Double-quantum ^{19}F-^{19}F dipolar recoupling under ultra-fast magic angle spinning: application to the assignment of ^{19}F NMR spectra of inorganic fluorides

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Electronic Supplementary Information

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Table 1. F-F distances ($d_{F-F} < 4.73$ Å) calculated from the optimized structure of β-$BaAlF_5$.[1]

Atom		Distance (Å)	Atom		Distance (Å)	Atom		Distance (Å)
F1	F6	2.4736	F3	F8	2.5296	F5	F6	2.5016
	F2	2.5774		F4	2.5800		F3	2.5838
	F7	2.5898		F5	2.5838		F2	2.5897
	F3	2.5925		F1	2.5925		F8	2.5952
	F4	2.5996		F7	2.8806		F9	2.5990
	F5	2.6108		F10	2.8947		F10	2.6045
	F10	2.6229		F10	2.8994		F1	2.6108
	F5	2.6382		F10	3.0361		F1	2.6382
	F9	3.0021		F9	3.3151		F4	2.9972
	F6	3.1199		F9	3.4378		F6	3.3252
	F8	3.6568		F2	3.5947		F4	3.6555
	F9	3.6573		F7	3.9342		F7	3.6808
	F6	4.0439		F4	4.1216		F2	3.8315
	F8	4.3270		F5	4.3018		F2	4.0386
	F10	4.3388		F8	4.4100		F7	4.2983
	F1	4.5080		F9	4.5139		F3	4.3018
	F2	4.5178		F4	4.5307		F8	4.5367
	F3	4.6139		F7	4.5512		F10	4.6391
				F1	4.6139			
				F9	4.6350			
F2	F4	2.5008	F4	F2	2.5008	F6	F1	2.4736
	F8	2.5564		F8	2.5105		F5	2.5016
	F1	2.5774		F3	2.5800		F9	2.5768
	F5	2.5897		F1	2.5996		F7	2.6043
	F6	2.7512		F8	2.7234		F2	2.7512
	F8	3.0141		F7	2.9115		F1	3.1199
	F4	3.0884		F5	2.9972		F6	3.1363
	F2	3.1129		F2	3.0884		F5	3.3252
	F2	3.2350		F10	3.3346		F6	3.3739
	F3	3.5947		F5	3.6555		F8	3.4909
	F5	3.8315		F10	3.8176		F10	3.6103
	F7	4.0187		F9	3.9923		F4	3.9941
	F5	4.0386		F6	3.9941		F1	4.0439
	F6	4.2447		F3	4.1216		F9	4.1901
	F6	4.3016		F2	4.3371		F2	4.2447
	F4	4.3371		F9	4.4001		F2	4.3016
	F9	4.3574		F9	4.4989		F9	4.3108
	F1	4.5178		F6	4.5131		F4	4.5131
	F8	4.6154		F3	4.5307		F7	4.6106
	F9	4.6310		F4	4.5956		F7	4.6691
	F8	4.6511						

Table 1. Continued.

Atom		Distance (Å)	Atom		Distance (Å)	Atom		Distance (Å)
F 7	F9	2.5787	F8	F4	2.5104	F9	F6	2.5768
	F1	2.5898		F3	2.5296		F7	2.5787
	F10	2.6029		F2	2.5564		F5	2.5990
	F6	2.6043		F5	2.5952		F10	2.6081
	F9	2.6591		F4	2.7234		F7	2.6591
	F3	2.8806		F9	2.8644		F8	2.8644
	F4	2.9115		F2	3.0141		F1	3.0021
	F8	3.3695		F7	3.3695		F3	3.3151
	F10	3.4472		F6	3.4909		F10	3.4101
	F5	3.6808		F10	3.5856		F3	3.4378
	F8	3.7527		F1	3.6568		F1	3.6573
	F3	3.9342		F7	3.7527		F4	3.9923
	F2	4.0187		F10	3.9429		F10	4.1272
	F5	4.2983		F1	4.3270		F6	4.1901
	F10	4.4773		F3	4.4100		F6	4.3108
	F3	4.5512		F5	4.5367		F2	4.3574
	F8	4.5979		F7	4.5979		F4	4.4001
	F6	4.6106		F2	4.6154		F4	4.4989
	F6	4.6691		F8	4.6421		F3	4.5139
F10	F7	2.6029		F2	4.6511		F2	4.6310
	F5	2.6045					F3	4.6350
	F9	2.6081						
	F1	2.6229						
	F3	2.8947						
	F3	2.8994						
	F3	3.0361						
	F4	3.3346						
	F9	3.4101						
	F7	3.4472						
	F8	3.5856						
	F6	3.6103						
	F4	3.8176						
	F8	3.9429						
	F9	4.1272						
	F1	4.3388						
	F7	4.4773						
	F5	4.6391						
	F10	4.7233						
	F10	4.7233						

Table 2. F-F distances ($d_{F-F} < 4.66$ Å) calculated from the optimized structure of $Ba_3Al_2F_{12}$.[1]

Atom		Distance (Å)	Atom		Distance (Å)	Atom		Distance (Å)
F1	F6 x 2	2.4945	F5	F2	2.5215	F 7	F6	2.5496
	F2 x 2	2.5564		F6	2.5420		F7	2.5551
	F1	2.5591		F7	2.6031		F8	2.5859
	F8 x 2	2.6022		F8	2.6201		F5	2.6031
	F7 x 2	2.6091		F6	2.7238		F1	2.6091
	F5 x 2	3.6254		F8	2.8516		F7	2.7931
	F8 x 2	3.7403		F3	3.1849		F4	2.9424
	F5 x 2	3.9829		F4	3.1895		F3	3.0129
	F6 x 2	4.0937		F1	3.6254		F6	3.5626
F2	F5 x 2	2.5215		F7	3.6878		F2	3.6492
	F1 x 2	2.5564		F1	3.9829		F5	3.6878
	F6 x 2	2.5589		F4	4.0883		F7	3.7855
	F8 x 2	2.5954		F5	4.2419		F6	3.9920
	F4	3.3262		F3	4.2965		F8	4.3951
	F4	3.5537		F4	4.3246		F5	4.4440
	F7 x 2	3.6492		F8	4.3394		F5	4.5019
	F3	4.4216		F7	4.4440		F6	4.5067
	F2	4.4263		F7	4.5019			
	F8 x 2	4.5329						
	F6 x 2	4.5582						
F3	F3	2.8954	F6	F1	2.4945	F8	F7	2.5859
	F7 x 2	3.0129		F5	2.5420		F2	2.5954
	F6 x 2	3.0575		F7	2.5496		F1	2.6022
	F5 x 2	3.1849		F2	2.5589		F5	2.6201
	F8 x 2	3.2642		F5	2.7238		F8	2.8208
	F8 x 2	3.3241		F3	3.0575		F5	2.8516
	F5 x 2	4.2965		F8	3.2090		F6	3.2090
	F2	4.4216		F4	3.2169		F3	3.2642
	F4	4.6542		F8	3.5262		F3	3.3241
F4	F7 x 2	2.9424		F7	3.5626		F6	3.5262
	F4	2.9883		F8	3.6257		F4	3.5295
	F5 x 2	3.1895		F7	3.9920		F6	3.6257
	F6 x 2	3.2169		F1	4.0937		F1	3.7403
	F2	3.3262		F6	4.1171		F5	4.3394
	F8 x 2	3.5295		F4	4.1234		F7	4.3951
	F2	3.5537		F7	4.5067		F2	4.5329
	F5 x 2	4.0883		F2	4.5582		F6	4.5811
	F6 x 2	4.1234		F8	4.5811			
	F5 x 2	4.3246						
	F3	4.6542						

Table 3. F-F distances (d_{F-F} < 3.75 Å) calculated from the optimized structure of α-$CaAlF_5$.[1]

Atom		Distance (Å)
F1	F2 x 2	2.5206
	F3 x 2	2.5699
	F3 x 2	2.5785
	F2 x 2	2.6970
	F3 x 2	3.4556
	F1 x 2	3.7478
F2	F3	2.5142
	F1	2.5206
	F3	2.5521
	F1	2.6970
	F2	2.7646
	F3	3.0321
	F3	3.1362
	F3	3.1850
	F2	3.2076
	F3	3.3356
	F2	3.6344
F3	F2	2.5142
	F2	2.5521
	F1	2.5699
	F1	2.5785
	F2	3.0321
	F2	3.1362
	F2	3.1850
	F2	3.3356
	F1	3.4556
	F3	3.5076
	F3	3.5300
	F3 x 2	3.6588
	F3 x 2	3.6814

Table 4. Experimental and calculated based on optimized periodic structure ^{19}F chemical shifts (in ppm) of α-$CaAlF_5$.

F site	F1	F2	F3
Experimental	-164	-146	-154
Calculated (δ_{cal})	-177	-150	-160
Fitted (δ_{fit})[a]	-167	-144	-152

[a] Fitted values derived from $\delta_{fit} = 0.86\ \delta_{cal} - 14.6$[2]

Computational details about calculations of ^{19}F chemical shifts of α-$CaAlF_5$

The DFT calculations were performed by Dr. Anmin Zheng, State Key laboratory of magnetic resonance and atomic and molecular physics, Wuhan center for magnetic resonance, Wuhan institute of physics and mathematics, Chinese academy of Sciences, Wuhan 430071, China.

In order to obtain the accurate ^{19}F chemical shift, the crystal structure of α-$CaAlF_5$[3] was optimized (unit cell parameters and atom coordinates) at GGA/PBE level with a plane-wave cutoff energy of 300 eV and a default medium level *k*-point grid in the CASTEP package.[4] The ^{19}F chemical shift was calculated by the GIPAW method,[5] and the integrals over the first Brillouin zone were performed using a 5×5×4 *k*-point grid with a plane-wave cutoff energy at 550 eV based on the optimized crystallographic structures. The detailed procedures involved in NMR calculation can be found elsewhere.[2,6] The calculated ^{19}F NMR chemical shifts were referenced to $CFCl_3$ with a known absolute shielding of 143.5 ppm. All the calculations for the structure optimization and chemical shift calculation were performed with 16 parallel CPU of an IBM-1350 cluster facilitated by the National Center for High-performance Computing (NCHC), Taiwan.

As shown in Table 4, theoretical ^{19}F chemical shifts predicted herein based on the optimized structure model offer an avenue for complete, unambiguous CS assignments. The ^{19}F chemical shift of the F3 site was found to be 10 ppm down-field to the F2 site. Moreover, the fitted values on the optimized structure for the F2 and F3 sites were -144 and -152 ppm, which are in good agreement with the MAS NMR experimental results. Therefore, the theoretical approaches adopted herein enable us to afford complementary supports for the complete spectral assignments of α-$CaAlF_5$.

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