What Quantum Chemical Simulations Tell Us about the Infrared Spectra, Structure and Hydrogen Bonding of a Bulk Ionic Liquid

Sergey A. Katsyuba,[a,]* Elena E. Zvereva,[a,b]

[a] *Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Centre of RAS, Arbuzov st. 8, 420088 Kazan, Russia.*

[b] *IFP Energies Nouvelles, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex – France*

Supporting information

Contents:

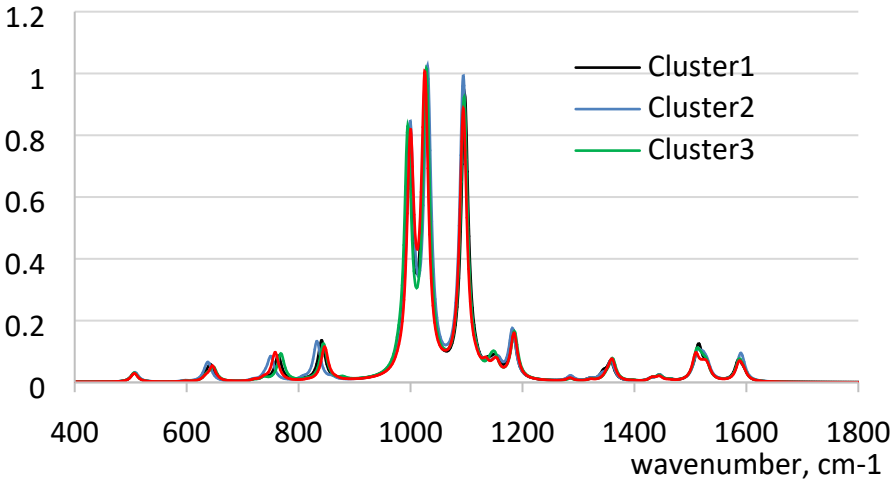

Figure S1. B97-3c simulated IR spectra for clusters $([Emim][BF_4])_8$ of lowest free energy (Cluster 1), of the second-lowest free energy (Cluster 2) of the third-lowest free energy (Cluster 3) and of the fourth-lowest free energy (Cluster 4). The spectra are normalized so that the maximum intensity is equal to unity.

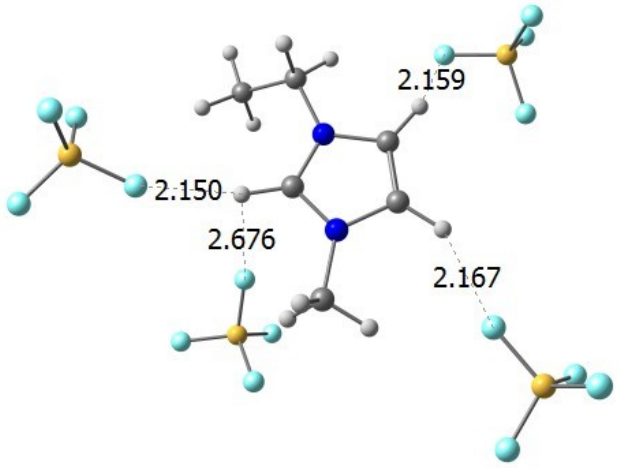

Figure S2: The H···F distances (in Å) computed for $[BF_4]^-$ anions closest to the ring protons of the solvated $[Emim]^+$ cation in the cluster $([Emim][BF_4])_8$ shown in Fig. 1, B (main text).

Table S1. Fundamental frequencies (cm^{-1}) of gaseous $[Emim]^+$ cation and $[BF_4]^-$ anion, and the corresponding B97-3c and B3LYP/6-31+G** computed values.

Assignment	B97-3c[a]	CIVP experiment[b]	B3LYP/6-31+G(d,p)[c]
$[BF_4]^-$			
ν_3 asym. str.	1045	1068	1052
$[Emim]^+$			
C2H oop bend	804	821	805
C4H/C5H ip bend	1099	1105	1099
N1C2N3 ring sym. str.	1109		
C2H ip bend	1143	1158	1146
Me CH_3 bend	1457	1450	1452
Et CH_3 bend	1468	1471	1467
N1C2N3 ring asym. str.	1548	1556	1555
C2N3/C4C5 ring asym. str.	1557		1563
Et CH_3 sym. str.	2958	2978	
Me CH_3 sym. str.	2981	2991	2972
Et CH_2 sym. str.	2984		2981
Et CH_3 asym. str.	3037	3008	3029
Et CH_2 asym. str.	3042		3039
C2H str.	3174	3132	3178
C4H/C5H asym. str.	3168	3163	3174
C4H/C5H sym. str.	3185	3180	3192

[a] Harmonic frequencies without scaling for the range $\nu < 1100$ cm^{-1}, and with a scaling factor of 0.979 for the range $\nu > 1100$ cm^{-1}; [b] Cryogenic Ion Vibrational Predissociation spectroscopy data from Ref.[1]; [c] Harmonic frequencies scaled by 0.97 for the range $\nu < 1800$ cm^{-1}, and with a scaling factor of 0.9639 for the range $\nu > 2900$ cm^{-1} (from Ref.[1]).

Cartesian coordinates of species shown in Fig. 1 (main text)

Ion pair

5	2.654574515	-0.527260468	0.159846778
9	3.938568335	-0.541514688	0.655340090
9	1.692265714	-0.420391959	1.205856248
9	2.450825642	0.571661758	-0.730792331
9	2.366918986	-1.723453405	-0.573758485
6	-0.314977792	-0.482613451	-0.698767027
7	-0.919157026	0.669800806	-0.414933109
7	-0.976310910	-1.466075191	-0.089044529
6	-1.993975128	0.416641463	0.411051144
6	-2.031713435	-0.923597924	0.611958954
1	0.591271548	-0.594564438	-1.263438781
6	-0.399410816	1.997202151	-0.772248664
6	-0.569567639	-2.866426409	-0.093897857
1	-2.625634171	1.200426291	0.782693951
1	-2.702708097	-1.530523710	1.189436682
6	0.154051662	2.721007326	0.436004884
1	0.384816981	1.833172471	-1.502933842
1	-1.209816923	2.548100454	-1.247281550
1	0.481976924	-2.912090326	-0.351893716
1	-0.703535702	-3.271066227	0.903485670
1	-1.168017265	-3.430303118	-0.804675259
1	0.576811906	3.671541193	0.117394163
1	0.940857416	2.131706096	0.895497353
1	-0.618114730	2.928621305	1.175099223

Cluster $([Emim][BF_4])_8$

5	-3.893410777	1.405345392	-2.449122533
9	-4.575970824	1.841000198	-1.288731353
9	-4.375093088	0.123833091	-2.817090484
9	-4.077470647	2.308053028	-3.494353885
9	-2.503522584	1.302563898	-2.145565031
6	0.003085315	0.297654074	-0.466889451
7	-0.169652612	-0.322399657	0.703480721
7	1.261856319	0.089803083	-0.859984056
6	1.004896054	-0.952621174	1.056301782
6	1.901933699	-0.694134434	0.073545287
1	-0.738252471	0.861752487	-1.000111445
6	-1.416761301	-0.401552963	1.477636873
6	1.852376483	0.576275204	-2.101501336
1	1.093273952	-1.475140998	1.989009546
1	2.933898620	-0.960395915	-0.039825187
6	-2.273517497	0.834765034	1.366167558
1	-1.950026793	-1.280109272	1.125456883
1	-1.123708142	-0.588889419	2.505185074
1	1.585184026	1.614015819	-2.246934469
1	2.928022027	0.490189681	-2.020600406
1	1.504766039	-0.020307981	-2.935857407

1	-3.113063204	0.728485282	2.048437384
1	-2.669825393	0.968914573	0.364378462
1	-1.724909574	1.728572317	1.651752275
5	1.118693659	-0.781080405	-6.530226358
9	0.146776131	-1.796021635	-6.291956258
9	1.516293668	-0.263601063	-5.252848942
9	2.237819809	-1.349284762	-7.155507043
9	0.561384649	0.242658837	-7.292100581
6	-1.586090284	0.212205363	-4.784198463
7	-2.609806744	-0.321571526	-5.445779315
7	-1.415406713	1.462679609	-5.210985169
6	-3.105751244	0.612968439	-6.326585580
6	-2.355211426	1.730762872	-6.176391287
1	-0.997832374	-0.293868240	-4.045488709
6	-3.128937981	-1.673778733	-5.234820820
6	-0.407919860	2.389108981	-4.709391565
1	-3.948953851	0.413407073	-6.957815323
1	-2.413351516	2.687587979	-6.657187786
6	-3.089414696	-2.506252197	-6.497967729
1	-2.523699848	-2.123546082	-4.454632217
1	-4.138131199	-1.570570664	-4.841871740
1	-0.479832143	3.314226675	-5.267419674
1	-0.593027474	2.593666235	-3.661211669
1	0.576025729	1.959153868	-4.853156619
1	-3.419486602	-3.517534738	-6.266691754
1	-2.080000653	-2.547094113	-6.895372535
1	-3.751325135	-2.113390605	-7.267845536
5	-0.491927108	4.332560657	4.163490124
9	0.600074300	4.816072095	3.416334637
9	-0.034027838	3.550354697	5.238419549
9	-1.274033423	5.404065638	4.639973405
9	-1.299860824	3.519297771	3.307329802
6	-2.134060977	1.599730828	5.703281267
7	-1.566225134	1.052456849	6.773211538
7	-3.035826466	2.490553958	6.110138861
6	-2.125931412	1.607441147	7.902608611
6	-3.047830889	2.509132694	7.486312706
1	-1.907900062	1.369675840	4.683315731
6	-0.548692925	-0.004619818	6.751627166
6	-3.932463989	3.231954700	5.235974258
1	-1.817571971	1.320157010	8.889127583
1	-3.704428193	3.153433919	8.038424000
6	-1.092782907	-1.330283107	7.235472409
1	-0.192992271	-0.093713264	5.732549558
1	0.287431624	0.335785227	7.358408539
1	-4.840103182	2.655995679	5.082054778
1	-4.156602712	4.186736547	5.698514861
1	-3.429539420	3.411185161	4.294246419
1	-0.302070736	-2.071839475	7.161236704
1	-1.930327101	-1.644703687	6.620238154
1	-1.422324938	-1.281760395	8.272224447
5	-0.493703164	-3.399807299	-2.066704847

9	-0.706601363	-3.224013480	-0.679895074
9	0.467276719	-4.425582630	-2.261116742
9	-1.698959664	-3.751162493	-2.692785722
9	0.002055795	-2.197292970	-2.625548503
6	2.287069970	-3.147225993	-4.677670807
7	1.961467785	-4.183365259	-5.449158906
7	3.573985954	-2.862591017	-4.878040269
6	3.069248058	-4.563241360	-6.174475824
6	4.078792876	-3.731553433	-5.818382287
1	1.611437858	-2.619388308	-4.032505986
6	0.619116230	-4.761529785	-5.560083157
6	4.275491573	-1.704186305	-4.334300523
1	3.040017084	-5.369111840	-6.881722387
1	5.094694436	-3.668050893	-6.157834639
6	0.583023082	-6.216059641	-5.148743823
1	-0.030618143	-4.163465898	-4.933801401
1	0.298350895	-4.616281531	-6.588888228
1	3.880939451	-1.470715478	-3.354957697
1	5.328104043	-1.934515693	-4.232018292
1	4.127416365	-0.858832688	-4.997043136
1	-0.436514402	-6.585155777	-5.238849505
1	0.888640311	-6.329703757	-4.112653314
1	1.217723857	-6.838474460	-5.777844484
5	-4.503811014	-0.695834040	4.747163469
9	-4.511486470	-0.188184997	6.045456621
9	-3.168205230	-0.943198533	4.324910918
9	-5.236379650	-1.906428250	4.682772690
9	-5.081924606	0.243246996	3.850148262
6	-5.019145287	-2.210697617	1.719266798
7	-4.154551092	-3.156120208	1.342813755
7	-5.218387475	-1.396570834	0.681950673
6	-3.792045610	-2.936512724	0.028690212
6	-4.461963608	-1.831817121	-0.387265452
1	-5.431167853	-2.104055564	2.708197051
6	-3.612665297	-4.194082781	2.227953235
6	-6.120108878	-0.248560364	0.680300079
1	-3.071841439	-3.545008758	-0.483300037
1	-4.448851797	-1.301746579	-1.323781440
6	-2.207584049	-3.877189007	2.693139583
1	-4.291782771	-4.270842307	3.072034795
1	-3.652098718	-5.131868699	1.677188682
1	-6.206561814	0.122145682	1.694606361
1	-5.704767017	0.518124197	0.037878952
1	-7.094898346	-0.549878737	0.305591786
1	-1.837481900	-4.696030172	3.306728054
1	-2.194892733	-2.975609461	3.296712533
1	-1.532897286	-3.752594986	1.850775303
5	6.198215128	-0.686973423	-1.482215568
9	6.556719903	-2.002047552	-1.853780067
9	6.346339741	0.196179177	-2.546350529
9	4.812595479	-0.707159397	-1.089911269
9	6.956549701	-0.278626395	-0.366214199

6	2.904757903	2.554677948	1.126765554
7	4.078829490	2.283806761	0.548219851
7	2.806562148	1.811018423	2.230795113
6	4.750737226	1.353255697	1.310930339
6	3.950490979	1.053694658	2.365295099
1	2.174101629	3.253306271	0.762110665
6	4.596353944	2.903633449	-0.680343636
6	1.676959167	1.799360961	3.153726464
1	5.699391825	0.956984320	0.999005396
1	4.054872122	0.340818835	3.160979420
6	5.576618194	4.015620389	-0.377965591
1	5.063426496	2.112491363	-1.259681718
1	3.744435179	3.275376064	-1.238975970
1	1.890369123	2.417657791	4.017193527
1	0.805553090	2.202055555	2.655662154
1	1.492999962	0.777985348	3.464322812
1	5.934695648	4.436334416	-1.314891717
1	6.438818947	3.649526488	0.176028208
1	5.102010894	4.812357260	0.190727286
5	1.989891345	-2.163403025	4.587863427
9	1.810717835	-3.524194651	4.222601376
9	2.138539817	-2.025784163	5.957560910
9	3.141112186	-1.672232037	3.903813164
9	0.859627480	-1.425623348	4.134359096
6	3.459070902	-3.890286652	1.702025616
7	4.495518086	-3.411445849	1.012163076
7	2.593035911	-4.418561617	0.835192784
6	4.292436083	-3.650400281	-0.331835982
6	3.094742521	-4.278534226	-0.443033188
1	3.306188843	-3.819263101	2.763650329
6	5.656974897	-2.731914511	1.599974112
6	1.323094700	-5.039177631	1.190923236
1	4.996027613	-3.312708153	-1.070302458
1	2.525131823	-4.585050802	-1.299820664
6	6.927639705	-3.536939223	1.444782750
1	5.750320494	-1.772816927	1.102062914
1	5.410065973	-2.553668071	2.642436475
1	0.547385476	-4.628495582	0.556406578
1	1.388825156	-6.113807737	1.043117977
1	1.114239965	-4.820492275	2.231377139
1	7.748263065	-2.996896108	1.911380270
1	7.181420498	-3.669746208	0.396569018
1	6.843707944	-4.512591943	1.920491982
5	1.025301791	4.428434250	-1.517343793
9	1.928268396	3.983345207	-2.487923894
9	1.717390124	5.091407171	-0.464764265
9	0.066126232	5.285039964	-2.061696385
9	0.370870277	3.296064486	-0.935856945
6	-1.183895376	5.891226309	0.904638837
7	-2.398983333	5.431580791	0.609923125
7	-1.306487509	6.823061443	1.852940210
6	-3.320657264	6.082911697	1.399207222

6	-2.636164904	6.951365171	2.183017001
1	-0.253293463	5.574151937	0.473678970
6	-2.731173478	4.463934370	-0.449066730
6	-0.207575158	7.558861399	2.462277991
1	-4.369635429	5.865665449	1.335088248
1	-2.964354570	7.615067553	2.959225223
6	-3.275106612	5.154334490	-1.679486428
1	-1.827037830	3.913532869	-0.675078365
1	-3.451381195	3.765926041	-0.034273054
1	-0.182532527	7.337633521	3.522135162
1	0.721753015	7.234844836	2.012378034
1	-0.349131972	8.622370761	2.289920759
1	-3.543475837	4.402529150	-2.415513639
1	-2.525925059	5.810343995	-2.113710159
1	-4.169139181	5.733516550	-1.451663245

References

[1] Johnson C.J., Fournier J.A., Wolke C.T., Johnson M.A. Ionic liquids from the bottom up: Local assembly motifs in [Emim][BF_4] through cryogenic ion spectroscopy. *J. Chem. Phys*. **2013**, *139*, 224305.