Electronic Supplementary Information

A Density Functional Theory Based Approach for Predicting Melting Points of Ionic Liquids

Lihua Chen[1,2], Vyacheslav S. Bryantsev[2*]

[1]*Department of Materials Science and Engineering, University of Connecticut, Storrs CT 06269 USA*

[2]*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN 37831 USA*

Email: bryantsevv@ornl.gov

Phone: (865) 576-4272

Fax: (865) 576 7956

Electronic Supplementary Information (ESI) Available: Full details of computing $^{\Delta G_{latt}}$, a description of the computational protocol based on the VBT approach, Table S1 showing the comparison of the computed and experimental lattice parameters and molecular volumes for 11 ILs, Table S2 listing the lattice enthalpies, entropies, and free energies, solvation free energies, and the resulting fusion free energies at standard conditions, Figure S1 showing a correlation of computed and experimental melting points, and Cartesian coordinates of all the polyatomic ions accompanied by their electronic energies obtained at the M06-2X/6-31+G(d, p) level of theory.

1. Full details of computing ΔG_{latt} based on the methodology in Section 2.

Eq. (1) $\Delta G_{latt} = \Delta H_{latt} - T\Delta S_{latt}$

Eq. (2) $\Delta H_{latt} = \Delta U_{latt} + P\Delta V = \Delta U_{latt} - 2RT$

Eq. (3) $\Delta U_{latt} = \Delta U_0 + \Delta U_{therm}$

Eq. (4) $\Delta U_0 = \left(\frac{E_{total}^{[C][A]_s}}{Z} + \frac{E_{ZPE}^{[C][A]_s}}{Z}\right) - \left(E_{total}^{C_g^+} + E_{ZPE}^{C_g^+}\right) - \left(E_{total}^{A_g^-} + E_{ZPE}^{A_g^-}\right)$, where Z is the the number of formula units included in the unit cell.

Eq. (5) $\Delta U_{therm} = \Delta U_{vib} + \Delta U_{rot} + \Delta U_{trans}$, where, vib, rot, and trans refer to the vibrational, rotational and translational contributions to internal thermal energy, respectively.

Eq. (6) $\Delta U_{vib} = \left(\frac{U_{vib}^{[C][A]_s}}{Z} + 6RT\right) - \left(U_{vib}^{C_g^+} + U_{vib}^{A_g^-}\right)$, where $6RT$ is the three acoustic modes of solids, i.e., $3RT$ per ion.

Eq. (7) $\Delta U_{rot} = -\left(U_{rot}^{C_g^+} + U_{rot}^{A_g^-}\right)$, where $U_{rot}^{monoatomic} = 0,\ and\ U_{rot}^{polyatomic}$ =1.5RT

Eq. (8) $\Delta U_{trans} = -\left(U_{trans}^{C_g^+} + U_{trans}^{A_g^-}\right) = -3RT$

Eq. (9) $\Delta S_{latt} = \left(\frac{S_{vib}^{[C][A]_s}}{Z}\right) - \left[\left(S_{vib}^{C_g^+} + S_{vib}^{A_g^-}\right) + \left(S_{rot}^{C_g^+} + S_{rot}^{A_g^-}\right) + \left(S_{trans}^{C_g^+} + S_{trans}^{A_g^-}\right)\right]$

Eq. (10) IL with polyatomic ions: $\Delta G_{latt}^{polyatomic} = \Delta U_0 + \Delta U_{vib} - 8RT - T\Delta S_{latt}$

Eq. (11) IL with monoatomic ions: $\Delta G_{latt}^{monoatomic} = \Delta U_0 + \Delta U_{vib} - 6.5RT - T\Delta S_{latt}$

2. A description of the computational protocol based on the VBT approach

Eq. (12) $\Delta U_0^{HSE06-D3} =$ -71.76$(V_m)^{-1/3}$ -417.83

Eq. (13) $\Delta U_{vib}^{VBT} = 6RT$

Eq. (14) $S_{[C][A]_s}^{monoatomic} = 3.267TV_m + 175.8V_m - 0.1057T + 12.28,\ R^2 = 0.996$

Eq. (15) $S_{[C][A]_s}^{polyatomic} = 3.164TV_m + 300.2V_m - 0.0156T + 7.85,\ R^2 = 0.997$

Eq. (16) $\Delta S_{latt}^{polyatomic} = S_{[C][A]_s}^{polyatomic} - \left[\left(S_{vib}^{C_g^+} + S_{vib}^{A_g^-}\right) + \left(S_{rot}^{C_g^+} + S_{rot}^{A_g^-}\right) + \left(S_{trans}^{C_g^+} + S_{trans}^{A_g^-}\right)\right]$

Eq. (17) $\Delta S_{latt}^{monoatomic} = S_{[C][A]_s}^{monoatomic} - \left[\left(S_{vib}^{C_g^+} + S_{vib}^{A_g^-}\right) + \left(S_{rot}^{C_g^+} + S_{rot}^{A_g^-}\right) + \left(S_{trans}^{C_g^+} + S_{trans}^{A_g^-}\right)\right]$

Eq. (18) IL with polyatomic ions: $\Delta G_{latt}^{polyatomic} = \Delta U_0^{HSE06-D3} + \Delta U_{vib}^{VBT} - 8RT - T\Delta S_{latt}^{polyatomic}$

Eq. (19) IL with monoatomic ions: $\Delta G_{latt}^{monoatomic} = \Delta U_0^{HSE06-D3} + \Delta U_{vib}^{VBT} - 6.5RT - TS_{latt}^{monoatomic}$

Table S1: Comparison of the computed and experimental lattice parameters and molecular volumes, V_m , for 11 ILs. The experimental values are taken from the CSD database.

ILs	space group	method	a (Å)	b (Å)	c (Å)	β (deg.)[a]	V_m (Å^3)
[C_1mim][Cl]	P21/n	Expt	8.65	7.86	10.54	106.34	171.89
		PBE-D3	8.65	7.83	10.22	106.71	170.65
		PBE	8.69	8.49	10.71	106.66	189.34
[C_2mim][Br]	P21/c	Expt	8.75	8.00	12.66	109.91	208.29
		PBE-D3	8.68	7.87	12.45	108.81	201.38
		PBE	8.94	8.79	12.85	110.67	236.31
[C_2mmim][Cl]	P21/c	Expt	6.68	16.43	8.24	105.10	218.15
		PBE-D3	6.66	16.26	8.09	103.97	212.53
		PBE	6.73	16.70	8.92	105.99	240.92
[C_2mim][BF_4]	P21/n	Expt	8.76	9.40	11.43	98.72	232.42
		PBE-D3	8.64	9.20	11.45	98.77	225.28
		PBE	8.91	9.69	13.95	101.25	261.01
[C_2mmim][Br]	P21/a	Expt	8.36	17.04	6.88	104.29	237.17
		PBE-D3	8.16	16.96	6.75	102.34	227.80
		PBE	8.93	17.37	6.87	104.40	258.12
[C4mim][Cl][b]	P21/c	Expt	9.92	11.45	9.65	118.81	240.15
		PBE-D3	9.81	11.46	9.54	118.44	235.78
		PBE	10.28	11.88	10.07	120.60	264.49
[C_2mim][PF_6]	P21/c	Expt	8.63	9.04	13.47	101.92	256.80
		PBE-D3	8.62	8.95	13.49	100.72	255.55
		PBE	8.91	9.69	13.95	101.25	295.29
[C_4mmim][Cl]	P21/n	Expt	8.31	11.66	10.67	90.74	259.03
		PBE-D3	8.21	11.66	10.72	91.88	256.34
		PBE	6.73	16.70	8.92	105.99	287.13
[C_3mim][PF_6]	P21/c	Expt	8.52	10.04	13.64	106.08	280.51
		PBE-D3	8.46	10.01	13.56	106.27	275.65
		PBE	8.78	10.51	14.11	105.12	314.36
[C_4mmim][PF_6]	Cc	Expt	15.35	8.60	11.60	122.25	323.58
		PBE-D3	15.39	8.60	11.58	122.37	323.66
		PBE	16.11	8.90	12.28	122.93	369.48
[C_1mpyr][Tf_2N]	P21/c	Expt	8.50	13.83	12.81	98.78	372.17
		PBE-D3	8.35	13.96	12.83	100.18	368.01
		PBE	8.82	14.34	13.64	99.71	425.35

[a]The other cell angles are $\alpha = \gamma = 90^o$. [b]The most stable polymorph with a monoclinic crystal.

Table S2: The lattice enthalpies $\Delta H^{HSE06-D3}_{latt}$, entropies ΔS_{latt}, and free energies ΔG_{latt}, solvation free energies ΔG^{o-l}_{solv}, and the resulting fusion free energies $\Delta G^{HSE06-D3}_{fus}$ at 298.15 K and 1 atm. Energies are in kJ/mol and entropies are in kJ/mol/K.

ILs	$\Delta H^{HSE06-D3}_{latt}$	ΔS_{latt}	ΔG_{latt}	ΔG^{o-l}_{solv}	$\Delta G^{HSE06-D3}_{fus}$
[C_1mim][Cl]	-574.986	-0.333	-475.830	-457.724	18.105
[C_4mim][Cl]	-579.021	-0.302	-489.010	-452.704	36.306
[C_2mmim][Cl]	-587.009	-0.356	-480.851	-444.698	36.154
[C_4mmim][Cl]	-575.487	-0.387	-460.122	-443.861	16.261
[C_2mim][Br]	-554.913	-0.340	-453.567	-441.379	12.188
[C_2mmim][Br]	-565.252	-0.348	-461.422	-432.560	28.861
[C_2mim][BF_4]	-519.598	-0.390	-403.411	-421.719	-18.308
[C_2mim][PF_6]	-512.209	-0.390	-395.896	-398.998	-3.102
[C_3mim][PF_6]	-510.114	-0.399	-391.224	-397.510	-6.286
[C_4mmim][PF_6]	-509.713	-0.425	-383.137	-388.879	-5.742
[C_1mpyr][Tf_2N]	-498.732	-0.412	-375.915	-355.909	20.006

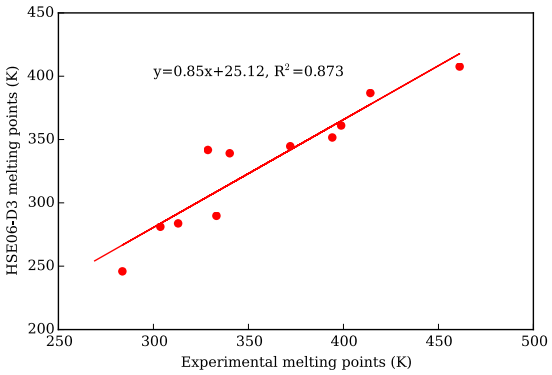

Figure S1: A correlation of computed based on the HSE06-D3 method and experimental melting points.

<u>Optimized geometries and absolute energies of polyatomic ions obtained at the M06-2X/6-31+G(d, p) level of theory</u>

C_1mim$^+$
Absolute Energy = -305.10011 Hartrees
Cartesian Coordinates

N	4.638062	4.154325	4.696078
N	3.813704	5.194066	6.422834
C	4.947959	4.909621	5.761798
C	2.756638	4.608311	5.757543
C	3.272858	3.954329	4.673219
C	5.603301	3.589217	3.751750
C	3.710432	5.968540	7.662985

H	5.944693	5.241586	6.027256
H	1.736929	4.717068	6.106409
H	2.788754	3.376267	3.894813
H	6.564538	4.095539	3.878219
H	5.721772	2.516747	3.948558
H	5.241261	3.743737	2.730020
H	4.242659	6.918975	7.554190
H	4.127603	5.394177	8.498726
H	2.651439	6.165996	7.851604

C_2mim$^+$

Absolute Energy = -344.40000 Hartrees

Cartesian Coordinates

N	7.993450	7.797313	7.885896
N	9.888882	7.780135	6.803777
C	8.861587	8.552176	7.191531
C	9.670509	6.495606	7.259470
C	8.482392	6.507012	7.939137
C	6.752770	8.318904	8.514183
C	11.039294	8.222708	6.013817
C	5.875344	7.226240	9.096010
H	8.752725	9.609485	6.980474
H	10.367901	5.689883	7.066249
H	7.958736	5.708024	8.446144
H	6.216666	8.880181	7.736989
H	11.016285	9.313124	5.925292
H	11.962111	7.919600	6.520792
H	10.998781	7.771703	5.015443
H	7.061900	9.027730	9.294581
H	6.382195	6.671749	9.896378
H	5.530674	6.521399	8.327864
H	4.990362	7.697930	9.540377

C_2mmim$^+$

Absolute Energy = -383.70883 Hartrees

Cartesian Coordinates

N	8.006355	7.822678	7.895074
N	9.903734	7.798436	6.824957
C	8.891836	8.600508	7.228337
C	9.654250	6.504081	7.241705
C	8.466990	6.519331	7.912009
C	6.759153	8.324246	8.517653
C	11.071841	8.192619	6.038735
C	8.750883	10.053556	6.976283
C	5.898540	7.221103	9.106527
H	10.337584	5.691780	7.028373
H	7.924570	5.717510	8.393087
H	6.206351	8.872069	7.742167
H	11.124732	9.281987	5.968347
H	11.977859	7.819704	6.529388
H	10.998560	7.770776	5.029035
H	7.049080	9.043477	9.297304
H	6.417150	6.672002	9.903113
H	5.558001	6.512236	8.340406
H	5.009953	7.682015	9.555055
H	8.135988	10.522045	7.752913

H	8.272606	10.245070	6.003529
H	9.727203	10.552112	6.977682

C_3mim^+

Absolute Energy = -383.69630 Hartrees

Cartesian Coordinates

N	8.012363	7.799170	7.874378
N	9.921981	7.793010	6.816190
C	8.877907	8.555827	7.178316
C	9.718149	6.513588	7.291986
C	8.521978	6.518079	7.956401
C	6.737124	8.293157	8.453358
C	11.070677	8.231242	6.020967
C	5.899627	7.188222	9.083092
C	4.582139	7.743133	9.626635
H	8.755849	9.607628	6.947316
H	10.429724	5.715284	7.121675
H	8.005781	5.720210	8.471958
H	6.182595	8.781513	7.639443
H	11.055158	9.321808	5.934300
H	11.994355	7.920508	6.521402
H	11.021216	7.781865	5.022081
H	6.991108	9.059444	9.199840
H	5.692505	6.408654	8.333430
H	6.463640	6.716600	9.902696
H	3.992458	6.937797	10.080982
H	3.976102	8.193815	8.828497
H	4.753204	8.506907	10.397657

C_4mim^+

Absolute Energy = -422.99236 Hartrees

Cartesian Coordinates

N	8.046461	7.787678	7.843805
N	9.952728	7.809089	6.779238
C	8.902530	8.558509	7.151939
C	9.761837	6.523250	7.243305
C	8.567593	6.510529	7.911295
C	6.777021	8.270962	8.446023
C	11.097638	8.269156	5.990891
C	5.936612	7.154335	9.046778
C	4.644145	7.696206	9.668274
C	3.785504	6.577542	10.257290
H	8.769930	9.611226	6.931731
H	10.480277	5.733141	7.063485
H	8.058992	5.703055	8.419641
H	6.222100	8.789082	7.651175
H	11.053892	9.358035	5.893521
H	12.024648	7.988191	6.502817
H	11.069590	7.809811	4.995848
H	7.042887	9.011432	9.214040
H	5.687656	6.413477	8.269590
H	6.510805	6.631339	9.828414
H	4.070504	8.246686	8.905030
H	4.896733	8.426740	10.453470
H	4.338502	6.010394	11.019661
H	3.465661	5.869212	9.479517

H	2.883416	6.981284	10.733621

C_4mmim$^+$

Absolute Energy = -462.30113 Hartrees

Cartesian Coordinates

N	8.056895	7.797669	7.855303
N	9.963375	7.809667	6.799533
C	8.924188	8.588357	7.179904
C	9.750819	6.517151	7.241468
C	8.558342	6.509803	7.902426
C	6.781041	8.264370	8.448330
C	11.120810	8.224140	6.007176
C	5.946231	7.144508	9.052946
C	4.651522	7.686025	9.670593
C	3.788175	6.570021	10.257798
C	8.749187	10.033043	6.900692
H	10.459722	5.721313	7.050624
H	8.037011	5.701787	8.395909
H	6.216263	8.771417	7.652995
H	11.134151	9.312309	5.906912
H	12.038639	7.898348	6.509083
H	11.066321	7.772961	5.009044
H	7.027212	9.012371	9.216845
H	5.699920	6.400729	8.277875
H	6.521715	6.625070	9.835898
H	4.080337	8.237026	8.905857
H	4.902443	8.416874	10.456352
H	4.339252	5.998024	11.018003
H	3.463058	5.865780	9.478858
H	2.888676	6.976992	10.736403
H	8.064006	10.485779	7.625326
H	8.336109	10.199776	5.894238
H	9.704662	10.567173	6.967041

C_1mpyr$^+$

Absolute Energy = -291.455702 Hartrees

Cartesian Coordinates

N	4.383873	7.452571	5.936785
C	4.736560	6.122450	5.249206
C	4.324620	5.001419	6.222777
C	3.837934	5.712501	7.502256
C	3.356313	7.059793	6.993408
C	5.604945	8.037502	6.591976
C	3.821830	8.449237	4.969510
H	4.176651	6.087938	4.308462
H	3.510755	4.413179	5.781143
H	3.028625	5.168397	8.002618
H	2.393563	6.969259	6.472667
H	6.023772	7.312743	7.296302
H	4.576885	8.675758	4.208810
H	5.806087	6.144507	5.014303
H	5.154129	4.314188	6.422773
H	4.646914	5.830133	8.235771
H	3.288583	7.860932	7.738420
H	6.342776	8.267408	5.816118
H	3.556910	9.362387	5.514132

H	5.318913	8.953381	7.120388
H	2.929961	8.023317	4.498178

BF_4^-
Absolute Energy = -424.42212 Hartrees
Cartesian Coordinates

B	7.787464	6.951249	5.157137
F	6.694483	6.931073	4.244648
F	7.485385	7.825493	6.239855
F	8.957185	7.410098	4.486807
F	8.012983	5.636888	5.657652

PF_6^-
Absolute Energy = -940.48703 Hartrees
Cartesian Coordinates

P	7.107745	7.107745	5.555006
F	7.107745	7.107745	7.198946
F	7.107745	7.107745	3.910980
F	5.945299	5.945299	5.554949
F	8.270189	8.270189	5.554949
F	8.270189	5.945299	5.554949
F	5.945299	8.270189	5.554949

Tf_2N^-
Absolute Energy = -1826.85832 Hartrees
Cartesian Coordinates

S	6.797417	5.490263	3.624038
S	4.206985	5.741618	4.806779
N	5.445042	6.256036	3.946222
C	6.459448	4.602791	1.991219
C	2.830351	5.925030	3.528407
O	7.164447	4.425146	4.529674
O	3.853549	6.729548	5.801563
O	7.787552	6.470863	3.244964
O	4.176392	4.341384	5.165195
F	5.541969	3.612320	2.127349
F	1.642244	5.567767	4.093946
F	7.610690	4.037746	1.524776
F	6.009711	5.463357	1.038247
F	2.707614	7.203385	3.085298
F	3.027888	5.126346	2.447223