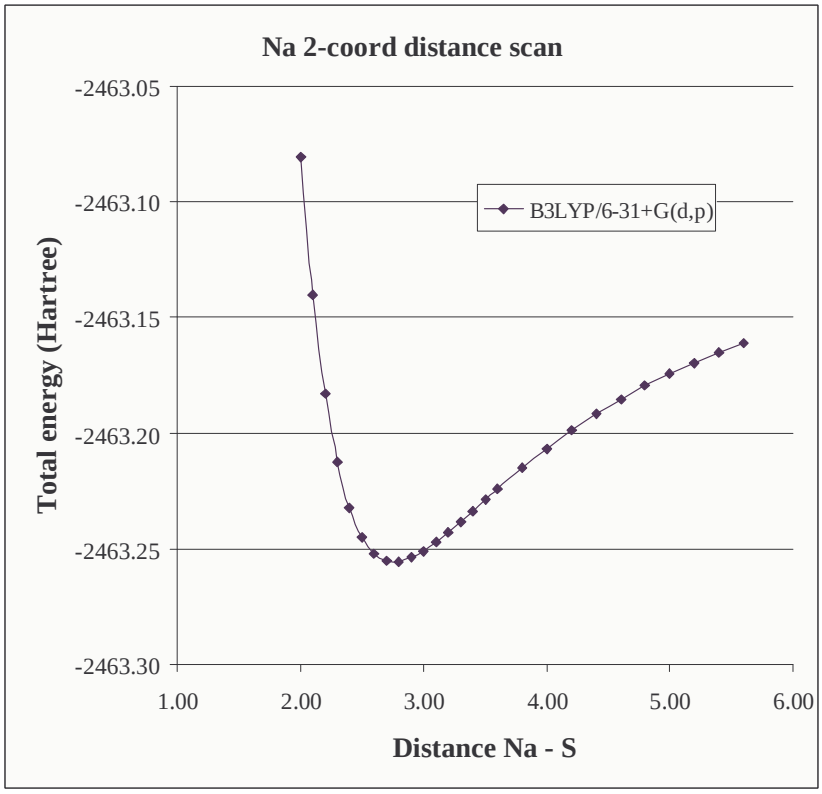
Energy well shape of Li^+ 2-coordinated to nafion sidechain. Fully optimized geometry, distance Li – S. BSSE corrected by Counterpoise method.



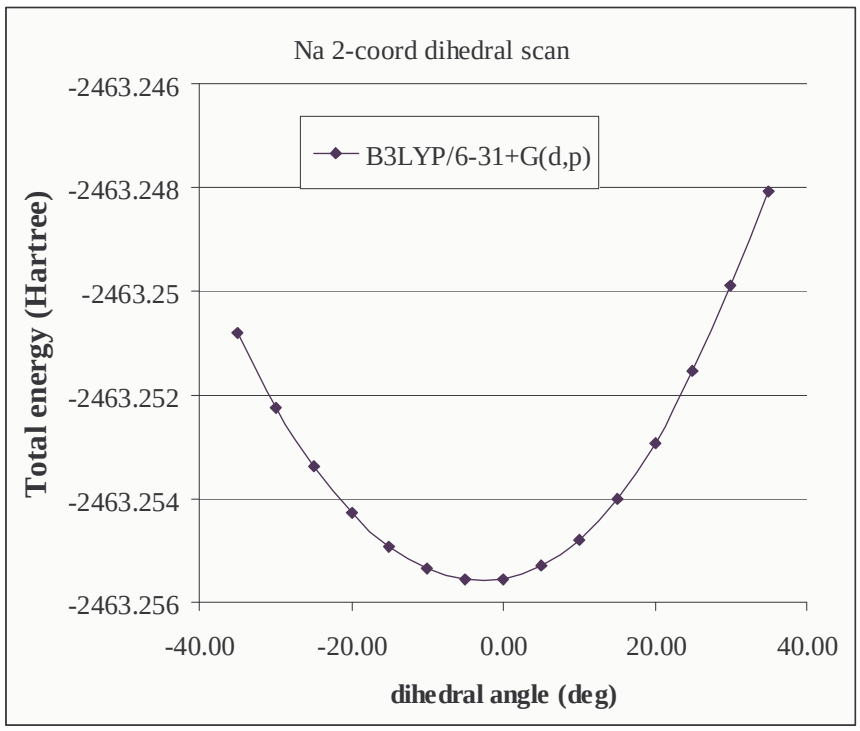
Energy well shape of Li^+ 2-coordinated to nafion sidechain. Fully optimized geometry, dihedral angle from O-S-0 plane. BSSE corrected by Counterpoise method. Lack of symmetry due to the influence of the nearest F-atom.



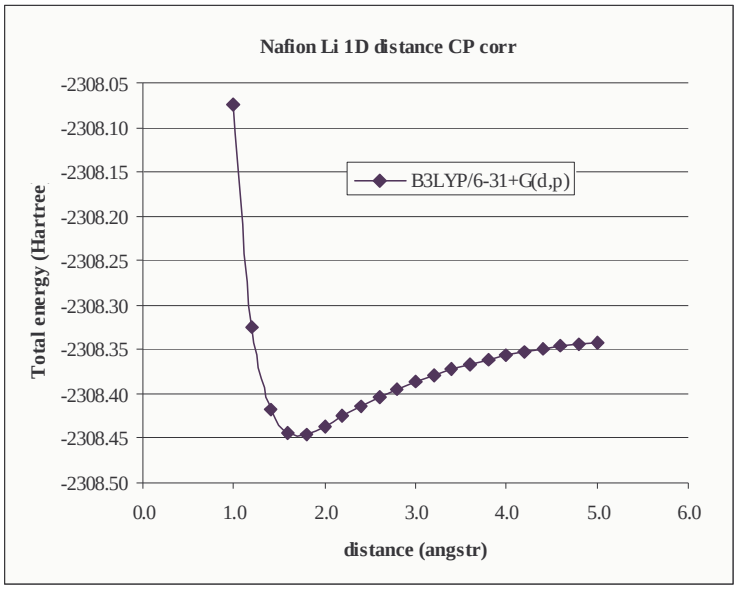
Energy well shape of Li^+ 2-coordinated to nafion sidechain. Fully optimized geometry, distance Li – S. BSSE corrected by Counterpoise method



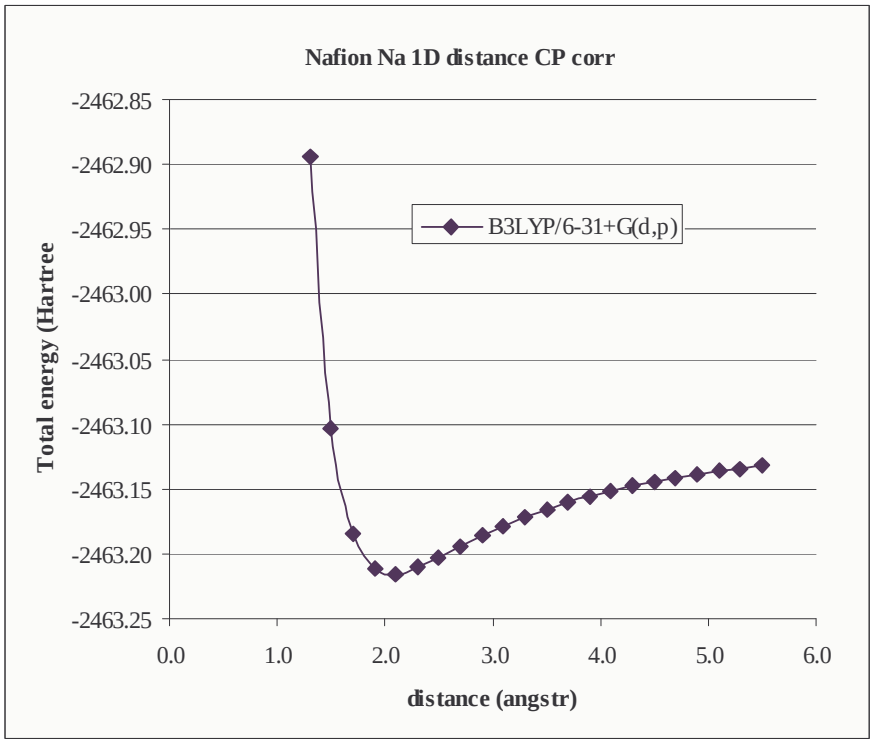
Energy well shape of Na^+ 2-coordinated to nafion sidechain. Fully optimized geometry, dihedral angle from O-S-0 plane. BSSE corrected by Counterpoise method.



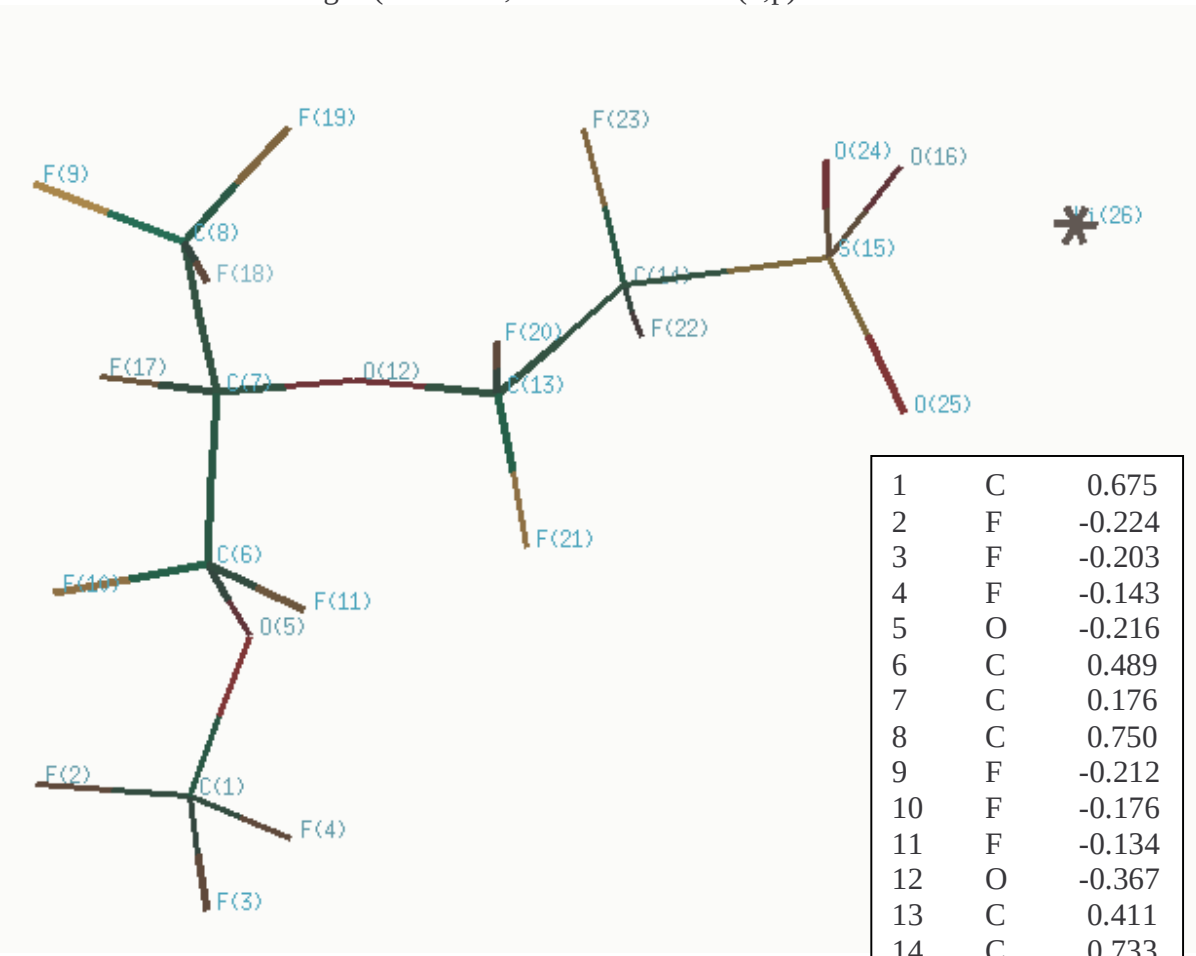
Energy well shape of Li^+ 1-coordinated to nafion sidechain. Fully optimized geometry, distance Li – O. BSSE corrected by Counterpoise method.



Energy well shape of Na^+ 1-coordinated to nafion sidechain. Fully optimized geometry, distance Li – O. BSSE corrected by Counterpoise method.



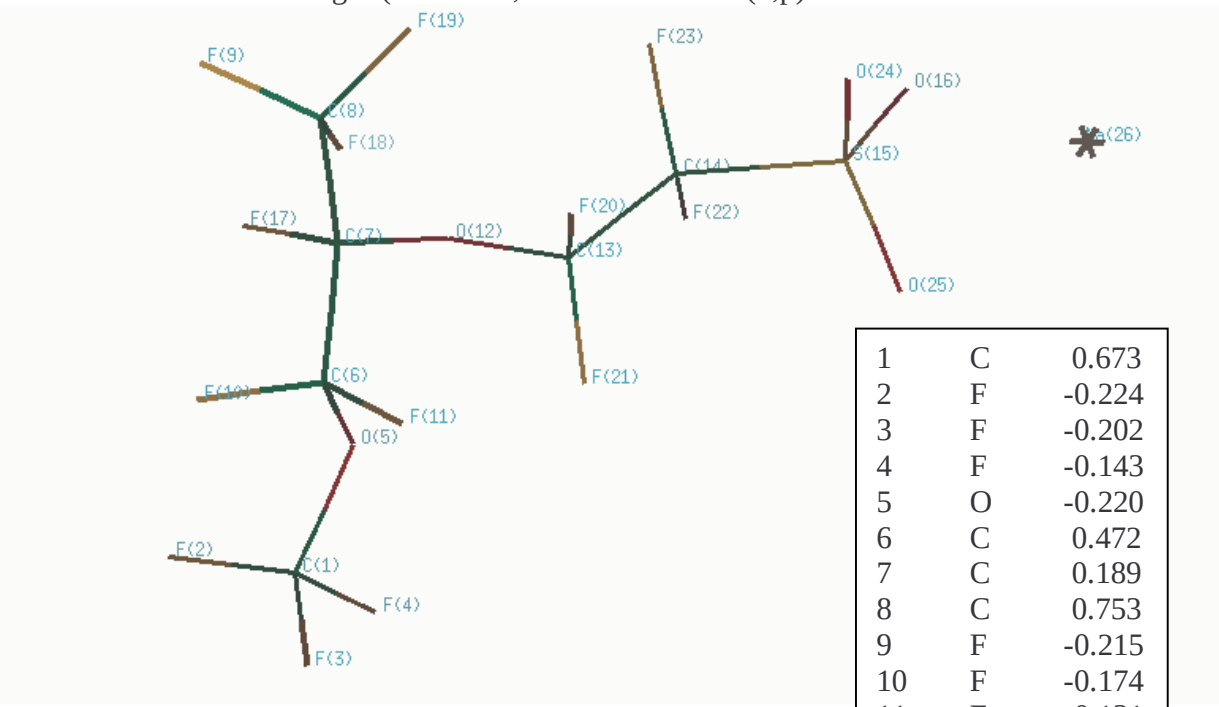
Li^+ -nafion sidechain charges (CHELPG, B3LYP/6-311+G(d,p)



1	C	0.675
2	F	-0.224
3	F	-0.203
4	F	-0.143
5	O	-0.216
6	C	0.489
7	C	0.176
8	C	0.750
9	F	-0.212
10	F	-0.176
11	F	-0.134
12	O	-0.367
13	C	0.411
14	C	0.733
15	S	0.737
16	O	-0.565
17	F	-0.157
18	F	-0.234
19	F	-0.218
20	F	-0.174
21	F	-0.166
22	F	-0.217
23	F	-0.214
24	O	-0.609
25	O	-0.601
26	Li	0.860

The charge distribution is relatively similar with both cations.

Na^+ -nafion sidechain charges (CHELPG, B3LYP/6-311+G(d,p)



1	C	0.673
2	F	-0.224
3	F	-0.202
4	F	-0.143
5	O	-0.220
6	C	0.472
7	C	0.189
8	C	0.753
9	F	-0.215
10	F	-0.174
11	F	-0.131
12	O	-0.347
13	C	0.439
14	C	0.609
15	S	0.848
16	O	-0.595
17	F	-0.165
18	F	-0.236
19	F	-0.219
20	F	-0.181
21	F	-0.170
22	F	-0.199
23	F	-0.199
24	O	-0.636
25	O	-0.631
26	Na	0.903

Total energy *vs* distance of 3-, 2-. 1-coordinated complexes.

	Li			**Na**		
distance	3D	2D	1D	3D	2D	1D
1.0			-2308.075			
1.2			-2308.325			
1.4	-2308.100		-2308.417			-2462.999
1.6	-2308.226	-2308.302	-2308.444	-2462.806		-2463.144
1.8	-2308.287	-2308.408	-2308.445	-2462.963		-2463.198
2.0	-2308.314	-2308.463	-2308.437	-2463.044	-2463.081	-2463.213
2.2	-2308.322	-2308.487	-2308.425	-2463.082	-2463.183	-2463.213
2.4	-2308.320	-2308.492	-2308.414	-2463.097	-2463.232	-2463.206
2.6	-2308.314	-2308.487	-2308.404	-2463.099	-2463.252	-2463.198
2.8	-2308.305	-2308.477	-2308.394	-2463.095	-2463.255	-2463.190
3.0	-2308.295	-2308.465	-2308.386	-2463.089	-2463.251	-2463.182
3.2	-2308.286	-2308.453	-2308.379	-2463.081	-2463.243	-2463.175
3.4	-2308.277	-2308.441	-2308.372	-2463.073	-2463.234	-2463.169
3.6	-2308.269	-2308.429	-2308.367	-2463.065	-2463.224	-2463.163
3.8	-2308.261	-2308.419	-2308.362	-2463.057	-2463.215	-2463.158
4.0	-2308.254	-2308.409	-2308.357	-2463.050	-2463.207	-2463.154
4.2	-2308.247	-2308.401	-2308.353	-2463.044	-2463.199	-2463.150
4.4	-2308.242	-2308.393	-2308.350	-2463.038	-2463.192	-2463.146
4.6	-2308.236	-2308.386	-2308.346	-2463.033	-2463.185	-2463.143
4.8	-2308.231	-2308.380	-2308.344	-2463.028	-2463.179	-2463.140
5.0	-2308.227	-2308.375	-2308.342	-2463.024	-2463.174	-2463.138
5.2	-2308.223	-2308.370		-2463.019	-2463.169	-2463.135
5.4	-2308.219	-2308.365		-2463.016	-2463.165	-2463.133
5.6	-2308.215			-2463.012	-2463.161	

Total energy *vs* dihedral angle

dihedral angle	Na 2-coord	Li 2-coord.
-35.00	-2463.25	-2308.47
-30.00	-2463.25	-2308.48
-25.00	-2463.25	-2308.49
-20.00	-2463.25	-2308.49
-15.00	-2463.25	-2308.49
-10.00	-2463.26	-2308.49
-5.00	-2463.26	-2308.49
0.00	-2463.26	-2308.49
5.00	-2463.26	-2308.49
10.00	-2463.25	-2308.49
15.00	-2463.25	-2308.49
20.00	-2463.25	-2308.48
25.00	-2463.25	-2308.48
30.00	-2463.25	-2308.48
35.00	-2463.25	-2308.48