

Understanding the ionic liquid [NC₄₁₁₁][NTf₂] from individual building blocks: an IR spectroscopic study

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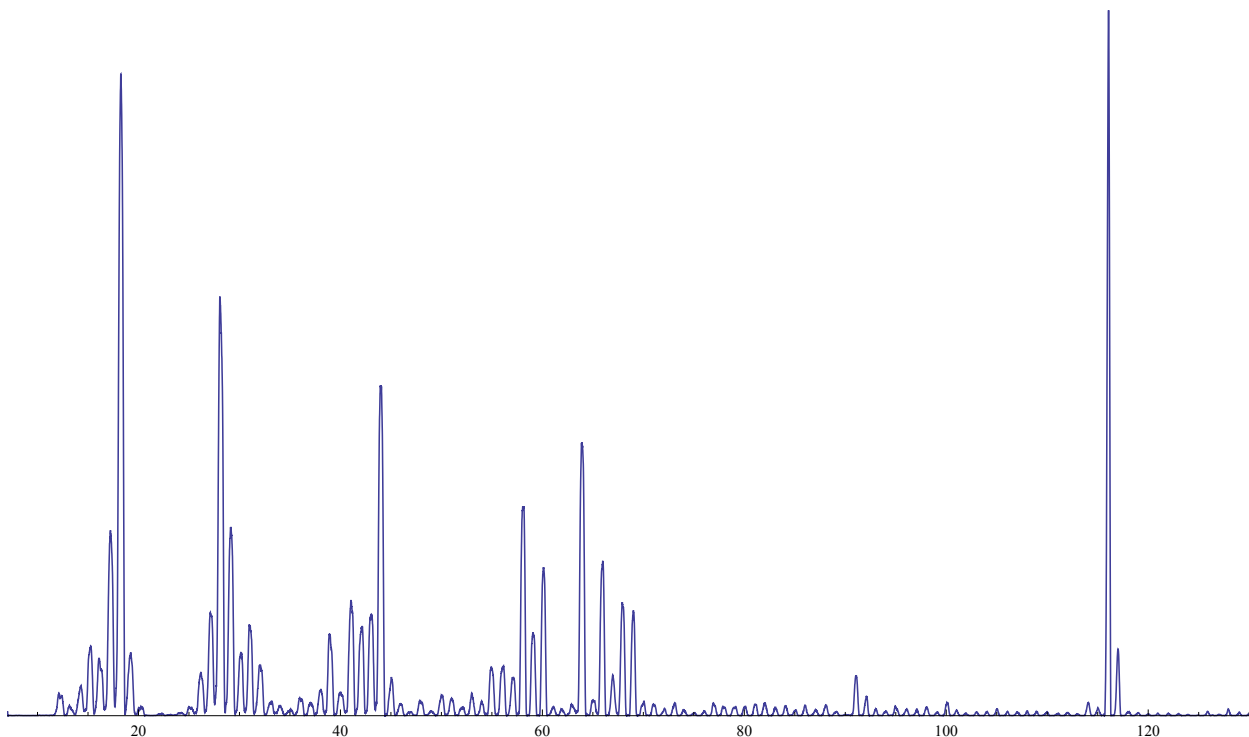


Fig. S 1. Gas phase mass spectrum of $[\text{NC}_{4111}][\text{NTf}_2]$. $m/z = 116$ is the cation mass. Peaks at $m/z = 58, 60, 64, 69$ result from the fragments $\text{Bu} + \text{H}^+$, $\text{N}(\text{CH}_3)_3 + \text{H}^+$, SO_2^+ and CF_3^+ of anion and cation, respectively. The water, nitrogen and CO_2 signals at $m/z = 18, 28, 44$ are due to the background in the QMS chamber.

Mass spectroscopic measurements This work present a line-of-sight mass spectroscopic measurement of the evaporated $[\text{NC}_{4111}][\text{NTf}_2]$ at an evaporation temperature of 450(1) K. In Figure S1 we show the gas phase mass spectrum of $[\text{NC}_{4111}][\text{NTf}_2]$. $m/z = 116$ corresponds to the cation mass. Peaks at $m/z = 58, 60, 64, 69$ result from the fragments $\text{Bu} + \text{H}^+$, $\text{N}(\text{CH}_3)_3 + \text{H}^+$, SO_2^+ and CF_3^+ of anion and cation, respectively. The water, nitrogen and CO_2 signals at $m/z = 18, 28, 44$ are due to the background in the QMS chamber. We observed a signal at $m/z = 116$ corresponding to the cation as well as fragments of the anion. After switching off the ionization filament no signal below $m/z = 1000$ could be observed. This supports the results of earlier studies that aprotic ILs evaporate in ultrahigh vacuum as classical ion pairs (see reference 27,74).

IR spectra for the IL using the deuterated cation Figure S2 displays the recorded IR spectra of the IL building blocks of the deuterated cation d_9 . From top to bottom: CIVP

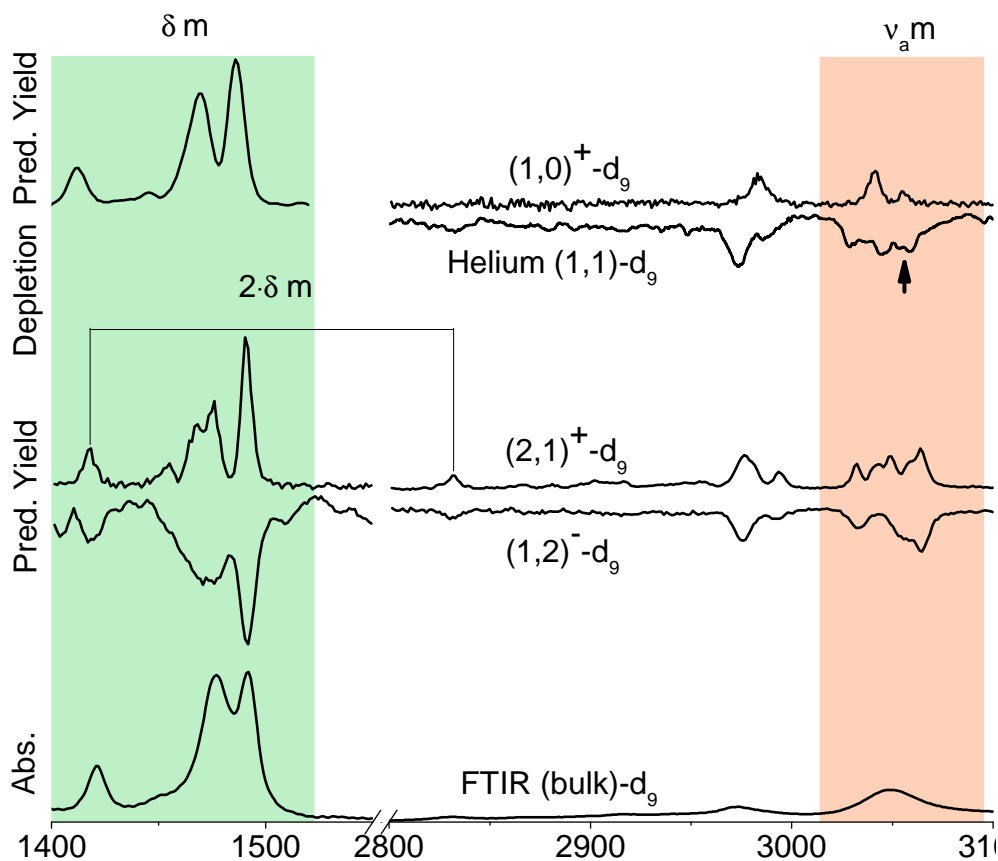


Fig. S 2. From top to bottom: CIVP spectra of the deuterated cation $(1,0)\text{-}d_9$; IR spectrum of $[d_9\text{-NC}_{4111}][\text{NTf}_2]$ measured in helium droplet Helium $(1,1)\text{-}d_9$; CIVP spectra of the deuterated $(2,1)$ and $(1,2)$ clusters and the FTIR bulk spectrum of $[d_9\text{-NC}_{4111}][\text{NTf}_2]$, labeled $(2,1)\text{-}d_9$, $(1,2)\text{-}d_9$ and FTIR (bulk)- d_9 , respectively. Note that the vertical axes are arbitrarily scaled on either side of the break in the abscissa. The arrow marks the position of the VTMA measurement.

spectrum of the deuterated cation $d_9 - (1,0)$. $[d_9 - \text{NC}_{4111}][\text{NTf}_2]$ ion pair measured in helium droplet Helium $d_9\text{-}(1,1)$; CIVP spectra of the deuterated $(2,1)$ and $(1,2)$ clusters and the FTIR bulk spectrum of $[d_9 - \text{NC}_{4111}][\text{NTf}_2]$, labeled $d_9 - (2,1)$, $d_9 - (1,2)$ and room temperature FTIR $d_9\text{-}(bulk)$, respectively. Vertical lines, corresponding to the most intense $(d_9\text{-}(1,0))$ features, aid to identify spectral changes. IR transitions are arbitrarily scaled on either side of. The arrow marks the position of the VTMA measurement.

Results of the theoretical predictions in comparison to the experimental results

TABLE I. Harmonic frequencies and assignments obtained by MP2/cc-pwCVTZ (scaled by 0.968) of the anion in trans ((0,1) *trans*) and cis ((0,1) *cis*) conformation; center frequencies of the anion ((0,1)) measured by CIVP; anion bands from two harmonic frequency calculations of an ion pair with the anion in trans ((1,1) *trans*) and cis ((1,1) *cis*) and the cation both in ap/ap conformation obtained by MP2/aug-cc-pwCVDZ (unscaled); center frequencies of anion bands in cm^{-1} . Band frequencies from resonances shifted due to different local environments are separated by a semicolon. Predicted frequencies in italics.

assignment ^a	(0,1) <i>trans</i>	(0,1) <i>cis</i>	(0,1) <i>cis</i>	(1,1) <i>trans</i>	(1,1) <i>cis</i>	(1,2)	(2,3)	(2,1)	(3,2)	bulk FTIR	Neon	Argon
δ_{CSN}	616	595 ^b	626	601	581 ^b	626	625	621	616	617	606;609;621;626	603;608;620;624
δ_{SNS}	615	642	—	615	637	—	669	—	643	656	656;672	655;670
$\delta_s \text{CF}_3$	734	735	—	726*	728*	737	740	—	—	741	742	741
ν_{CS}	748	749	—	739*	743*	756	760	—	—	763	769	767
$\nu_s \text{SN}$	788	784	—	777*	772*	788	793	—	—	791	794	792
$\nu_a \text{SN}$	1077	1080	1069	1022	1029	1063;1074	1059;1073	1055	1057	1060	1053;1058;1065	1056;1063
—	—	—	—	1100*	1102*	—	—	—	—	—	—	—
$\nu_a^{o,p} \text{SO}_2$	1144	1142	—	1105* ^b	1106* ^b	1144	1148	1140	1130	1139	1134;1141	1132;1139
$\nu_s^{i,p} \text{SO}_2$	1148	1148	—	1118* ^b	1115* ^b	1153	1152	1149	1142	—	1146;1151	1143;1149
ν_{CF_3}	1173	1176 ^b	1178	1142 ^b	1152 ^b	1171	1184	1182	—	1177	—	—
ν_{CF_3}	1179	1178 ^b	—	1148 ^b	1166 ^b	—	—	1190	—	—	—	—
ν_{CF_3}	1181	1187	1186	1190	1191	1183	—	1202	1195	—	1197;1200	1193
ν_{CF_3}	1207	1203	1205	1202	1198	1204;1215	1202;1216	1216	1212;1220	1199	1208;1213	1203
$\nu_a \text{CF}_3$	1234	1238	1229	1214	1213	1234	1235	—	1226	1226	1222	—
$\nu_s \text{CF}_3$	1246	1245	1236	1225	1222	1249	—	1255	1241	—	1237	1234
$\nu_a^{o,p} \text{SO}_2$	1359	1358	1348	1322*	1314*	1347;1368	1330	1342	1327	1335	1321;1332	1321;1331
$\nu_a^{i,p} \text{SO}_2$	1379	1375	1370	1352*	1338*	1362;1379	1361;1368	1368	1349	1355	1350;1361	1345 sh;1348 sh;1355

^a The symbols have their usual meaning: ν , stretching; δ , bending; s , symmetric; a , antisymmetric; i,p , in-phase; o,p , out-of-phase; sh, shoulder. ^b Vibration is localized on either moiety. * Strongly coupled band.

TABLE II. Harmonic frequencies and group assignments obtained by MP2/cc-pVTZ (scaled by 0.94) of the cation in ap/ap conformation (ap/ap); center frequencies of cation bands as shown in the main document and in argon matrix in cm^{-1} . Band frequencies from resonances shifted due to different local environments are separated by a semicolon. Calculated frequencies are written in italics.

assignment ^a	ap/ap	(1,0)	(2,1)	(3,2)	(1,2)	(2,3)	bulk FTIR	Helium (1,1)	Helium (2,2)+	Neon	Argon
ν_s b	<i>2889</i>	2884	2880 sh	2885	2869	2874 sh	2880 sh	2880 sh	2882 sh	2875 sh	
	<i>2897</i>	2895	2889	-	2886	2883	2889	2889	2891	2887	
	<i>2902</i>	-	2901	-	-	-	-	-	-	-	
	<i>2911</i>	-	-	-	-	-	-	-	-	-	
ν_s m	<i>2915</i>	-	2914	2916	2912	-	2913	2913	2918 sh	-	
	<i>2918</i>	-	-	-	-	-	-	-	-	-	
	<i>2921</i>	-	-	-	-	-	-	-	-	-	
	<i>2933</i>	2950 sh	2939	-	-	2935	-	2931	2930 sh	2929	2924
ν_a b	<i>2956</i>	2959	2950	2949	2946	2947	2942	2949	2948	2951	2946
	<i>2975</i>	-	-	-	-	-	-	-	-	-	-
	<i>2979</i>	2979	2976; 2978 sh	2973	2970	2971; 2977 sh	2972	2975	2975	2979	2975
	<i>2991</i>	2996	2988; 2990 sh	2979 sh	2980 sh	2985 sh	2984	2984	2982 sh	2990 sh	2984 sh
	<i>3018</i>	-	3014	-	3014	3006	-	3009	3009	3017	-
	<i>3019</i>	-	-	-	-	-	-	-	-	-	-
ν_a m	<i>3023</i>	3039	3031	3030	3032	3024	-	3030	3034	3037 sh	3029 sh
	<i>3023</i>	-	-	-	-	-	-	-	-	-	-
	<i>3035</i>	-	-	-	-	-	-	-	-	-	-
	<i>3038</i>	3055	3042; 3048	3040; 3048	3053	3050	3048	3046	3051	3048	3043 sh
	-	-	3057; 3064	3060	3063	3063 sh	-	3058	3057 sh	3057	3053

^a The symbols have their usual meaning: ν , stretching; s , symmetric; a , antisymmetric; sh, shoulder.

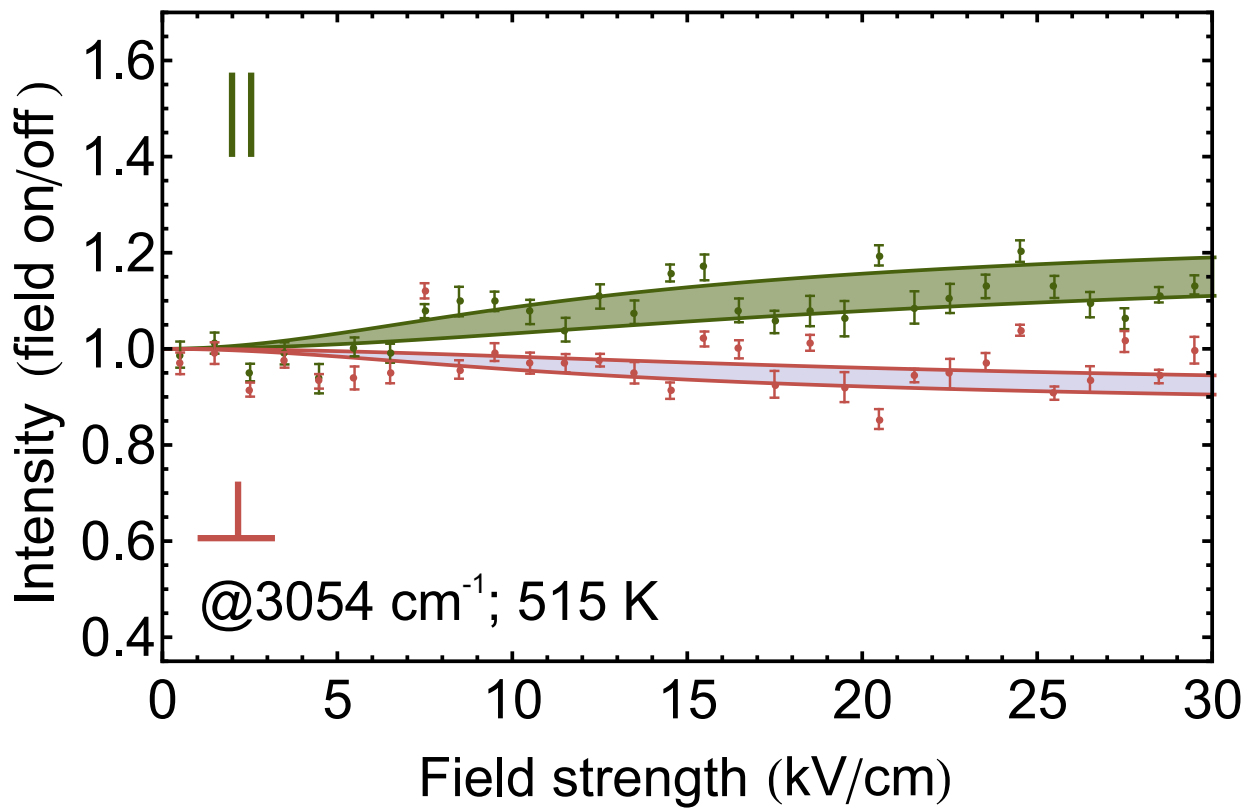


Fig. S 3. Recorded intensity ratio with field on/off as a function of the electric field strength for the 3054 cm⁻¹ band at an evaporation temperature of 515 K. Results for the laser polarization parallel/perpendicular to the electric field are displayed in green and red, respectively.

TABLE III. Harmonic frequencies and group assignments obtained by MP2/cc-pVTZ (scaled by 0.94) of the cation in different conformations; cation bands from two harmonic frequency calculations of an ion pair with the anion in trans ((1,1) *trans*) and cis ((1,1) *cis*) and the cation both in ap/ap conformation obtained by MP2/aug-cc-pwCVDZ (scaled by 0.945).

assignment ^a	ap/ap	ap/sc	sc/ap	ac/ap	sc/sc	ac/sc	(1,1) <i>trans</i>	(1,1) <i>cis</i>
ν_{sb}	2889	2891	2880	2892	2892	2892	2880	2885
	2897	2900	2894	2896	2894	2905	2888	2887
	2902	2903	2897	2904	2900	2906	2889	2890
	2911	2913*	2911*	2912*	2914*	2914*	2907	2906
ν_{sm}	2915	2915*	2914*	2915*	2917*	2918*	2911	2911
	2918	2918	2917	2918	2918*	2918*	2917	2916
	2921	2921	2924**	2921	2924*	2922*	2924	2920
ν_{ab}	2933	2951	2924**	2933	2941	2947	2955	2958
	2956	2957	2945	2952	2947	2952	2968	2969
	2975	2973	2974	2974	2971	2972	2976	2979
	2979	2981	2979	2976	2978	2978	2995	2986
	2991	2987	2992	2991	2987	2989	–	–
ν_{am}	3018	3018	3017	3019	3017	3018	3015	3015
	3019	3019	3018	3020	3018	3019	3019	3018
	3023	3023	3022	3023	3022	3023	3025	3024
	3023	3023	3024	3024	3024	3024	3029	3026
	3035	3035	3032	3033	3032	3034	3032	3029
	3038	3038	3056	3037	3054	3037	3035	3034
	–	–	–	–	–	–	3059	3054

^a The symbols have their usual meaning: ν , stretching; s , symmetric; a , antisymmetric. * ν_{sb} and ν_{sm} coupled band. ** ν_{sm} and ν_{ab} coupled band.

TABLE IV. Harmonic frequencies and group assignments obtained by MP2/cc-pVTZ (scaling factors see computational methods) of the deuterated cation in ap/ap conformation (ap/ap - d₉); center frequencies of deuterated cation bands in cm⁻¹. Band frequencies from resonances shifted due to different local environments are separated by a semicolon. Calculated frequencies are written in italics.

assignment ^a	ap/ap - d ₉	(1,0) - d ₉	(2,1) - d ₉	(1,2) - d ₉	Helium (1,1) - d ₉	bulk FTIR - d ₉
	<i>1419</i>		1418	1418		1421
	<i>1420</i>		–	–		–
	<i>1461</i>		1455	1455 sh		1455 sh
	<i>1461</i>		–	–		–
δ m	<i>1470</i>	no data	–	–	no data	–
	<i>1471</i>		–	–		–
	<i>1491</i>		1467	1470		
	<i>1493</i>		1476	1476		1476
	<i>1508</i>		1491	1491		1492
	<i>2082</i>		2078	2078		2078
ν _s b	<i>2104</i>	no data	–	–	no data	–
	<i>2112</i>		2115	2116		2117
	<i>2116</i>		–	–		–
	<i>2177</i>		–	2145		2147
	<i>2195</i>		2221	2215		2226
ν _a b	<i>2207</i>	no data	–	–	no data	–
	<i>2210</i>		–	–		–
	<i>2216</i>		2231	2235 sh		–
	<i>2915</i>	–	–	–	–	–
ν _s m	<i>2918</i>	–	–	–	–	–
	<i>2920</i>	–	–	–	–	–
	–	2983	2976;2980 sh	2976	2974	2972
	–	–	2994	2994	2987	2983 sh
	<i>3018</i>	–	–	–	–	–
	<i>3019</i>	–	–	–	–	–
	<i>3023</i>	–	–	–	–	–
ν _a m	<i>3023</i>	3041	3032	3033	3029	–
	<i>3035</i>	–	–	–	–	–
	<i>3037</i>	3055	3043;3049	3055 sh	3044	3049
	–	–	3059 sh;3064	3064	3059	–

^a The symbols have their usual meaning: δ bending; ν , stretching; _s, symmetric; _a, antisymmetric; sh, shoulder.