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

Supporting Information

Ab Initio Molecular Dynamics Study of Sodium NMR Chemical Shifts in the Methylamine Solution of [$Na^+(C_{222})$ Na^-]

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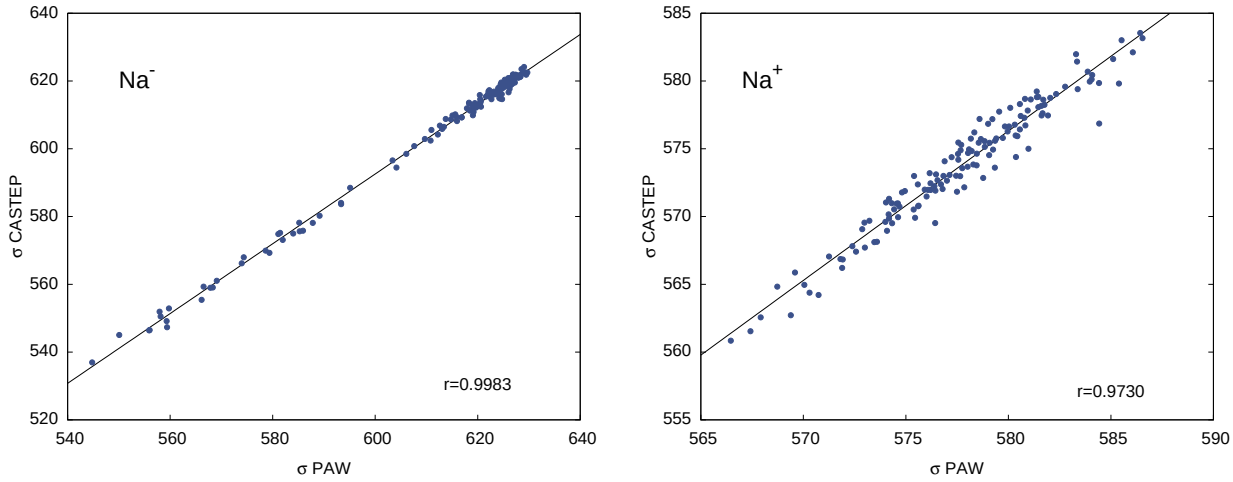

Figure S1: Shielding constants (in ppm) at $^{23}Na^{-}$ and $^{23}Na^{+}$ nuclei for one of the trajectories. PAW vs. CASTEP calculations. The straight line indicates where PAW = CASTEP. Correlation coefficients *r* are given inside of the plot panels.

For QE calculations, one trajectory with a production phase of 20 ps was selected to study the most appropriate grid spacing of time steps, computing 84, 140 and 538 configurations. As NMR chemical shieldings calculated with the GIPAW NMR code of CASTEP allow us a reduced computational cost due to the use of USPP, three trajectories were chosen to test the number of configurations, which varying from 140 up to 1114 along a total time of production phase of 20 ps. The code to generate the different sets of configurations was set up as taking a configuration every X frames, for example, being X as 2000 frames (∼84 conf.), 1200 frames (∼140 conf.), 600 frames (∼279 conf.), 300 frames (∼557 conf.) and 150 frames (∼1114 conf.).

Table S1: Sodium nuclear magnetic shielding constants*, standard error (SE) and chemical shift for one solvated [Na^{+}c222Na^{-}] trajectory at 258 K. Comparisons between different numbers of configurations extracted from the production phase.

Configurations	Ion	σ	SE	$\Delta\sigma$
84	Na^{-}	611.5	2.4	33.7
	Na^{+}	577.8	0.4	
140	Na^{-}	611.6	1.8	33.8
	Na^{+}	577.8	0.4	
538	Na^{-}	616.5	0.7	38.4
	Na^{+}	578.0	0.2	

* Shielding constants (in ppm) calculated with PAW method.

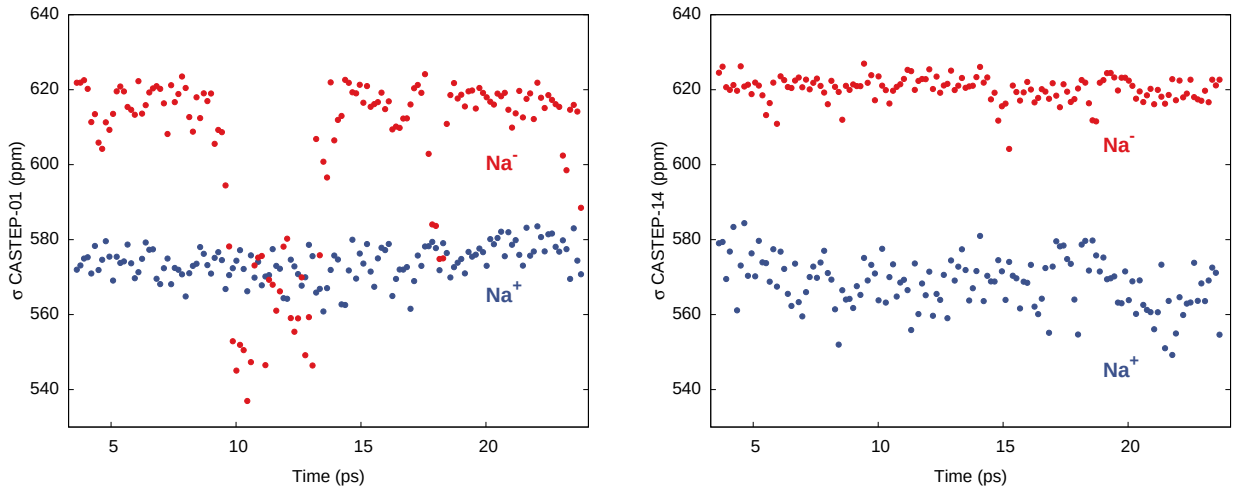

Figure S2: Shielding constants (in ppm) at $^{23}Na^{-}$ and $^{23}Na^{+}$ nuclei along two trajectories; MD-01 (left) and MD-14 (right). Calculations using GIPAW NMR code of CASTEP.

Table S2: Sodium nuclear magnetic shielding constants*, standard error (SE) and chemical shift for three solvated [Na^{+}c222Na^{-}] trajectories at 258 K. Comparisons between different numbers of configurations extracted from the production phase.

MD	Configurations	Ion	σ	SE	$\Delta\sigma$
1	140	Na^{-}	604.5	1.9	30.6
		Na^{+}	573.8	0.4	
	279	Na^{-}	603.8	1.4	30.2
		Na^{+}	573.6	0.3	
	557	Na^{-}	603.8	1.0	30.2
		Na^{+}	573.7	0.2	
	1114	Na^{-}	603.9	0.7	30.2
		Na^{+}	573.7	0.1	
2	140	Na^{-}	601.6	1.5	26.9
		Na^{+}	574.6	0.4	
	551	Na^{-}	601.4	0.8	27.0
		Na^{+}	574.4	0.2	
3	140	Na^{-}	601.4	1.4	26.0
		Na^{+}	575.4	0.4	
	554	Na^{-}	601.3	0.7	26.1
		Na^{+}	575.2	0.2	

* Shielding constants (in ppm) calculated with the GIPAW NMR code of CASTEP.

Table S3: Sodium nuclear magnetic shielding constants* and chemical shifts using PAW and GIPAW NMR code of CASTEP for a set of fifteen solvated [Na^+c222Na^-] trajectories at 258 K. Standard error is given in parenthesis.

MD	Ion	$\Delta\nu^b$	σ^c	$\Delta\sigma^c$	σ^d	$\Delta\sigma^d$
1	Na^-	1.88	611.6 (1.8)	33.8	604.5 (1.9)	30.6
	Na^+	42.09	577.8 (0.4)		573.8 (0.4)	
2	Na^-	0.11	622.0 (0.6)	44.2	615.6 (0.6)	41.8
	Na^+	52.81	577.8 (0.4)		573.8 (0.4)	
3	Na^-	0.26	620.8 (0.7)	43.9	614.6 (0.7)	41.4
	Na^+	25.02	576.9 (0.4)		573.2 (0.4)	
4	Na^-	0.02	624.0 (0.4)	54.0	616.6 (0.4)	51.9
	Na^+	4.75	570.0 (0.7)		564.7 (0.7)	
5	Na^-	4.18	613.7 (1.3)	37.3	607.3 (1.4)	34.9
	Na^+	55.13	576.3 (0.3)		572.4 (0.4)	
6	Na^-	0.03	624.4 (0.4)	45.6	619.1 (0.4)	43.2
	Na^+	40.27	578.9 (0.3)		575.9 (0.4)	
7	Na^-	2.39	617.1 (1.1)	44.7	610.5 (1.1)	43.2
	Na^+	6.76	572.4 (0.6)		567.2 (0.8)	
8	Na^-	0.04	621.7 (0.6)	53.6	615.9 (0.6)	53.5
	Na^+	6.58	568.1 (0.4)		562.4 (0.5)	
9	Na^-	1.14	620.1 (1.0)	41.5	613.2 (1.1)	38.7
	Na^+	29.81	578.5 (0.3)		574.5 (0.4)	
10	Na^-	9.79	610.3 (1.6)	31.2	603.2 (1.7)	27.9
	Na^+	32.00	579.0 (0.3)		575.3 (0.4)	
11	Na^-	13.89	608.0 (1.5)	29.8	601.6 (1.5)	26.9
	Na^+	46.02	578.2 (0.3)		574.6 (0.4)	
12	Na^-	0.66	622.1 (0.6)	44.5	616.5 (0.7)	42.3
	Na^+	49.90	577.6 (0.3)		574.2 (0.4)	
13	Na^-	7.36	607.8 (1.3)	29.1	601.4 (1.4)	26.0
	Na^+	44.02	578.7 (0.4)		575.4 (0.4)	
14	Na^-	0.06	625.8 (0.3)	53.5	620.2 (0.3)	51.7
	Na^+	1.79	572.4 (0.5)		568.5 (0.6)	
15	Na^-	0.06	624.2 (0.4)	45.8	618.8 (0.4)	43.6
	Na^+	36.73	578.4 (0.3)		575.2 (0.4)	
Average	Na^-	2.79	618.2 (0.9)	42.2	611.9 (0.9)	39.9
	Na^+	31.58	576.1 (0.4)		572.1 (0.5)	

* Calculated values with 24 molecules per simulation cell. Shielding constants were computed for 140 snapshot clusters from the aiMD simulations. All quantities are averaged over a set of 15 trajectories. Shielding constants are given in ppm. Experimental chemical shift is 51.2 ppm. [b] Line widths in Hertz are from Ref. 1. Values extracted from PAW calculations. [c] Calculations performed using PAW method. [d] Calculations performed using the GIPAW NMR code of CASTEP.

Table S4: Sodium nuclear magnetic shielding constants* and chemical shift for one solvated [Na^+c222Na^-] snapshot at 258 K using PAW and GIPAW NMR code of CASTEP.

Ion	PAW	CASTEP
σ-Na^-	627.3	621.9
σ-Na^+	576.1	572.0
$\Delta\sigma$	51.2	49.8

* Shielding and chemical shift are in ppm.

Table S5: Sodium nuclear magnetic shielding constants* and chemical shift for one solvated [Na^+c222Na^-] trajectory at 258 K using PAW and STO methods.

Ion	PAW-01	STO-01
σ-Na^-	611.6	608.7
σ-Na^+	577.8	582.4
$\Delta\sigma$	33.8	26.2

* Values averaged for 140 configurations. Shielding and chemical shift are in ppm. STO calculations at PBE/(A)TZP level.

Table S6: Sodium nuclear magnetic shielding constants* and chemical shift for two solvated [Na^+c222Na^-] snapshots at 258 K using PAW and STO methods and, varying the functional and basis for the latter.

	PAW/PBE	STO/PBE/TZP	STO/PBE/QZ4P	STO/PBE0/TZP
Snapshot 1				
σ-Na^-	556.0	546.1	546.5	540.2
σ-Na^+	574.2	577.9	578.2	580.8
$\Delta\sigma$	-18.2	-31.8	-31.7	-40.6
Snapshot 2				
σ-Na^-	626.0	627.8	627.5	627.7
σ-Na^+	581.0	585.5	586.5	586.0
$\Delta\sigma$	45.0	42.3	41.0	41.7

* Shielding and chemical shift are in ppm.

Table S7: ^{23}Na NMR shielding constants (in ppm) and chemical shift for the free sodium ions in gas phase using different methods. Comparison with the Hartree-Fock (HF) calculation values extracted from ref. 2.

Ion	PAW	STO*	CASTEP	HF[2]
σ-Na^-	631.5	631.7	630.2	631.5
σ-Na^+	622.9	623.3	619.1	623.8
$\Delta\sigma$	8.7	8.4	11.1	7.7

* STO calculations at PBE/(A)TZP level.

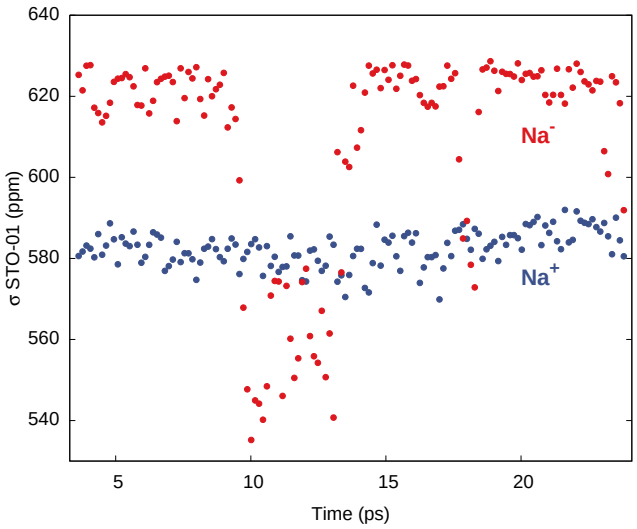

Figure S3: Shielding constants (in ppm) at $^{23}Na^{-}$ and $^{23}Na^{+}$ nuclei along one trajectory; MD-01. Calculations using STO method.

Table S8: Comparison between TZP and QZ4P basis sets using STO. ^{23}Na NMR shielding constants (in ppm) and chemical shift of the free sodium ions in gas phase.

Ion	TZP	QZ4P
σ-Na^{-}	631.7	631.6
σ-Na^{+}	623.3	623.3
$\Delta\sigma$	8.4	8.3

Table S9: ^{23}Na NMR chemical shifts (in ppm) for the free sodium anion using different box sizes (in Å) and PAW method.

Box Size	σ
5.29	717.57
10.58	646.71
12.71	639.36
15.87	634.66
21.17	632.12
26.46	631.54

Table S10: ^{23}Na NMR chemical shifts (in ppm) for the free sodium cation using different box sizes (in Å) and PAW method.

Box Size	σ
5.29	622.21
10.58	622.82
12.71	622.81
15.87	622.82
21.17	622.84
26.46	622.85

Table S11: ^{23}Na NMR chemical shifts (in ppm) for the free sodium anion using different box sizes (in Å) and GIPAW NMR code of CASTEP.

Box Size	σ
5.29	725.77
10.58	647.38
12.71	635.05
15.87	630.32
21.17	630.17
26.46	625.84

Table S12: ^{23}Na NMR chemical shifts (in ppm) for the free sodium cation using different box sizes (in Å) and GIPAW NMR code of CASTEP.

Box Size	σ
5.29	619.94
10.58	617.09
12.71	616.91
15.87	619.25
21.17	622.68
26.46	619.31
37.04	619.08
42.33	619.06

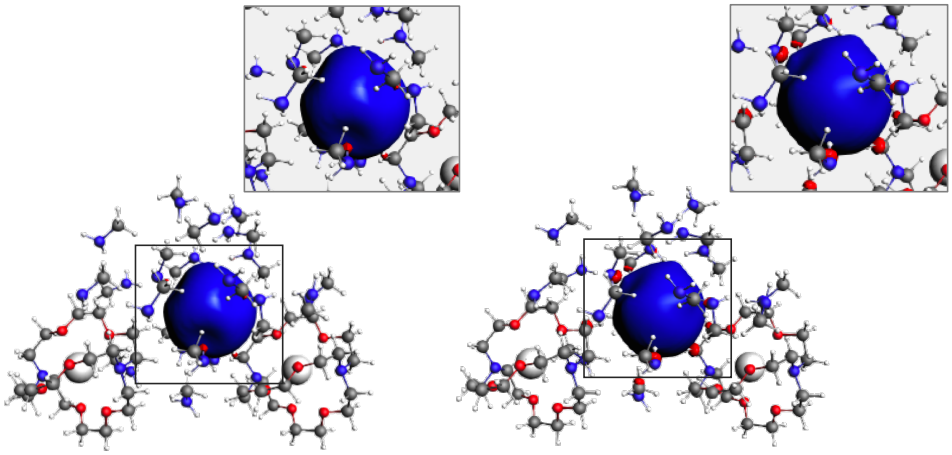

Figure S4: Isosurface (±0.022 au) of the 3*s* NBO and NLMO from snapshot 1 for Na^-.

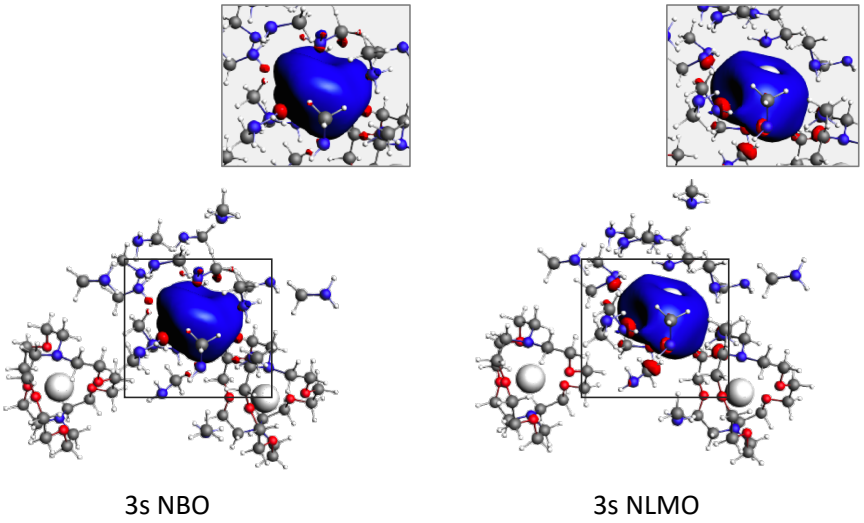

Figure S5: Isosurface (±0.022 au) of the 3*s* NBO and NLMO from snapshot 5 for Na^-.

Table S13: ^{23}Na NMR shielding analysis for a selected trajectory snapshot using PBE and PBE0 functionals.[a]

Functional	PBE	PBE0
Na^- Isotropic Shielding Tensor analysis		
Σ 1s,2s	441.7	441.9
2p	139.4	143.4
3s	-24.3	-27.2
Σ 2p,3s	115.1	116.2
Diffuse[b]	16.8	18.0
Other[c]	-23.0	-16.9
Σ analysis[d]	550.6	559.2
Total calcd.	543.9	543.2
Na^+ Isotropic Shielding Tensor analysis		
Σ 1s,2s	441.8	442.0
2p	153.0	154.0
3s	0.0	0.0
Σ 2p,3s	153.0	154.0
Diffuse[b]	-7.8	-6.5
Other[c]	-12.9	-12.5
Σ analysis[d]	574.1	576.9
Total calcd.	578.2	581.9
^{23}Na NMR shift		
STO	-34.3	-38.7

[a] PBE vs. PBE0 STO calculations. All shielding data in ppm. Shielding tensor contributions from Na 1s, Na 2s, Na 2p, Na 3s, diffuse Na centered NBOs, and contributions from other atoms are listed. [b] Sum of contributions from diffuse Na-centered NBOs ('Rydberg' NBOs). [c] Sum of contributions from other atoms. [d] Sum of all NBO contributions with a print threshold above 1% of shielding tensor.

Table S14: ^{23}Na NMR shielding and shift for a selected trajectory snapshot using PBE/(A)TZP, PBE/QZ4P and PBE0 functionals.[a]

Functional	PBE/(A)TZP	PBE/QZ4P	PBE0
σ-Na^-	543.9	543.9	543.2
σ-Na^+	578.2	578.8	581.9
^{23}Na NMR shift	-34.3	-34.8	-38.7

[a] STO calculations. All shielding data in ppm.

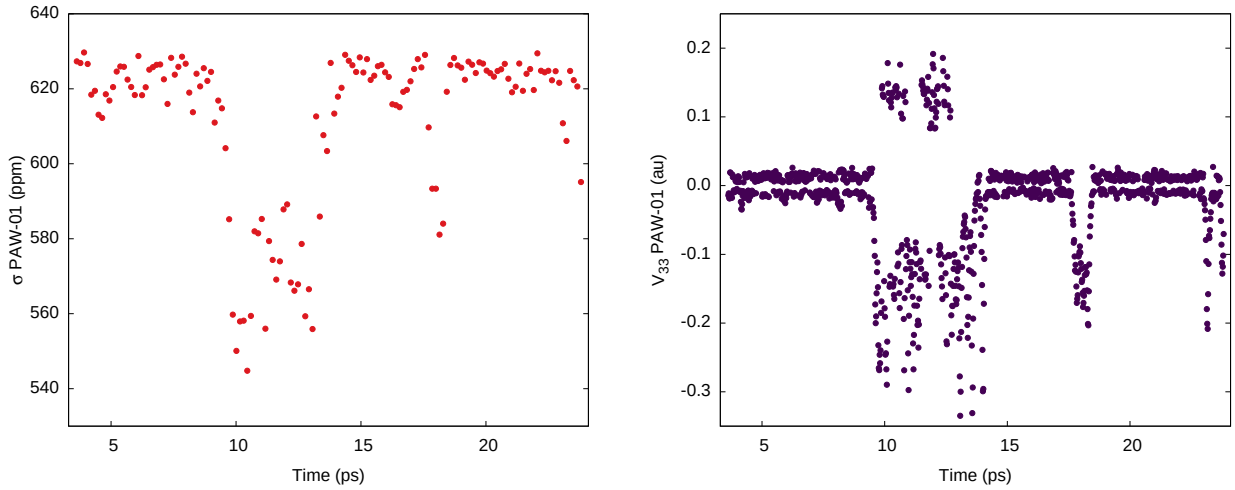

Figure S6: Shielding vs. V_{33} EFG component at $^{23}Na^{-}$ nuclei for one of the trajectories; MD-01.

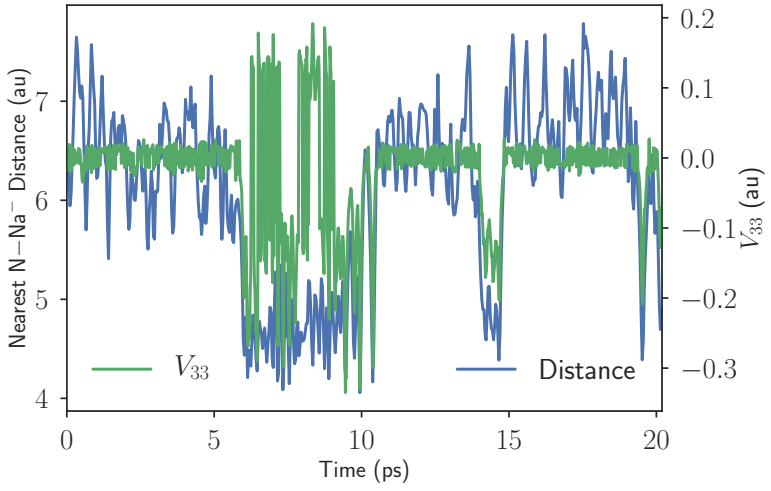

Figure S7: Nearest N-Na^{-} distance vs. V_{33} EFG component at $^{23}Na^{-}$ nuclei for one of the trajectories; MD-01.

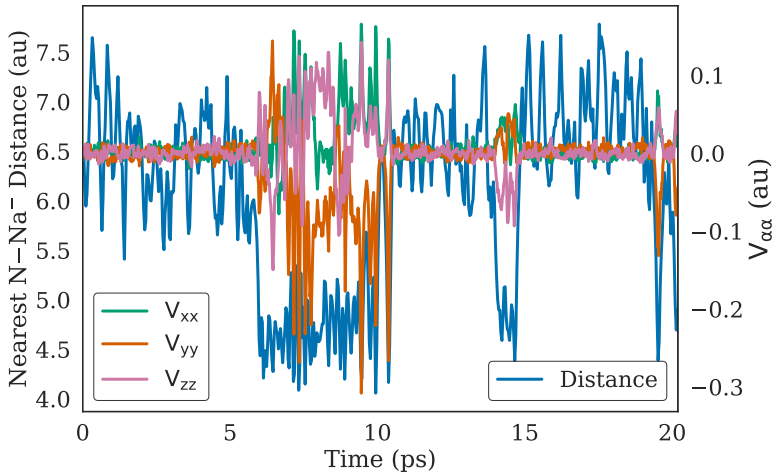

Figure S8: Nearest N-Na^- distance vs. V_{xx}, V_{yy} and V_{zz} EFG components at $^{23}Na^-$ nuclei for one of the trajectories; MD-01.

References

(1) L. Abella, A. Philips and J. Autschbach, *J. Phys. Chem. Lett.*, 2020, **11**, 843–850.

(2) G. Malli and S. Fraga, *Theor. Chim. Acta*, 1967, **7**, 75–79.