Electronic Supplementary Information

Interactions in the ionic liquid [EMIM][FAP]: A coupled experimental and computational analysis

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Table S1. The B3LYP/6-31+G(2df,p) calculated frequencies (v_{calc}, cm^{-1}), infrared normalized intensities (I_{IR}), and mode assignments PED (%) for RTIL [EMIM][FAP-f1] and [EMIM][FAP-m1].

v_{calc}	I_{IR}	PED	Interpretation	Attribution to ion
			[EMIM][FAP-f1]	
3301	2.58	s2(51), s87(36)	$v(C_rH)$+ring bending	cation
3282	7.28	s3(60), s88(19)	$v(C_rH)$+ring bending	cation
3244	236.91	s1(82)	$v(C_rH)$	cation
3178	3.48	s6(70)	$v(C_mH)$	cation
3141	2.99	s10(-17), s55(48)	$v(C_\beta H)$+$\delta(HC_\beta H)$	cation
3137	3.34	s4(-45), s51(25)	$v(C_\alpha H)$+$v(C_mH)$+ $\delta(HC_mH)$	cation
3128	1.51	s7(-48), s51(-17)	$v(C_\alpha H)$+$v(C_mH)$+ $\delta(HC_mH)$	cation
3105	11.33	s9(-55)	$v(C_\beta H)_{asym}$	cation
3058	15.1	s4(10), s5(13), s89(29)	$v(C_\alpha H)$+ethyl bending	cation
3058	18.14	s8(57), s53(-12)	$v(C_{al}H)$+ $\delta(HC_\beta H)$	cation
3038	15.71	s11(32), s89(15)	$v(C_{al}H)$+ethyl bending	cation
1607	40.25	s86(17), s122(-24)	ring bending	cation
1598	30.18	s13(-11), s98(37), s99(-10)	$v(C_rC_r)$+ring bending	cation
1504	7.38	s7(-14), s54(38)	$v(C_\alpha H)$+$v(C_mH)$+ $\delta(HC_\alpha H)$	cation
1504	19	s51(-12), s54(13), s91(20)	$\delta(HC_mH)$+ $\delta(HC_\alpha H)$+ring bending	cation
1491	10.1	s96(39)	ring bending	cation
1484	3.73	s50(-14), s90(-24)	$\delta(HC_mH)$+ethyl bending	cation
1478	16.62	s50(-10), s90(26)	$\delta(HC_mH)$+ethyl bending	cation
1465	9.34	s50(24), s92(17), s108(14)	$\delta(HC_mH)$+ring bending	cation
1446	5.65	s49(-14)	ethyl bending	cation
1424	8.44	s10(37), s53(24), s91(-10)	$v(C_\beta H)$+ $\delta(HC_\beta H)$+ring bending	cation
1413	2.01	s15(22)	$v(NC_r)$	cation
1385	10.8	s5(34), s89(-15)	ethyl bending	cation
1347	9.07	s16(-12)	$v(NC_r)$	cation
1323	0.09	s46(-23), s88(25)	ring bending	cation
1300	2.92			
1281	13.5	s44(-10)	degenerated deformation	cation
1275	261.79	s110(15)	$\gamma(FCFC)$	anion
1274	237.51	s36(-13), s118(-15)	$v(CC)$+ $\gamma(FCFC)$	anion
1203	419.86	s23(-19), s101(10)	$v(C_\beta F)$+$\tau(FCCP)$	anion
1199	319.05	s18(-24), s116(-12)	$v(C_\beta F)$+ $\gamma(FCFC)$	anion
1194	10.79			
1191	46.52	s17(-29)	$v(CF)$	anion
1172	608	s115(28), s116(15)	$\gamma(FCFC)$	anion
1162	42.17	s22(15), s67(12), s117(-15)	$v(C_\beta F)$+$\delta(FCF)$+ $\gamma(FCFC)$	anion
1159	3.45	s8(-10), s11(-12), s50(10)	$v(C_{al}H)$+ $\delta(HC_mH)$	cation
1157	46.44	s19(-17), s65(10), s109(16)	$v(C_\beta H)$+ $\delta(FCF)$+ $\gamma(FCFC)$	anion
1152	497.67	s68(-13)	$\delta(FC_\alpha F)$	anion
1144	4.31	s97(27)	$\tau(HC_{al}C_{al}H)$	cation
1127	28.6	s30(-13), s68(-11)	$\delta(FC_\alpha F)$	anion

1126	19.62	s26(10), s111(-15), s119(-11)	$\nu(C_\alpha F)+ \gamma(FPFC)$	anion
1125	9.42	s16(-12), s47(-15), s87(17)	ring bending	cation
1109	3.57	s52(-13), s92(-10)	$\delta(HC_m H)+$ring bending	cation
1103	22.06	s32(15), s68(-15), s119(-15)	$\delta(FC_\alpha F)+ \gamma(FPFC)$	anion
1101	47.23	s30(-25), s112(-11)	$\nu(C_\alpha F)+ \gamma(FPFC)$	anion
1100	55.39	s29(11), s119(-11)	$\nu(FC)+ \gamma(FPFC)$	anion
1084	2.98	s29(10), s33(24)	$\nu(FC)$	anion
1046	3.58	s16(19), s103(-17)	$\nu(NC_r)+$ring bending	cation
1039	4.4	s16(18), s58(33)	$\nu(NC_r)+$ring bending	cation
965	2.8	s123(-15)	ring bending	cation
955	85.51	s102(19), s113(35)	$\gamma(FFPC)+\tau(FCCP)$	anion
954	82.87	s79(-14)	$\delta(CCP)$	anion
950	0.79			
930	24.89	s56(21)	$\delta(FC_\beta F)$	anion
869	0.04	s2(-24), s47(42), s87(15)	$\nu(C_r H)+$ring bending	cation
811	3.21	s49(28)	ethyl bending	cation
758	49.72	s3(16), s46(-15), s88(-11)	$\nu(C_r H)+$ring bending	cation
744	47.33	s60(14), s102(10)	$\delta(FC_\beta F)+ \gamma(FFPC)$	anion
743	4.53	s19(32), s65(16)	$\delta(FC_\beta F)$	
742	4.35	s83(10), s105(11)	$\tau(CCPF)+ \tau(CCPC)$	anion
709	177.51	s38(14)	$\nu(PF)$	anion
705	7.4	s45(16)	ring bending	cation
669	54.24	s14(-12), s999(-20)	$\nu(NC_r)+$ring bending	cation
664	194.08	s38(11), s114(27)	$\nu(PF)asym$	anion
655	176.75	s81(13), s126(-10)	$\delta(CPF)+ \gamma(CFFP)$	anion
641	11.68	s13(10), s57(36)	$\nu(C_r C_r)+$ring bending	cation
627	6.36	s26(11)	$\nu(CC)+\nu(CF)$	anion
619	29.43	s102(12)	$\gamma(FFPC)$	anion
617	46.05	s74(14)	$\delta(FC_\alpha F)+d(CCF)$	anion
600	1.85			
585	0.08			
584	0.35	s20(-24)	$\nu(FC_\beta)_{asym}$	anion
584	0.34	s94(10)	ring bending	cation
535	9.59	s66(-15), s84(-11)	$\delta(FC_\beta F)+ \delta(FPF)+ \delta(CPF)$	anion
528	4.37	s17(-11), s64(-27)	$\nu(FC)+ \delta(FCF)$	anion
527	4.98	s61(33)	$\delta(FC_\beta F)$	anion
522	26.82	s61(18)	$\delta(FC_\beta F)$	anion
		[EMIM][FAP-m1]		
3299	1.32	s3(-12), s44(39), s87(16)	$\nu(C_r H)$	cation
3287	266.3	s3(27), s44(18), s87(-20)	$\nu(C_r H)$	cation
3280	7.53	s2(15), s3(10), s47(12), s87(51)	$\nu(C_r H)+$ring bending	cation
3166	5.86	s51(34), s92(24)	$\delta(HC_\alpha H)+$ring bending	cation
3139	1.57	s4(-11), s5(-13), s49(21), s89(12)	$\nu(C_\alpha H)+$ethyl bending/torsion	cation

3134	2.56	s9(29), s10(12), s91(13)	$\nu(C_\beta H)$+ring bending	cation
3118	10.48	s10(-37), s91(25)	$\nu(C_\beta H)$+$\tau(HC_{al}NC_r)$	cation
3103	15.34	s9(21), s10(-16)	$\nu(C_\beta H)_{asym}$	cation
3070	9.7	s5(75)	$\nu(C_\beta H)$	cation
3055	17.84	s52(49), s91(19)	$\delta(HC_m H)_{asym} + \tau(HC_{al}NCr)$	cation
3034	12.44	s9(-14), s11(-29), s96(33)	$\nu(C_\beta H)+ \tau(HCaCaN)$	cation
1604	33.24	s15(-12), s88(12), s98(20)	$\nu(NC_r)$+ring bending	cation
1596	35.65	s98(-12), s123(12)	ring bending and out-of-plane vibration	cation
1506	7.22	s48(-47)	ethyl torsion	cation
1504	10.42	s50(44), s108(-10)	$\delta(HC_{al}H)_{asym}$ (methyl group) + $\tau(HC_{al}NC_r)$	cation
1489	7.91	s7(67)	$\nu(C_m H)$	cation
1488	9.87	s6(20), s51(-12), s92(16)	$\nu(C_m H) + \delta(HC_m H) + \tau(HC_{al}NC_r)$	cation
1485	6.1	s9(-14), s53(-22), s94(27)	$\nu(C_\beta H)+ \delta(HC_\beta H)$+ethyl radical torsion	cation
1463	9.57	s53(11), s95(35)	$\delta(HC_\beta H)$+ethyl radical torsion + ring bending	cation
1451	3.17	s13(-10), s123(-12)	$\nu(C_r C_r)$+ring bending and out-of-plane vibration	cation
1420	6.21	s11(-12), s89(-13)	$\nu(C_{al}H)$+ethyl bending	cation
1412	3.2	s55(12), s94(19)	ethyl radical bending and torsion	cation
1389	11.53	s4(12), s89(41)	ethyl radical stretching and bending	cation
1350	8.45	s34(11), s122(-25)	$\nu(C_r N)$ + out-of-plane ring vibration	cation
1315	0.45	s47(10), s88(16)	$\delta(HC_r C_r)$+ring bending	cation
1297	32.48	s17(12), s77(15)	$\nu(C_\beta F)+\delta(CCP)$	anion
1287	154.87	s36(-14)	$\nu(CC)_{asym}$	anion
1274	89.51	s37(-14)	$\nu(CC)$	anion
1273	142.67	s49(10)	$\delta(HC_\alpha H)$	anion
1211	338.17	s22(25), s66(36)	$\nu(C_\beta F)_{asym}+ \delta(FC_\beta F)$	anion
1201	346.24	s19(10), s109(-38)	$\nu(C_\beta F)_{asym}+\gamma(FCFC)$	anion
1192	321.51	s115(19)	$\gamma(FCFC)$	anion
1182	26.89	s20(13), s115(-33)	$\nu(C_\beta F)_{asym}+\gamma(FCFC)$	anion
1176	268.72	s65(24), s101(-14), s110(15)	$\delta(FC_\beta F)+\tau(FCCP)+\gamma(FCFC)$	anion
1163	220.89	s8(40)	$\nu(C_m H)$	cation
1161	2.56	s24(24), s117(22), s118(-11)	$\nu(C_\beta F)+ \gamma(FCFC)$	anion
1155	15.51	s68(-11), s102(17)	$\tau(FCCP)$	anion
1145	186.14	s27(-15)	$\nu(C_\alpha F)$	anion
1140	103.89	s27(-17), s120(-11)	$\nu(C_\alpha F)+\gamma(FPCC)$	anion
1138	187.45			
1125	28.18	s72(29), s112(-12)	$\delta(FC_\alpha F)+\gamma(FPCC)$	anion
1123	39.1	s121(12)	$\gamma(FPCC)$	anion
1110	8.14	s121(18)	$\gamma(FPCC)$	anion
1106	67.87	s90(24)	ethyl radical torsion	cation
1103	2.8	s71(16), s72(11)	$\delta(FC_\alpha F)$	anion

1092	40.55	s88(15)	ring bending	cation
1048	102.51	s74(34), s119(-17)	δ(FCC)+γ(FPFC)	anion
1045	46.62	s13(17), s93(-10)	ν(C$_r$C$_r$), ring deformation	cation
1038	2.75	s73(28)	ring bending	cation
964	4.68	s33(-25), s103(-18)	ν(C$_{al}$C$_{al}$)+τ(C$_{al}$C$_{al}$NC$_r$)	cation
958	92.53			
952	86.56	s113(16)	γ(FPFC)	anion
948	2.55			
923	29.03	s1(51)	ν(C$_{al}$H)	cation
869	0.03	s3(-34), s46(-45)	ν(C$_{al}$H)$_{asym}$+ring bending	cation
809	3.5	s4(-24), s48(-16), s49(-11), s55(18)	ethyl bending and torsion	cation
802	163.68	s38(59), s114(16)	ν(PF)$_{asym}$	anion
757	36.11	s2(-41), s47(33)	ν(C$_r$H)+ring bending	cation
744	8.3	s61(-20), s63(13), s65(15)	δ(FCF)	anion
741	7.03	s60(10), s118(-17), s124(11)	δ(FC$_\beta$F)+ γ(FCFC)+ γ(FCFP)	anion
734	3.2	s60(18), s118(11)	δ(FC$_\beta$F)+ γ(FCFC)	anion
704	7.52	s86(-16), s99(-16)	ring bending	cation
671	31.08	s14(-11), s16(23), s58(-11)	ring bending	cation
657	237.12	s126(-17)	γ(C$_\alpha$FFP)	anion
640	23.43	s57(59)	ring bending	cation
632	9.27	s119(-24)	γ(FPFC$_\alpha$)	anion
627	0.85	s29(17), s111(-15)	ν(C$_\alpha$F)+ γ(FPFC$_\alpha$)	anion
622	66.14	s28(26)	ν(CF)	anion
608	210.66	s80(-10), s106(11)	δ(FPF)+τ(CCPC)	anion
597	2.99	s105(-15)	τ(CCPF)	anion
586	0.48	s59(18), s117(-16)	δ(FC$_\beta$F)$_{asym}$+ γ(FCFC)	anion
584	0.21	s23(10), s109(-10)	ν(C$_\beta$F)+ γ(FCFC)	anion
573	44.63	s39(32)	ν(PF)	anion
550	15.59	s34(11), s39(19)	ν(NC)+ν(PF)	anion+cation
530	5.9	s23(17), s101(13)	ν(C$_\beta$F)+τ(FCCP)	anion
528	7.94	s22(14), s119(10)	ν(C$_\beta$F)+ γ(FPFC)	anion
523	23.9	s25(53), s67(15)	ν(CF)+δ(FC$_\beta$F)	anion

Notations: ν: stretching vibrations; δ: bending vibrations; γ: out-of-plane vibrations; τ: torsion vibrations; sym: symmetric; asym: asymmetric; r: ring; al: aliphatic; m: methyl.

Table S2.1. The internal mode definitions for [EMIM][FAP-f1].

Coord. No.	Coef.	Mode type	Atom	Nos	Atom types	Struct. par. value	Freq. to which the coord. participates and PED%
s 1	1.00	STRE	27	26	CH	1.079692	f3243 82
s 2	1.00	STRE	30	32	CH	1.076315	f3297 51 f869 24
	1.00		33	34	CH	1.076718	
s 3	1.00	STRE	33	34	CH	1.076718	f3270 60 f777 16
	-1.00		30	32	CH	1.076315	
s 4	-1.00	STRE	35	38	CH	1.091468	f3138 45 f3056 10
	1.00		31	41	CH	1.090809	
s 5	1.00	STRE	31	40	CH	1.094147	f3056 13 f1388 34
s 6	1.00	STRE	35	36	CH	1.088447	f3172 70
s 7	1.00	STRE	31	41	CH	1.090809	f3125 48 f1525 14
	-1.00		35	37	CH	1.092007	
s 8	1.00	STRE	35	37	CH	1.092007	f3043 57 f1162 10
	1.00		35	38	CH	1.091468	
	1.00		35	36	CH	1.088447	
	-1.00		39	44	CH	1.094549	
s 9	1.00	STRE	39	42	CH	1.093553	f3086 55
	-1.00		39	44	CH	1.094549	
s 10	1.00	STRE	39	43	CH	1.092083	f3157 17 f1423 37
	-1.00		39	42	CH	1.093553	
s 11	1.00	STRE	39	42	CH	1.093553	f3003 32 f1162 12
	1.00		35	37	CH	1.092007	
	1.00		35	38	CH	1.091468	
	1.00		35	36	CH	1.088447	
s 12	1.00	STRE	7	26	FH	2.001488	f48 47
s 13	1.00	STRE	33	30	CC	1.361347	f1597 11 f641 10
s 14	1.00	STRE	28	27	NC	1.334427	f669 12 f85 11 f78 12
s 15	1.00	STRE	29	27	NC	1.334670	f1412 22 f46 13
s 16	1.00	STRE	28	30	NC	1.382040	f1348 12 f1120 12 f1046 19 f1040 18
s 17	1.00	STRE	24	21	FC	1.333650	f1188 29 f527 11
	-1.00		22	21	FC	1.341792	
	1.00		14	11	FC	1.330196	
	-1.00		19	16	FC	1.342742	
s 18	1.00	STRE	19	16	FC	1.342742	f1200 24
	-1.00		17	16	FC	1.343437	
s 19	1.00	STRE	12	11	FC	1.347313	f1156 17 f742 32
s 20	1.00	STRE	20	16	FC	1.332562	f584 24
	-1.00		17	16	FC	1.343437	
s 21	1.00	STRE	15	11	FC	1.342344	f307 18
s 22	-1.00	STRE	22	21	FC	1.341792	f1163 15
	1.00		25	21	FC	1.345225	
s 23	-1.00	STRE	12	11	FC	1.347313	f1206 19
	1.00		14	11	FC	1.330196	
	-1.00		20	16	FC	1.332562	
s 24	1.00	STRE	24	21	FC	1.333650	f219 12
	1.00		25	21	FC	1.345225	
s 25	1.00	STRE	18	9	FC	1.362935	f307 13 f251 10
s 26	1.00	STRE	10	9	FC	1.356908	f1125 10 f623 11
	1.00		13	1	FC	1.356947	
s 27	1.00	STRE	23	4	FC	1.357389	
s 28	1.00	STRE	19	16	FC	1.342742	f73 42
	1.00		17	16	FC	1.343437	
s 29	-1.00	STRE	31	39	CC	1.526648	f1097 11 f1077 10
	1.00		2	1	FC	1.362615	

	1.00		5	4		FC	1.361350	
	-1.00		10	9		FC	1.356908	
	1.00		18	9		FC	1.362935	
s 30	1.00	STRE	13	1		FC	1.356947	f1128 13 f1100 25
k 31	1.00	STRE	29	35		NC	1.465387	f243 28
	-1.00		28	27		NC	1.334427	
s 32	1.00	STRE	5	4		FC	1.361350	f1101 15
s 33	1.00	STRE	2	1		FC	1.362615	f1077 24
	1.00		5	4		FC	1.361350	
	-1.00		10	9		FC	1.356908	
	1.00		18	9		FC	1.362935	
s 34	1.00	STRE	28	31		NC	1.477043	f373 10 f358 18
s 35	1.00	STRE	4	21		CC	1.566363	f54 11
	-1.00		6	9		FC	2.604656	
k 36	1.00	STRE	9	16		CC	1.565636	f1274 13 f364 18
s 37	1.00	STRE	1	11		CC	1.565873	f358 10 f138 14 f9 10
s 38	1.00	STRE	3	6		PF	1.661909	f710 14 f664 11 f477 10
s 39	1.00	STRE	3	8		PF	1.665894	f202 17
	1.00		3	7		PF	1.674474	
s 40	1.00	STRE	3	7		PF	1.674474	f477 16 f425 13 f347 10
s 41	1.00	STRE	3	9		PC	1.980570	f9 37
	1.00		1	11		CC	1.565873	
	1.00		3	7		PF	1.674474	
s 42	-1.00	STRE	3	1		PC	1.983025	f176 14 f170 11
	1.00		3	9		PC	1.980570	
s 43	1.00	STRE	3	4		PC	1.983031	f236 14 f217 11
s 44	1.00	BEND	27	26	7	CHF	160.23	f1280 10 f46 11
s 45	1.00	BEND	27	28	30	CNC	108.52	f692 16
s 46	-1.00	BEND	26	27	29	HCN	125.31	f1325 23 f777 15
	1.00		32	30	33	HCC	130.78	
s 47	1.00	BEND	34	33	29	HCN	121.99	f1120 15 f869 42
	1.00		32	30	28	HCN	122.15	
s 48	-1.00	TORS	27	26	7	3	CHFP	-30.70	f288 12
	1.00		43	39	31	28	HCCN	60.27	
	-1.00		29	27	26	7	NCHF	-63.54	
s 49	1.00	BEND	41	31	28	HCN	106.41	f1439 14 f822 28
	1.00		43	39	44	HCH	109.32	
s 50	1.00	BEND	36	35	37	HCH	110.34	f1481 14 f1479 10 f1477 24 f1162 10
s 51	1.00	BEND	37	35	38	HCH	110.31	f3138 25 f3125 17 f1506 12
s 52	1.00	BEND	36	35	38	HCH	108.63	f1114 13
	-1.00		36	35	37	HCH	110.34	
s 53	1.00	BEND	42	39	44	HCH	107.88	f3043 12 f1423 24
s 54	1.00	BEND	40	31	41	HCH	108.40	f1525 38 f1506 13
	1.00		41	31	28	HCN	106.41	
	-1.00		43	39	44	HCH	109.32	
	1.00		42	39	43	HCH	108.31	
	1.00		37	35	38	HCH	110.31	
s 55	1.00	BEND	42	39	43	HCH	108.31	f3157 48
s 56	1.00	BEND	26	27	28	HCN	125.82	f926 21 f46 10
s 57	1.00	BEND	27	29	33	CNC	108.59	f641 36
	1.00		27	28	30	CNC	108.52	
s 58	1.00	BEND	27	28	30	CNC	108.52	f1040 33
	1.00		33	30	28	CCN	107.06	
s 59	1.00	BEND	22	21	25	FCF	107.15	f74 30
s 60	1.00	BEND	19	16	17	FCF	107.21	f743 14
s 61	1.00	BEND	14	11	12	FCF	108.43	f526 33 f522 18
s 62	-1.00	TORS	26	7	3	9	HFPC	-23.86	f475 10 f349 14
	1.00	OUT	17	9	20	16	FCFC	55.61	
	1.00		18	10	3	9	FFPC	56.65	

s 63	1.00	BEND	12	11	15		FCF	106.99	f71 46
s 64	1.00	BEND	17	16	20		FCF	107.43	f527 27
	-1.00		5	4	23		FCF	106.87	
	-1.00		22	21	24		FCF	107.44	
	-1.00		19	16	20		FCF	108.53	
s 65	1.00	BEND	14	11	15		FCF	107.60	f1156 10 f742 16
	1.00		12	11	15		FCF	106.99	
s 66	-1.00	BEND	19	16	20		FCF	108.53	f535 15
	1.00		17	16	20		FCF	107.43	
	-1.00		24	21	25		FCF	108.30	
s 67	1.00	BEND	22	21	24		FCF	107.44	f1163 12
	1.00		24	21	25		FCF	108.30	
	1.00		22	21	25		FCF	107.15	
	1.00		19	16	20		FCF	108.53	
	1.00		5	4	23		FCF	106.87	
s 68	1.00	BEND	10	9	18		FCF	106.86	f1154 13 f1128 11 f1101 15
s 69	1.00	BEND	5	4	23		FCF	106.87	f254 22
	-1.00		21	4	5		CCF	104.34	
s 70	1.00	BEND	9	16	19		CCF	111.66	f219 16
	1.00		16	9	18		CCF	104.27	
s 71	1.00	BEND	2	1	11		FCC	104.25	
s 72	1.00	BEND	13	1	2		FCF	106.89	f307 10
s 73	1.00	BEND	33	30	28		CCN	107.06	f422 37
	1.00		33	29	35		CNC	126.20	
	-1.00		30	28	31		CNC	126.38	
s 74	1.00	BEND	5	4	23		FCF	106.87	f616 14 f364 11
	1.00		21	4	5		CCF	104.34	
s 75	1.00	BEND	39	31	28		CCN	112.23	f104 17
s 76	1.00	BEND	30	28	31		CNC	126.38	f288 11 f226 16
	1.00		33	29	35		CNC	126.20	
s 77	1.00	BEND	21	4	3		CCP	118.17	
s 78	1.00	BEND	16	9	3		CCP	118.13	f170 10 f54 15
s 79	1.00	BEND	11	1	3		CCP	118.44	f955 14
s 80	1.00	BEND	8	3	6		FPF	87.63	f349 33
s 81	1.00	BEND	1	3	7		CPF	90.61	f653 13
s 82	1.00	BEND	3	7	26		PFH	105.41	f19 14
s 83	-1.00	TORS	26	7	3	9	HFPC	-23.86	f736 10
	1.00		16	9	3	7	CCPF	59.05	
s 84	1.00	BEND	6	3	7		FPF	87.34	f535 11 f22 17
	1.00		1	3	6		CPF	87.10	
s 85	1.00	BEND	4	3	6		CPF	173.79	f347 12
s 86	1.00	TORS	26	27	28	30	HCNC	-177.66	f1606 17
s 87	1.00	TORS	32	30	33	29	HCCN	-179.82	f3297 36 f1120 17 f869 15
	1.00		34	33	30	28	HCCN	-180.24	
s 88	1.00	TORS	26	27	28	30	HCNC	-177.66	f3270 19 f1325 25 f777 11
	1.00		34	33	30	28	HCCN	-180.24	
s 89	1.00	BEND	40	31	39		HCC	111.68	f3056 29 f3003 15 f1388 15
	-1.00		41	31	28		HCN	106.41	
s 90	1.00	BEND	40	31	41		HCH	108.40	f1481 24 f1479 26
	1.00		43	39	44		HCH	109.32	
	1.00		41	31	28		HCN	106.41	
s 91	1.00	TORS	44	39	31	28	HCCN	-61.85	f1506 20 f1423 10
	1.00		36	35	29	33	HCNC	-178.14	
s 92	1.00	TORS	38	35	29	33	HCNC	-59.71	f1477 17 f1114 10 f122 20
s 93	1.00	TORS	28	27	26	7	NCHF	-246.18	f19 11
s 94	1.00	TORS	42	39	31	28	HCCN	-180.88	f577 10
s 95	1.00	TORS	42	39	31	28	HCCN	-180.88	f288 12 f226 12
	1.00		43	39	31	28	HCCN	60.27	
s 96	1.00	TORS	36	35	29	33	HCNC	-178.14	f1498 39

Coord. No.	Coef.	Mode type	Atom	Nos	Atom types	Struct. par. value	Freq. to which the coord. participates and PED%
s 97	1.00	TORS	40	31	39	42	HCCH	-60.35	f1138 27
s 98	1.00	TORS	33	30	28	27	CCNC	-0.04	f1597 37
s 99	1.00	TORS	30	28	27	29	CNCN	0.07	f1597 10 f669 20
s 100	1.00	TORS	22	21	4	3	FCCP	-173.11	f74 17
s 101	1.00	TORS	12	11	1	3	FCCP	-55.55	f1206 10 f217 13
s 102	1.00	OUT	10	18	3	9	FFPC	54.49	f955 19 f743 10 f619 12
s 103	1.00	TORS	39	31	28	30	CCNC	63.54	f1046 17 f104 20
s 104	1.00	TORS	9	3	4	21	CPCC	-99.79	f54 11
s 105	1.00	TORS	16	9	3	7	CCPF	59.05	f736 11
	1.00		9	3	4	21	CPCC	-99.79	
s 106	1.00	TORS	11	1	3	9	CCPC	-194.27	f55 19
s 107	1.00	TORS	6	3	7	26	FPFH	48.39	
s 108	1.00	TORS	37	35	29	27	HCNC	-121.84	f1477 14 f122 34
	1.00		38	35	29	33	HCNC	-59.71	
	1.00		38	35	29	27	HCNC	-242.76	
s 109	1.00	OUT	15	1	14	11	FCFC	55.28	f1156 16
s 110	1.00	OUT	14	1	12	11	FCFC	50.99	f1274 15
s 111	1.00	OUT	13	3	2	1	FPFC	54.60	f1125 15 f373 11
s 112	1.00	OUT	2	3	11	1	FPCC	56.36	f1100 11
s 113	1.00	OUT	10	18	3	9	FFPC	54.49	f955 35
	1.00	TORS	17	16	9	3	FCCP	-173.39	
s 114	1.00	TORS	26	8	3	1	HFPC	-39.14	f664 27 f475 15 f202 11
s 115	-1.00	OUT	19	9	17	16	FCFC	54.94	f1172 28
	1.00		20	9	19	16	FCFC	51.03	
s 116	1.00	OUT	20	9	19	16	FCFC	51.03	f1200 12 f1172 15
s 117	1.00	OUT	25	4	24	21	FCFC	51.66	f1163 15
s 118	1.00	OUT	24	4	22	21	FCFC	53.51	f1274 15
s 119	1.00	OUT	23	3	5	4	FPFC	54.46	f1125 11 f1101 15 f1097 11
s 120	1.00	OUT	5	3	21	4	FPCC	56.21	
s 121	1.00	OUT	18	3	16	9	FPCC	56.46	
s 122	1.00	OUT	35	27	33	29	CCCN	2.12	f1606 24
	1.00	TORS	30	28	27	29	CNCN	0.07	
s 123	1.00	TORS	27	28	31	39	CNCC	-113.43	f969 15
	-1.00		31	28	27	29	CNCN	-182.51	
s 124	1.00	OUT	4	9	6	3	CCFP	2.26	f202 11 f116 17
s 125	1.00	OUT	1	9	6	3	CCFP	84.36	
s 126	1.00	OUT	9	7	6	3	CFFP	5.57	f653 10

Table S2.2. The internal mode definitions for [EMIM][FAP-m1].

Coord. No.	Coef.	Mode type	Atom	Nos	Atom types	Struct. par. value	Freq. to which the coord. participates and PED%
s 1	1.00	STRE	27	26	CH	1.077323	f923 51 f17 15
s 2	1.00	STRE	30	33	CH	1.076687	f3265 15 f758 41
s 3	-1.00	STRE	30	33	CH	1.076687	f3301 12 f3281 27 f3265 10 f870 34
	1.00		32	34	CH	1.076715	
s 4	1.00	STRE	31	41	CH	1.091167	f3150 11 f1394 12 f820 24
s 5	1.00	STRE	31	40	CH	1.093120	f3150 13 f3069 75
s 6	1.00	STRE	35	37	CH	1.089705	f1484 20 f150 16 f143 14
	1.00		35	38	CH	1.091593	
s 7	1.00	STRE	35	37	CH	1.089705	f1491 67
	1.00		35	36	CH	1.092155	
s 8	1.00	STRE	35	38	CH	1.091593	f1166 40
	1.00		35	36	CH	1.092155	
s 9	1.00	STRE	39	42	CH	1.093598	f3126 29 f3087 21 f3023 14 f1482 14
s 10	1.00	STRE	39	43	CH	1.093511	f3126 12 f3114 37 f3087 16

	1.00		39	44	CH	1.094637	
s 11	1.00	STRE	39	44	CH	1.094637	f3023 29 f1419 12
	1.00		31	41	CH	1.091167	
s 12	1.00	STRE	3	26	FH	2.149477	f83 24
s 13	1.00	STRE	32	30	CC	1.361663	f1445 10 f1044 17
s 14	1.00	STRE	28	27	NC	1.333895	f670 11 f240 14 f17 12
s 15	1.00	STRE	29	27	NC	1.334516	f1609 12
s 16	1.00	STRE	28	30	NC	1.382134	f670 23 f83 10 f17 19
s 17	1.00	STRE	23	20	FC	1.329480	f1298 12 f64 23
s 18	-1.00	STRE	9	6	FC	1.352100	f111 10 f74 15
	1.00		10	6	FC	1.334334	
s 19	-1.00	STRE	16	13	FC	1.337486	f1203 10 f373 10 f210 19
	1.00		18	13	FC	1.343136	
s 20	1.00	STRE	11	6	FC	1.340532	f1186 13
	-1.00		9	6	FC	1.352100	
s 21	1.00	STRE	18	13	FC	1.343136	f48 47
s 22	-1.00	STRE	23	20	FC	1.329480	f1211 25 f525 14
	1.00		25	20	FC	1.338808	
s 23	1.00	STRE	17	13	FC	1.335357	f576 10 f530 17 f431 11
	1.00		18	13	FC	1.343136	
s 24	1.00	STRE	25	20	FC	1.338808	f1164 24
	1.00		24	20	FC	1.348292	
s 25	1.00	STRE	10	6	FC	1.334334	f523 53
	1.00		9	6	FC	1.352100	
	-1.00		8	5	FC	1.362217	
s 26	-1.00	STRE	7	5	FC	1.356213	
	1.00		8	5	FC	1.362217	
	-1.00		15	12	FC	1.359505	
s 27	1.00	STRE	22	19	FC	1.353716	f1146 15 f1140 17
s 28	1.00	STRE	8	5	FC	1.362217	f622 26
	1.00		9	6	FC	1.352100	
s 29	1.00	STRE	14	12	FC	1.360267	f626 17
s 30	1.00	STRE	15	12	FC	1.359505	f250 16
s 31	1.00	STRE	29	35	NC	1.465947	f304 19
s 32	1.00	STRE	21	19	FC	1.381122	f308 18
s 33	1.00	STRE	39	31	CC	1.527086	f959 25
s 34	1.00	STRE	28	31	NC	1.476924	f1344 11 f543 11
s 35	1.00	STRE	20	19	CC	1.560978	f12 14
k 36	-1.00	STRE	5	6	CC	1.567061	f1287 14
	-1.00		12	13	CC	1.567579	
	1.00		19	20	CC	1.560978	
s 37	1.00	STRE	13	12	CC	1.567579	f1273 14 f373 16
s 38	1.00	STRE	1	4	PF	1.622444	f802 59
	-1.00		1	2	PF	1.679319	
s 39	1.00	STRE	1	2	PF	1.679319	f552 32 f543 19
	1.00		1	4	PF	1.622444	
s 40	1.00	STRE	1	3	PF	1.680771	f319 21
s 41	1.00	STRE	1	5	PC	1.982327	f104 18
s 42	-1.00	STRE	1	12	PC	1.987908	f5 29
	1.00		1	5	PC	1.982327	
	1.00		1	19	PC	1.990115	
s 43	1.00	STRE	1	19	PC	1.990115	f193 14 f155 16
s 44	1.00	BEND	27	26	3	CHF	142.75	f3301 39 f3281 18
s 45	-1.00	BEND	32	29	35	CNC	126.52	f240 23
	1.00		27	28	30	CNC	108.56	
s 46	1.00	BEND	33	30	32	HCC	130.85	f870 45
	-1.00		34	32	30	HCC	131.02	
s 47	1.00	BEND	34	32	30	HCC	131.02	f3265 12 f1318 10 f758 33
	1.00		33	30	32	HCC	130.85	

s 48	1.00	TORS	40	31	39	42	HCCH	-59.63	f1514 47 f820 16
	1.00		43	39	31	28	HCCN	61.66
s 49	1.00	BEND	41	31	40		HCH	108.03	f3150 21 f1270 10 f820 11
s 50	1.00	BEND	36	35	38		HCH	109.98	f1505 44
	-1.00		37	35	38		HCH	109.36
s 51	1.00	BEND	37	35	38		HCH	109.36	f3174 34 f1484 12
	1.00		36	35	37		HCH	110.05
s 52	1.00	BEND	36	35	38		HCH	109.98	f3044 49
	1.00		37	35	38		HCH	109.36
	-1.00		36	35	37		HCH	110.05
s 53	1.00	BEND	42	39	44		HCH	108.12	f1482 22 f1471 11
s 54	1.00	BEND	42	39	43		HCH	108.03	f304 10 f230 28
	-1.00		43	39	44		HCH	108.86
s 55	1.00	BEND	43	39	44		HCH	108.86	f1416 12 f820 18 f230 10
s 56	1.00	BEND	26	27	28		HCN	125.54	f41 12
	1.00		27	26	3		CHF	142.75
s 57	1.00	BEND	32	30	28		CCN	107.07	f641 59
	1.00		28	27	29		NCN	108.82
	1.00		27	28	30		CNC	108.56
s 58	1.00	BEND	27	28	30		CNC	108.56	f670 11 f385 15 f41 12
	1.00		32	30	28		CCN	107.07
	-1.00		28	27	29		NCN	108.82
s 59	-1.00	BEND	23	20	24		FCF	107.55	f584 18
	1.00		23	20	25		FCF	109.02
s 60	1.00	BEND	10	6	9		FCF	108.10	f741 10 f732 18 f360 11
s 61	1.00	BEND	17	13	16		FCF	107.93	f744 20
s 62	1.00	BEND	11	6	10		FCF	107.31	f74 15
s 63	1.00	BEND	16	13	18		FCF	107.46	f744 13 f210 10
s 64	-1.00	BEND	23	20	24		FCF	107.55	f64 28
	1.00		24	20	25		FCF	107.20
s 65	1.00	BEND	17	13	18		FCF	107.55	f1177 24 f744 15
	1.00		16	13	17		FCF	107.93
	1.00		16	13	18		FCF	107.46
s 66	1.00	BEND	23	20	25		FCF	109.02	f1211 36
	1.00		23	20	24		FCF	107.55
s 67	1.00	BEND	9	6	11		FCF	106.67	f523 15
s 68	-1.00	BEND	6	5	1		CCP	118.78	f1157 11
	1.00		7	5	8		FCF	107.54
s 69	-1.00	BEND	21	19	22		FCF	104.80	f295 17
	1.00		2	1	4		FPF	179.48
	-1.00		7	5	8		FCF	107.54
	1.00		12	1	2		CPF	92.03
s 70	1.00	BEND	6	5	8		CCF	103.96	f462 11 f409 11
	-1.00		6	5	7		CCF	103.92
	1.00		5	6	10		CCF	112.89
s 71	1.00	BEND	14	12	13		FCC	104.90	f1101 16
s 72	1.00	BEND	15	12	14		FCF	105.98	f1124 29 f1101 11
s 73	1.00	BEND	32	29	35		CNC	126.52	f1019 28
	-1.00		27	29	32		CNC	108.61
s 74	1.00	BEND	21	19	20		FCC	104.30	f1046 34
s 75	1.00	BEND	39	31	28		CCN	112.30	f143 12
	1.00		30	28	31		CNC	126.71
s 76	1.00	BEND	30	28	31		CNC	126.71	f385 34
	1.00		28	27	29		NCN	108.82
	-1.00		32	30	28		CCN	107.07
s 77	1.00	BEND	20	19	1		CCP	118.40	f1298 15
s 78	1.00	BEND	6	5	1		CCP	118.78	f360 11
s 79	1.00	BEND	13	12	1		CCP	122.12	f131 11 f85 10
s 80	1.00	BEND	4	1	2		FPF	179.48	f607 10 f319 26

s 81	1.00	BEND	2	1	3	FPF	89.28	f268 33	
s 82	1.00	BEND	1	3	26	PFH	102.10	f12 11	
s 83	1.00	BEND	5	1	2	CPF	88.61		
s 84	1.00	BEND	12	1	2	CPF	92.03	f417 11 f373 10 f223 10	
	1.00		2	1	3	FPF	89.28		
s 85	1.00	BEND	19	1	2	CPF	87.56		
s 86	1.00	TORS	26	27	28	30	HCNC	-181.63	f690 16
s 87	1.00	TORS	33	30	32	29	HCCN	-180.65	f3301 16 f3281 20 f3265 51
s 88	1.00	TORS	34	32	30	28	HCCN	-179.22	f1609 12 f1318 16 f1066 15
s 89	1.00	BEND	40	31	39	HCC	111.58	f3150 12 f1419 13 f1394 41	
	-1.00		41	31	28	HCN	106.49		
s 90	1.00	TORS	40	31	39	42	HCCH	-59.63	f1106 24
	1.00		41	31	28	30	HCNC	-158.03	
	-1.00		43	39	31	28	HCCN	61.66	
s 91	1.00	TORS	36	35	29	32	HCNC	-67.54	f3126 13 f3114 25 f3044 19
s 92	1.00	TORS	37	35	29	32	HCNC	-187.78	f3174 24 f1484 16
s 93	1.00	TORS	27	26	3	1	CHFP	-141.34	f1044 10
	-1.00		27	26	2	1	CHFP	-217.17	
s 94	1.00	TORS	42	39	31	28	HCCN	-179.51	f1482 27 f1416 19
s 95	1.00	TORS	43	39	31	28	HCCN	61.66	f1471 35
	1.00		41	31	28	30	HCNC	-158.03	
s 96	1.00	TORS	44	39	31	28	HCCN	-60.05	f3023 33
s 97	1.00	TORS	27	26	3	1	CHFP	-141.34	
	1.00		29	27	26	3	NCHF	-207.20	
s 98	1.00	TORS	32	30	28	27	CCNC	-0.19	f1609 20 f1598 12
s 99	1.00	TORS	29	27	28	30	NCNC	0.18	f690 16
s 100	1.00	TORS	23	20	19	1	FCCP	66.54	f421 13 f219 13
s 101	1.00	TORS	16	13	12	1	FCCP	57.30	f1177 14 f530 13
s 102	1.00	TORS	9	6	5	1	FCCP	53.76	f1157 17 f462 26
s 103	1.00	TORS	39	31	28	30	CCNC	79.85	f959 18
s 104	1.00	TORS	5	1	19	20	CPCC	-260.66	f34 14
	1.00		6	5	1	3	CCPF	16.13	
s 105	1.00	TORS	6	5	1	3	CCPF	16.13	f590 15 f53 13
s 106	1.00	TORS	13	12	1	5	CCPC	-267.98	f607 11
s 107	1.00	TORS	2	1	3	26	FPFH	-5.26	
s 108	1.00	TORS	38	35	29	32	HCNC	53.09	f1505 10 f150 15 f143 14
s 109	1.00	OUT	18	12	17	13	FCFC	55.96	f1203 38 f576 10
s 110	1.00	OUT	17	12	16	13	FCFC	51.84	f1177 15 f48 19
s 111	1.00	OUT	15	1	14	12	FPFC	59.60	f626 15
s 112	1.00	OUT	14	1	13	12	FPCC	53.32	f1124 12
s 113	1.00	OUT	7	1	8	5	FPFC	53.96	f953 16 f360 10
s 114	1.00	OUT	4	5	2	1	FCFP	0.48	f802 16 f476 10
s 115	1.00	OUT	11	5	10	6	FCFC	55.25	f1197 19 f1186 33
	-1.00		10	5	9	6	FCFC	51.04	
s 116	1.00	OUT	10	5	9	6	FCFC	51.04	
	1.00		11	5	10	6	FCFC	55.25	
s 117	1.00	OUT	25	19	24	20	FCFC	55.03	f1164 22 f584 16
s 118	1.00	OUT	24	19	23	20	FCFC	55.61	f1164 11 f741 17 f732 11
s 119	1.00	OUT	22	1	21	19	FPFC	55.35	f1046 17 f632 24 f525 10
s 120	1.00	OUT	21	1	20	19	FPCC	56.30	f1140 11
s 121	1.00	OUT	8	1	6	5	FPCC	54.82	f1113 12 f1110 18 f462 11
s 122	1.00	OUT	35	32	27	29	CCCN	1.04	f1344 25
s 123	1.00	OUT	31	30	27	28	CCCN	0.08	f1598 12 f1445 12
s 124	1.00	OUT	19	5	2	1	CCFP	9.03	f741 11 f376 11
s 125	1.00	OUT	12	5	2	1	CCFP	85.73	f250 11
s 126	1.00	OUT	5	3	2	1	CFFP	86.46	f657 17

Coordinates of the equilibrated [FAP-f1]⁻ anion

```
P    0.030142    0.021918   -0.599342
F    1.237601    0.694196   -1.482177
F    0.053154   -1.287210   -1.586970
F   -1.071125    0.732455   -1.585506
C    1.462651   -0.793324    0.528702
C    2.242128   -2.020979   -0.046300
F    1.022991   -1.199781    1.754893
F    2.437259    0.135542    0.761998
F    1.482919   -3.112254   -0.160150
F    3.251775   -2.336949    0.799992
F    2.796788   -1.756797   -1.232575
C   -0.080354    1.670509    0.521997
C    0.641534    2.958056    0.005208
F   -1.387749    2.049776    0.639661
F    0.381118    1.495451    1.794306
F    0.244056    3.301470   -1.222945
F    1.971265    2.845531    0.011410
F    0.335488    3.994166    0.822802
C   -1.439556   -0.896573    0.393461
C   -2.862833   -0.913256   -0.254583
F   -1.632213   -0.410063    1.653819
F   -1.127831   -2.218931    0.539164
F   -3.426748    0.295229   -0.302087
F   -2.850744   -1.431329   -1.485665
F   -3.679229   -1.693492    0.493885
```

Coordinates of the equilibrated [FAP-m1]⁻ anion

```
P   -0.070340   -0.326280   -0.022976
F   -0.391516    0.216227   -1.542395
F   -0.369061   -1.883657   -0.452851
F    0.263602   -0.806883    1.509809
C   -2.004461   -0.178787    0.397656
C   -2.972230   -1.239049   -0.227872
F   -2.258556   -0.251799    1.735733
F   -2.501237    1.018249   -0.034679
F   -2.845852   -1.336534   -1.553759
F   -2.821104   -2.452620    0.311854
F   -4.251775   -0.867363    0.017940
C    0.318522    1.532260    0.614957
C    0.305139    2.766276   -0.348361
F   -0.566204    1.863595    1.602613
F    1.547030    1.556926    1.208690
F    1.179739    2.656557   -1.350203
F   -0.901409    2.992488   -0.872401
F    0.644520    3.874740    0.351891
C    1.786196   -0.702774   -0.620616
C    2.707746   -1.555676    0.305814
F    1.730093   -1.400587   -1.793078
F    2.508658    0.419441   -0.904249
F    3.014252   -0.923294    1.442236
F    3.877091   -1.808095   -0.328581
F    2.165019   -2.738427    0.608669
```