Electronic Supporting Information

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Thermodynamics of Imidazolium-Based Ionic Liquids Containing PF_6 Anion

Dzmitry H. Zaitsau,[a,]* Andrei V. Yermalayeu,[a] Vladimir N. Emel´yanenko,[a,b] Simon Butler,[c] Thomas Schubert,[d] Sergey P. Verevkin[a]

[a]*Department of Physical Chemistry and Department „Science and Technology of Life, Light and Matter“, University of Rostock, D-18059, Rostock, Germany*
[b]*Department of Physical Chemistry, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia*
[c]*Eduard-Zintl-Institut für Anorganische und Physikalische Chemie. Technische Universität Darmstadt, Alarich-Weiss-Str. 4, 64287 Darmstadt, Germany*
[d]*IoLiTec Ionic Liquids Technologies GmbH, Salzstrasse 184, D-74076 Heilbronn, Germany*

Table S1. Provenance and Purity af the IL Used in This Study.

Sample	CAS	Origin	Purity
$[C_2mim][PF_6]$	155371-19-0	IoLiTec GmbH	99%
$[C_4mim][PF_6]$	174501-64 -5	IoLiTec GmbH	99%
$[C_6mim][PF_6]$	304680-35-1	IoLiTec GmbH	99%
$[C_8mim][PF_6]$	304680-36-2	IoLiTec GmbH	99%
$[C_{10}mim][PF_6]$	362043-46-7	IoLiTec GmbH	98%

Table S2. The Results of the Temperature Dependence of Frequency Shift Velocity *df/dt* of the QCM for [$C_n$mim][PF_6] and Vaporization Enthalpies $\Delta_l^g H^o_m(T)$ Determination.

Run	T / K	$10^6 \cdot p^*_{sat}$ / Pa	T^{-1} / K^{-1}	$R\cdot\ln(p^*_{sat}/p^o)$	$\frac{\Delta_l^g H^o_m(T)}{kJ\cdot mol^{-1}}$
			[C_2mim][PF_6]		
$\ln(p^*_{sat}/p^o) = -\frac{78196}{R} - \frac{129904}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) - \frac{74}{R}\left(\frac{T_0}{T} - 1 - \ln\left(\frac{T}{T_0}\right)\right)$, T_0 = 435.2 K					
1	456.79	224	0.002189	-165.6	128.3
	451.80	153	0.002213	-168.8	128.7
	446.81	105	0.002238	-171.9	129.0
	441.84	71	0.002263	-175.2	129.4
	436.82	47	0.002289	-178.6	129.8
	431.85	31	0.002316	-181.9	130.2
	426.85	20	0.002343	-185.6	130.5
	421.85	13	0.002370	-189.2	130.9
	416.85	8.3	0.002399	-193.0	131.3
2	454.34	185	0.002201	-167.2	128.5
	450.31	136	0.002221	-169.7	128.8
	444.31	85	0.002251	-173.6	129.2
	439.29	57	0.002276	-177.0	129.6
	434.32	38	0.002302	-180.4	130.0
	429.33	25	0.002329	-183.8	130.3
	424.34	17	0.002357	-187.3	130.7
	419.34	11	0.002385	-190.9	131.1
	414.05	6.5	0.002415	-195.0	131.5
			[C_4mim][PF_6]		
$\ln(p^*_{sat}/p^o) = -\frac{78587}{R} - \frac{137095}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) - \frac{74}{R}\left(\frac{T_0}{T} - 1 - \ln\left(\frac{T}{T_0}\right)\right)$, T_0 = 425.7 K					
1	447.43	148	0.002235	-169.0	135.5
	442.43	98	0.002260	-172.5	135.9
	437.44	64	0.002286	-176.0	136.2
	432.45	41	0.002312	-179.6	136.6
	427.47	27	0.002339	-183.3	137.0
	422.50	17	0.002367	-187.1	137.3
	417.53	11	0.002395	-191.0	137.7
	412.53	6.6	0.002424	-194.9	138.1
	407.54	4.0	0.002454	-199.0	138.4
	402.56	2.4	0.002484	-203.2	138.8
2	449.91	183	0.002223	-167.3	135.3
	444.92	120	0.002248	-170.8	135.7
	439.94	79	0.002273	-174.3	136.0
	434.93	51	0.002299	-177.8	136.4
	429.94	33	0.002326	-181.5	136.8
	424.95	21	0.002353	-185.1	137.2
	419.97	13	0.002381	-189.1	137.5
	414.98	8.2	0.002410	-193.1	137.9
	409.99	5.0	0.002439	-197.2	138.3
	405.01	3.2	0.002469	-200.9	138.6

[C_6mim][PF_6]

$$\ln(p^*_{sat}/p^o) = -\frac{78728}{R} - \frac{140029}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{81}{R}\left(\frac{T_0}{T} - 1 - \ln\left(\frac{T}{T_0}\right)\right),\ T_0 = 430.7\ \text{K}$$

1	452.44	185	0.002210	-167.2	138.3
	447.44	121	0.002235	-170.7	138.7
	442.43	79	0.002260	-174.3	139.1
	437.44	51	0.002286	-177.8	139.5
	432.45	33	0.002312	-181.6	139.9
	427.46	21	0.002339	-185.4	140.3
	422.46	13	0.002367	-189.1	140.7
	417.48	8.3	0.002395	-193.0	141.1
	412.50	5.0	0.002424	-197.2	141.5
	407.51	3.1	0.002454	-201.2	141.9
2	454.94	229	0.002198	-165.4	138.1
	449.93	151	0.002223	-168.9	138.5
	444.92	99	0.002248	-172.4	138.9
	439.91	64	0.002273	-176.0	139.3
	434.90	41	0.002299	-179.7	139.7
	429.88	26	0.002326	-183.5	140.1
	424.87	16	0.002354	-187.3	140.5
	419.84	10	0.002382	-191.3	140.9
	414.84	229	0.002411	-165.4	141.3
	409.85	151	0.002440	-168.9	141.7

[C_8mim][PF_6]

$$\ln(p^*_{sat}/p^o) = -\frac{80218}{R} - \frac{143395}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{85}{R}\left(\frac{T_0}{T} - 1 - \ln\left(\frac{T}{T_0}\right)\right),\ T_0 = 433.7\ \text{K}$$

1	458.06	182	0.002183	-167.3	142.2
	453.03	118	0.002207	-170.9	142.7
	448.00	77	0.002232	-174.5	143.1
	442.96	50	0.002258	-178.1	143.5
	437.93	32	0.002283	-181.8	143.9
	432.90	20	0.002310	-185.6	144.4
	427.87	13	0.002337	-189.5	144.8
	422.84	8.0	0.002365	-193.3	145.2
	417.82	4.7	0.002393	-197.7	145.6
	412.79	2.8	0.002423	-201.9	146.1
2	455.54	146	0.002195	-169.1	142.4
	450.51	95	0.002220	-172.8	142.9
	445.47	60	0.002245	-176.5	143.3
	440.45	40	0.002270	-180.0	143.7
	435.42	25	0.002297	-183.7	144.1
	430.39	16	0.002323	-187.5	144.6
	425.37	10	0.002351	-191.2	145.0
	420.34	6.3	0.002379	-195.3	145.4
	415.31	3.6	0.002408	-199.9	145.9
	410.29	2.2	0.002437	-203.9	146.3

[C_{10}mim][PF_6]

$$\ln(p^*_{sat}/p^o) = -\frac{81747}{R} - \frac{148515}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{93}{R}\left(\frac{T_0}{T} - 1 - \ln\left(\frac{T}{T_0}\right)\right),\ T_0 = 436.3\ \text{K}$$

1	458.07	115	0.002183	-171.1	146.5
	453.09	74	0.002207	-174.8	147.0
	448.10	48	0.002232	-178.5	147.4
	443.08	30	0.002257	-182.2	147.9
	438.08	19	0.002283	-186.0	148.4
	433.07	12	0.002309	-189.9	148.8
	428.06	7.3	0.002336	-194.0	149.3
	423.05	4.6	0.002364	-197.9	149.8
	418.04	2.6	0.002392	-202.6	150.2
	413.03	1.6	0.002421	-206.6	150.7
2	460.61	140	0.002171	-169.5	146.3
	455.58	90	0.002195	-173.1	146.7
	450.58	59	0.002219	-176.7	147.2
	445.58	38	0.002244	-180.3	147.7
	440.58	24	0.002270	-184.1	148.1
	435.57	15	0.002296	-187.9	148.6
	430.57	9.5	0.002323	-191.9	149.1
	425.56	5.8	0.002350	-196.0	149.5
	420.56	3.5	0.002378	-200.2	150.0
	415.55	2.1	0.002406	-204.4	150.4

Table S3. The Volumetric Properties of $[C_n mim][PF_6]$ Used for $\Delta_l^g C_p^{\circ}{}_m$ Calculations.

IL (M, g·mol^{-1})	$C_P^{\circ}{}_m$(l), J·K^{-1}·mol^{-1}	$10^4 V_m$, m^3·mol^{-1}	$10^4 \alpha_T$, K^{-1}	W, m·s^{-1}	$10^{10} \kappa_T$, Pa^{-1}	C_P-C_V J·K^{-1}·mol^{-1}	$\Delta_l^g C_p^{\circ}{}_m$	Ref
$[C_2mim][PF_6]$ (256.13) 353 K	289	***1.80***	***5.94***		***3.95***	***56.9***	***-74***	1 2
$[C_4mim][PF_6]$ (284.18)	**408.7**	**2.080**	**6.056**	1421				3 4
		2.078	**6.054**	**1442**				5
				1441				6
		2.079		**1442**				7
		2.078	**6.242**	**1443**				8
		2.078	**6.294**	**1443**				9
		2.078	**6.294**	**1443**				10
		2.080		**1444**				11
		2.078	**6.247**	**1442**				12
		2.090						13
		2.077	**5.928**					14
		2.089	**5.905**					15
		2.078						16
		2.082	**6.182**					17
		2.078	**6.203**					18
		2.080	**6.278**					19
		2.077	**6.357**					20
		2.078	**6.178**					21
		2.080	**6.308**					22
		2.079	**6.324**					23
		2.078	**5.943**					24
		2.078						25
		2.081	**6.159**					26
		2.078	**6.225**					27
		2.080	**6.313**					28
		2.092	6.638					29
		2.077						30
		2.078	**6.170**					31
		2.084	**5.497**					32
		2.078	**6.225**					33
		2.078	**5.960**					34
average	**408.7**	***2.080***	***6.145***	***1443***	***4.088***	***57.3***	***-74***	
$[C_6mim][PF_6]$ (312.24)				**1424**				8
				1424				9
				1424				10
	424							35
		2.405	9.510					14
		2.414						36
		2.414	**6.385**					37
		2.414						9
		2.411	**7.073**					38
		2.414	**6.416**					10
		2.414	**6.211**					39
		2.419	**5.890**					40
		2.419	**6.184**					41
		2.414	**5.987**					42
		2.415	**6.165**					1
		2.413	**6.493**					34
average	**424**	***2.414***	***6.303***	***1424***	***4.419***	***64.7***	***-81***	
$[C_8mim][PF_6]$ (340.29)		**2.754**	**6.234**	**1407.8**				8
		2.754	**6.234**	**1408**				9
		2.754	**6.234**	**1408**				10
					4.856			1

				(312.8K)			
	2.748	6.946		**4.880**			38
	2.757	6.073		**4.887**			40
	2.780	5.484					15
	2.751	**6.221**					43
	2.758	5.668		**4.858**			41
	2.771	10.12					14
	2.779	**6.150**					15
	2.751	**6.396**					1
	2.751						44
	2.756						45
	2.746						46
	2.751	**6.477**					34
average	***2.755***	***6.248***	***1408***	***4.681***	***68.5***	***-85***	
$[C_{10}mim][PF_6]$ (368.34)	***3.132***	***6.530***		***5.240***	***76.0***	***-93***	Estimated[a]

[a] the isothermal compressibility was evaluated according to ref [47], molecular volume and thermal expansion were linearly extrapolated according to experimental data from ref [34].

[b] $[C_2mim][PF_6]$ have fusion temperature of 332.8 K and the lowest temperature at which liquid density is available is 353.15 K. Therefore, the evaluated heat capacity difference for $[C_2mim][PF_6]$ corresponds to this temperature (T = 353.15 K).

TABLE S4 Comparison of Molar Enthalpies of Vaporization for $[C_nmim][PF_6]$ Family Derived from QCM Method and Results of Predictive Scheme of Deyko *et al.*

IL	$\Delta_l^g H_m^o$(298 K)[a]	$\Delta_l^g H_m^o$(298 K)[b]
	kJ·mol^{-1}	kJ·mol^{-1}
$[C_2mim][PF_6]$	140.0 ± 2.8	160
$[C_4mim][PF_6]$	146.5 ± 2.6	157
$[C_6mim][PF_6]$	150.8 ± 2.7	161
$[C_8mim][PF_6]$	154.9 ± 2.8	169
$[C_{10}mim][PF_6]$	161.4 ± 2.8	-

[a] This work

[b] Ref 48

Table S5. The Results of the Temperature Dependence of Frequency Shift Velocity *df/dt* of the QCM at different *T* for [C_{10}mim][NTf_2] Determination.

T / K	df/dt / Hz·s^{-1}
T_{QCM} = 303.15 K (Ref 22)	
407.33	0.1307
402.25	0.07788
397.30	0.04669
392.31	0.02762
387.30	0.01598
412.37	0.2083
417.36	0.3315
422.30	0.5207
427.35	0.8153
422.30	0.5307
417.36	0.3324
412.37	0.2055
407.33	0.1277
402.25	0.07758
397.30	0.04606
392.31	0.02759
422.30	0.5258
417.19	0.3301
412.20	0.2048
407.33	0.1264
402.25	0.07660
397.30	0.04660
392.31	0.02759
422.30	0.5249
417.19	0.3298
412.20	0.2042
407.17	0.1259
402.25	0.07705
397.30	0.04643
392.31	0.02740
387.30	0.01579
382.26	0.009400
T_{QCM} = 306.15 K	
402.94	0.08397
397.89	0.04971
392.86	0.02870
387.83	0.01677
382.82	0.009677
377.82	0.005511
372.82	0.003117
T_{QCM} = 323.15 K	
403.06	0.08435
398.09	0.04985
393.08	0.02951
388.05	0.01693
383.14	0.009741
378.07	0.005599
373.13	0.003189
T_{QCM} = 343.15 K	
403.06	0.08159
397.93	0.04954
392.93	0.02882
387.90	0.01649
383.00	0.009563
377.93	0.005480
373.00	0.003175

Table S6. The Value of *K´* Constant Evaluated from the Frequency Change Rates and Vapor Pressures of ILs.

Compound	$10^6 \cdot K'$ / $Pa \cdot s \cdot kg^{1/2} \cdot Hz^{-1} \cdot K^{-1/2} \cdot mol^{-1/2}$	T_{QCM} / K	References
$[C_1C_1im][NTf_2]$	7.363	323.15	[49,50]
$[C_2C_1im][NTf_2]$	11.34	303.15	[51,52]
$[C_3C_1im][NTf_2]$	11.18	303.15	[51,49]
$[C_4C_1im][NTf_2]$	8.886	303.15	[51,53]
$[C_5C_1im][NTf_2]$	7.132	303.15	[51,49]
$[C_6C_1im][NTf_2]$	8.071	303.15	[51,53]
$[C_7C_1im][NTf_2]$	6.817	303.15	[51,49]
$[C_8C_1im][NTf_2]$	7.532	303.15	[51,53]
$[C_{10}C_1im][NTf_2]$	13.90	303.15	[51,53]
$[C_{10}C_1im][NTf_2]$	12.27	306.15	[51], this work
$[C_{10}C_1im][NTf_2]$	11.59	323.15	[51], this work
$[C_{10}C_1im][NTf_2]$	12.72	343.15	[51], this work
$[C_{12}C_1im][NTf_2]$	7.494	303.15	[51,53]
$[C_2Py][NTf_2]$	8.059	303.15	[54,55]
$[C_3Py][NTf_2]$	6.370	303.15	[54,55]
$[C_4Py][NTf_2]$	7.896	303.15	[54,55]
$[C_2C_2im][NTf_2]$	9.020	313.15	[56]
$[C_4C_4im][NTf_2]$	11.24	313.15	[56]
$[C_6C_6im][NTf_2]$	11.80	313.15	[56]
Average	9.5 ± 1.1		

Table S7. The Solution Calorimetry Results.

m / mmol·kg^{-1}	$\Delta_{soln}H$ / kJ·mol^{-1}
$LiPF_6$ (cr)	
0.0185	-21.87
0.0474	-23.55
0.0298	-21.28
mean value	-22.23 ± 1.9
$[C_2mim][PF_6]$ (cr)	
0.00684	46.36
0.00992	45.85
0.00740	45.54
0.01411	45.82
0.00887	46.45
mean value	46.00 ± 0.7

Table S8. G3MP2 Total Energies at 0 K and Enthalpies at 298.15 K (in Hartree) of the Molecules Studied in This Work

Compounds	G3MP2	
	E_0	H_{298}
$[C_2mim][PF_6]$	-1283.874044	-1283.856483
$[C_3mim][PF_6]$	-1323.109917	-1323.090904
$[C_4mim][PF_6]$	-1362.345172	-1362.324749

DLPNO-CCSD(T) ***calculations.***

Geometry optimization of $[C_2mim][PF_6]$ was carried out at B3LYP/def2-TZVP level of theory[57-58] with D3 dispersion correction[59] and Becky-Jonson damping.[60] The same level of theory was used while computing the spectral properties of the molecules. The initial geometry of the close ion pair was taken from the results of quantum chemical study.[61]

Total energies for all reaction participants were obtain from DLPNO-CCSD(T) method.[62] It has to be noted that the total energies have to be extrapolated to complete basis set (CBS),[63] to minimize basis set incompleteness error (BSIE). We used the direct extrapolation, where two single point calculations DLPNO-CCSD(T) with def2-TZVPP and def2-QZVPP basis sets were performed.[58] Subsequently Hartree—Fock and correlation energies were extrapolated to CBS.[63] Thermal correction was calculated at rigid rotator, harmonic oscillator approximation. All computations were carried out by using ORCA 3.0.2 package.[64] Results of DFT calculations are listed in Table S9. Enthalpies of formation were calculated using isodesmic reactions R1-R7. The total energies, ZPVE and thermal corrections, as well as the enthalpies of formation for reaction participants can be found in Table S10.

Table S9. The Computed Enthalpies of Formation for $[C_2mim][PF_6]$ in the ideal Gas Phase, kJ·mol^{-1}.

#	Reaction	$\Delta_f H_m^o(g)$
R1	1-methyl-imidazole + C_2H_5Cl + HF + PF_5 = $[C_2mim][PF_6]$ + HCl	-1916.9
R2	1-methyl-imidazole + C_2H_5Br + HF + PF_5 = $[C_2mim][PF_6]$ + HBr	-1919.4
R3	1-methyl-imidazole + C_2H_4 + HF + PF_5 = $[C_2mim][PF_6]$	-1922.7
R4	10 C_2H_6 + 2 NH_3 + HF + PF_5 = $[C_2mim][PF_6]$ + 14 CH_4	-1907.9
R5	1-methyl-imidazole + C_2F_6 + PH_3 + 2 CH_4 = $[C_2mim][PF_6]$ + C_2H_6	-1923.5
R6	α,α,α-Trifluorotoluene + N_2H_4 + PH_3 + 2 H_2 = = $[C_2mim][PF_6]$ + Benzene + C_2H_4	-1908.8
R7	α,α,α-Trifluorotoluene + 2 NH_3 + PH_3= $[C_2mim][PF_6]$ + Benzene + C_2H_2	-1906.6
Average value		-1915.1
Max absolute deviation from the experimental value		8.9

Table S10. DLPNO-CCSD(T) Calculation of the Enthalpy of Formation in the Ideal Gas State for [C_2mim][PF_6]

Compound	E_{tot} (DLPNO-CCSD(T)/CBS) / Hartree	ZPVE / Hartree	$\Delta_0^{298.15}H^o_m$ / Hartree	$\Delta_f H^o_m$	Ref.
[C_2mim][PF_6]	-1284.215917	0.18937777	0.01692281		
1-methyl-imidazole	-265.1878677	0.09868266	0.0062762	125.7 ± 1.1	[65]
PF_5	-840.0586287	0.01685823	0.00629413	-1593.3 ± 1.3	[66]
C_2H_5Cl	-538.8907179	0.06609793	0.00505754	-107.53	[66]
C_2H_5Br	-2651.802376	0.06555812	0.00518868	-61.92	[66]
HCl	-460.3812509	0.00668729	0.00330467	-92.30 ± 0.04	[66]
HBr	-2573.289607	0.00596257	0.0033047	-36.28 ± 0.38	[66]
HF	-100.3940024	0.0092883	0.00330466	-272.55	[66]
C_2H_4	-78.47522598	0.05096598	0.00397964	52.47 ± 0.33	[66]
CH_4	-40.45888678	0.04452669	0.00381313	-74.81 ± 0.33	[66]
C_2H_6	-79.71365038	0.07434774	0.00448048	-84.73 ± 0.50	[66]
NH_3	-56.50552157	0.03414853	0.00381525	-46.19 ± 0.29	[66]
PH_3	-342.7196479	0.02384987	0.00385363	5.44 ± 1.67	[66]
N_2H_4	-111.7587839	0.05323249	0.00418121	95.27 ± 0.42	[66]
C_2F_6	-674.8392266	0.02903141	0.00763643	-1344 ± 5	[66]
C_6H_6	-231.9085784	0.10005518	0.00535819	82.9 ± 0.9	[66]
C_2H_2	-77.22172974	0.02539188	0.00363424	226.73 ± 0.8	[66]
α,α,α-Trifluorotoluene	-568.7381751	0.10470475	0.00797571	-587.7 ± 1.2	[67-68]
H_2	-1.174678204	0.01007058	0.00330466	0	

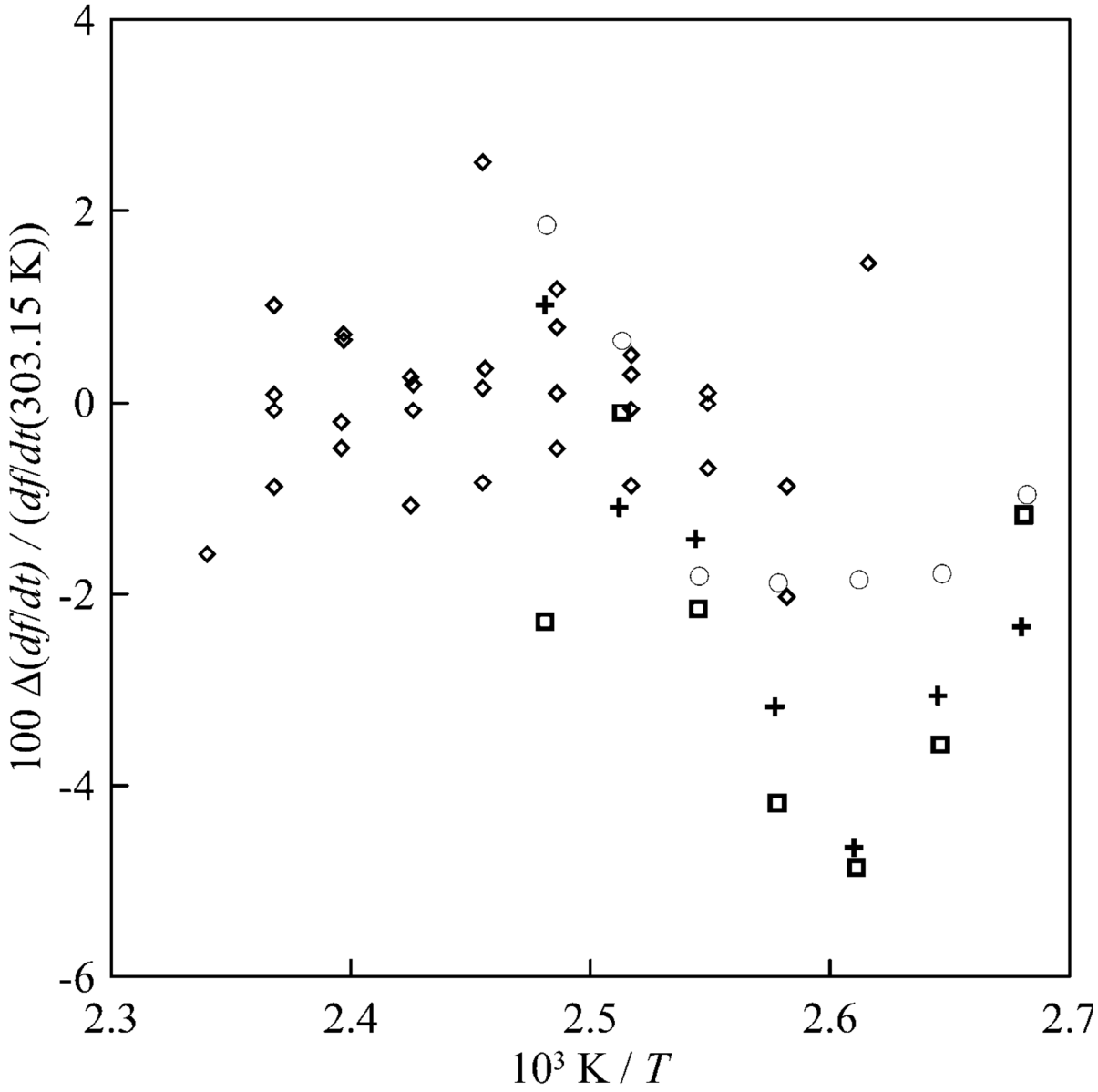

Figure S1. Temperature dependence of deviation of the experimental frequency change rates at different temperatures of the QCM sensor for $[C_{10}mim][NTf_2]$:

◇ - results at $T = 303.15$ K;[53] ○ - results at $T = 306.15$ K; + results at $T = 323.15$ K; ◘ results at $T = 343.15$ K.

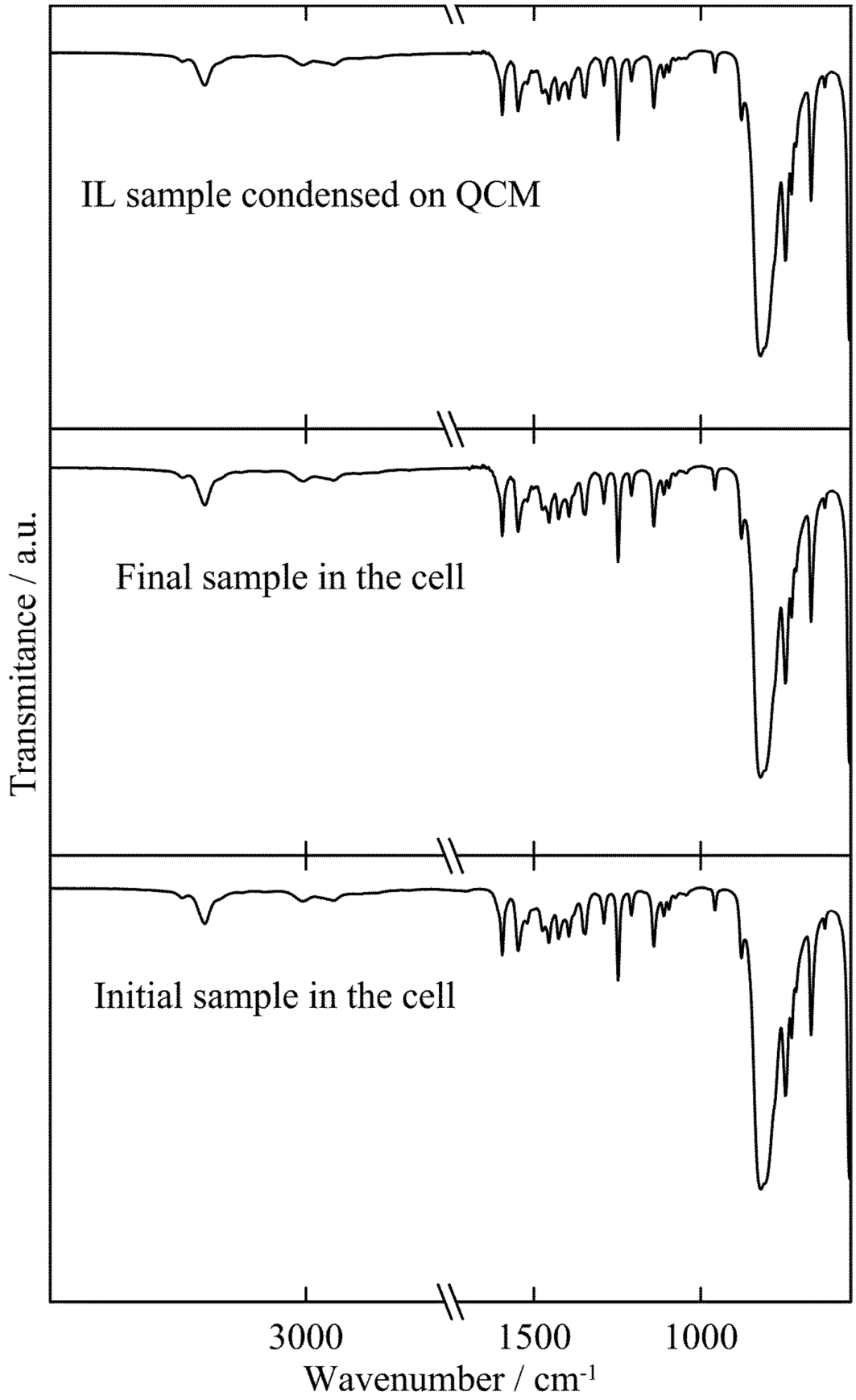

Figure S2. The IR spectra for $[C_2mim][PF_6]$ during enthalpy of vaporization investigation with QCM method

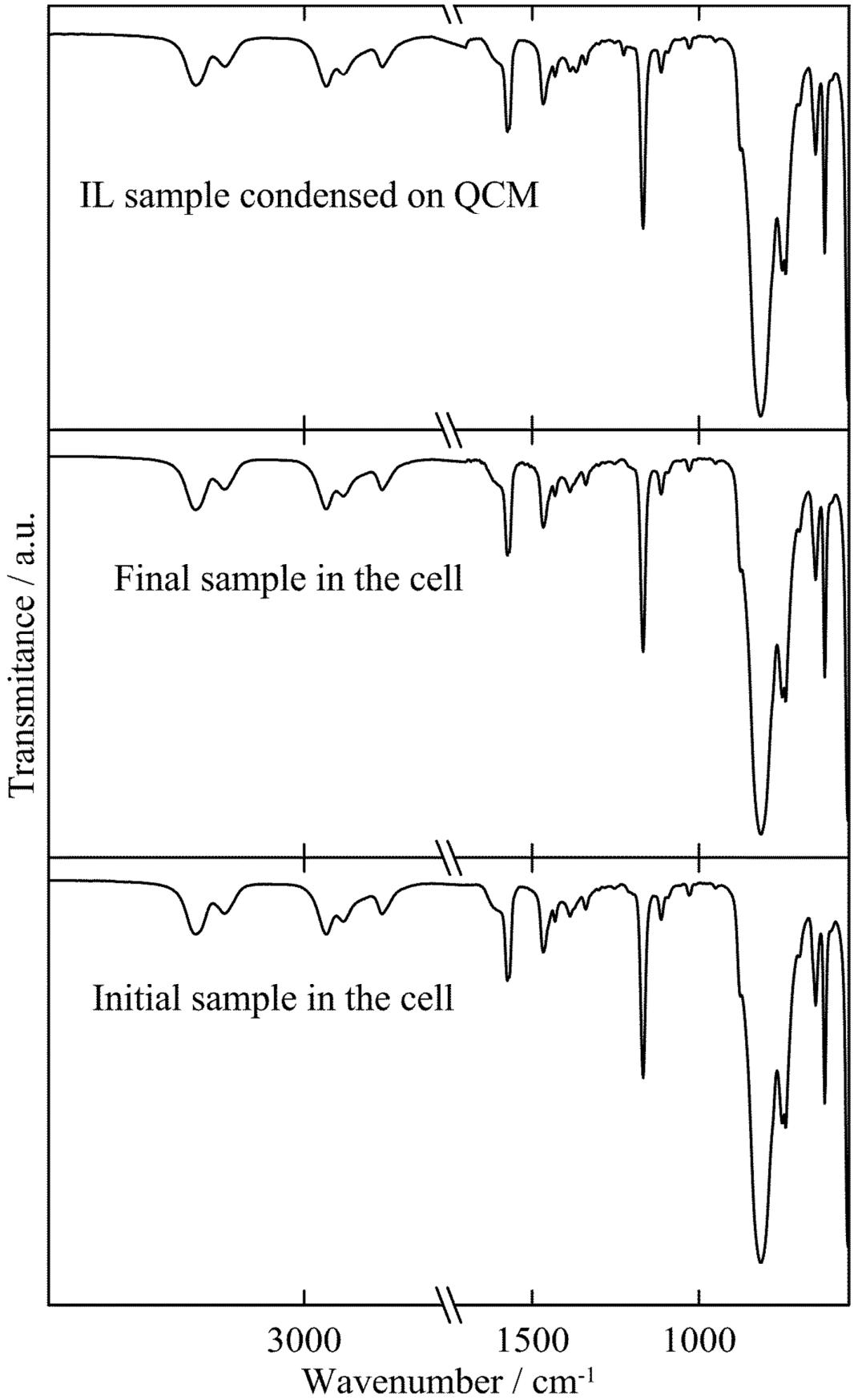

Figure S3. The IR spectra for $[C_4mim][PF_6]$ during enthalpy of vaporization investigation with QCM method

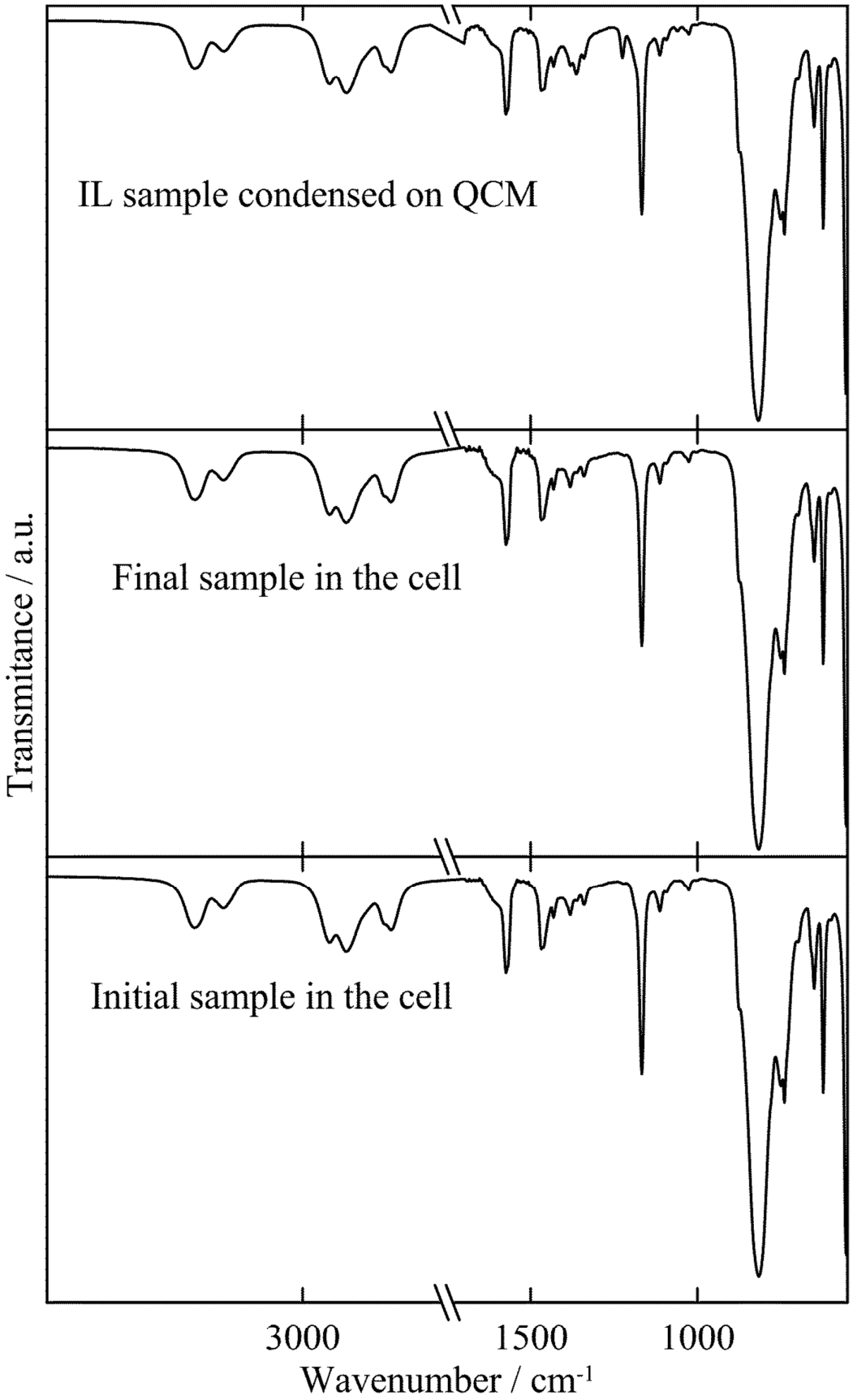

Figure S4. The IR spectra for $[C_6mim][PF_6]$ during enthalpy of vaporization investigation with QCM method

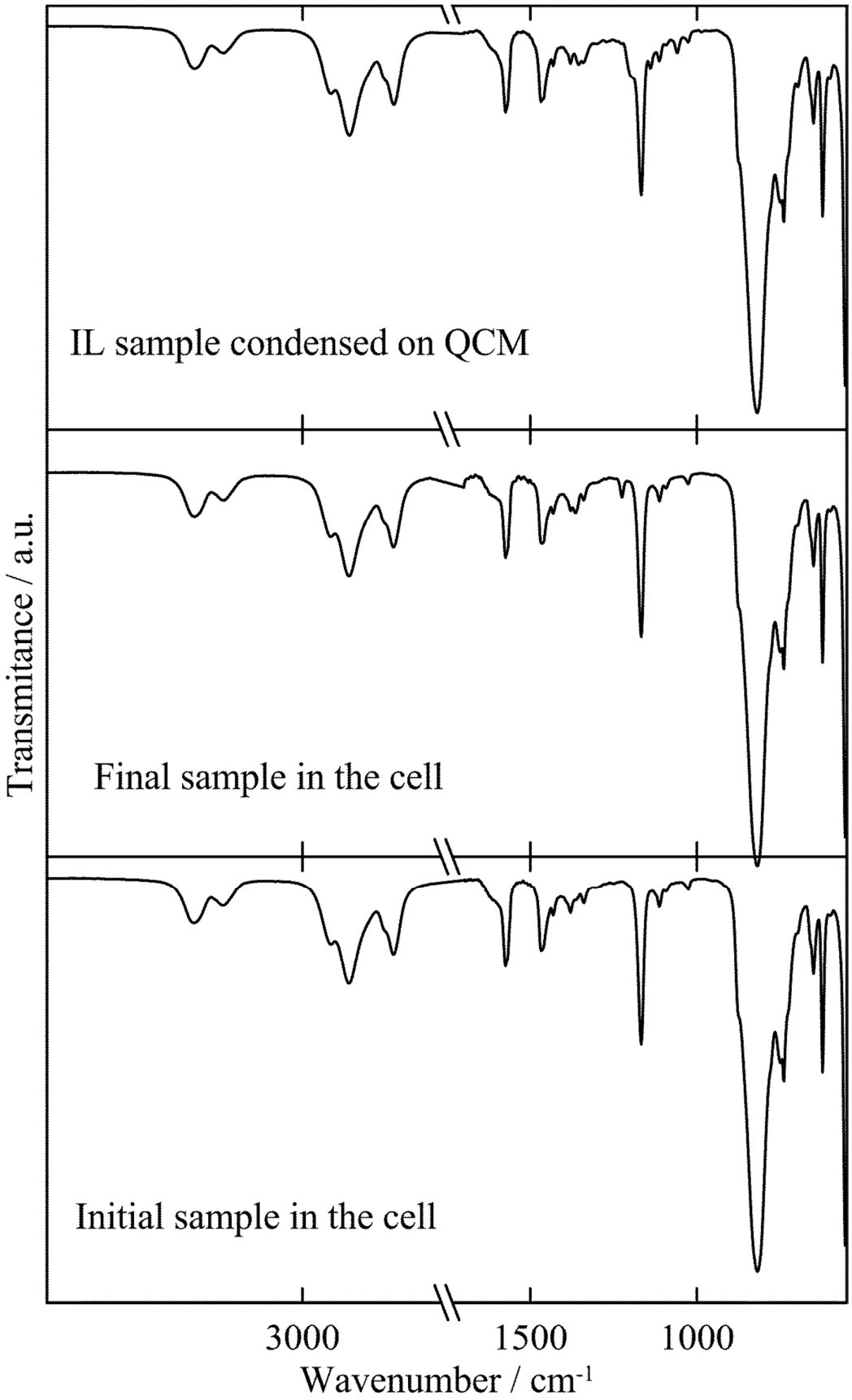

Figure S5. The IR spectra for $[C_8mim][PF_6]$ during enthalpy of vaporization investigation with QCM method

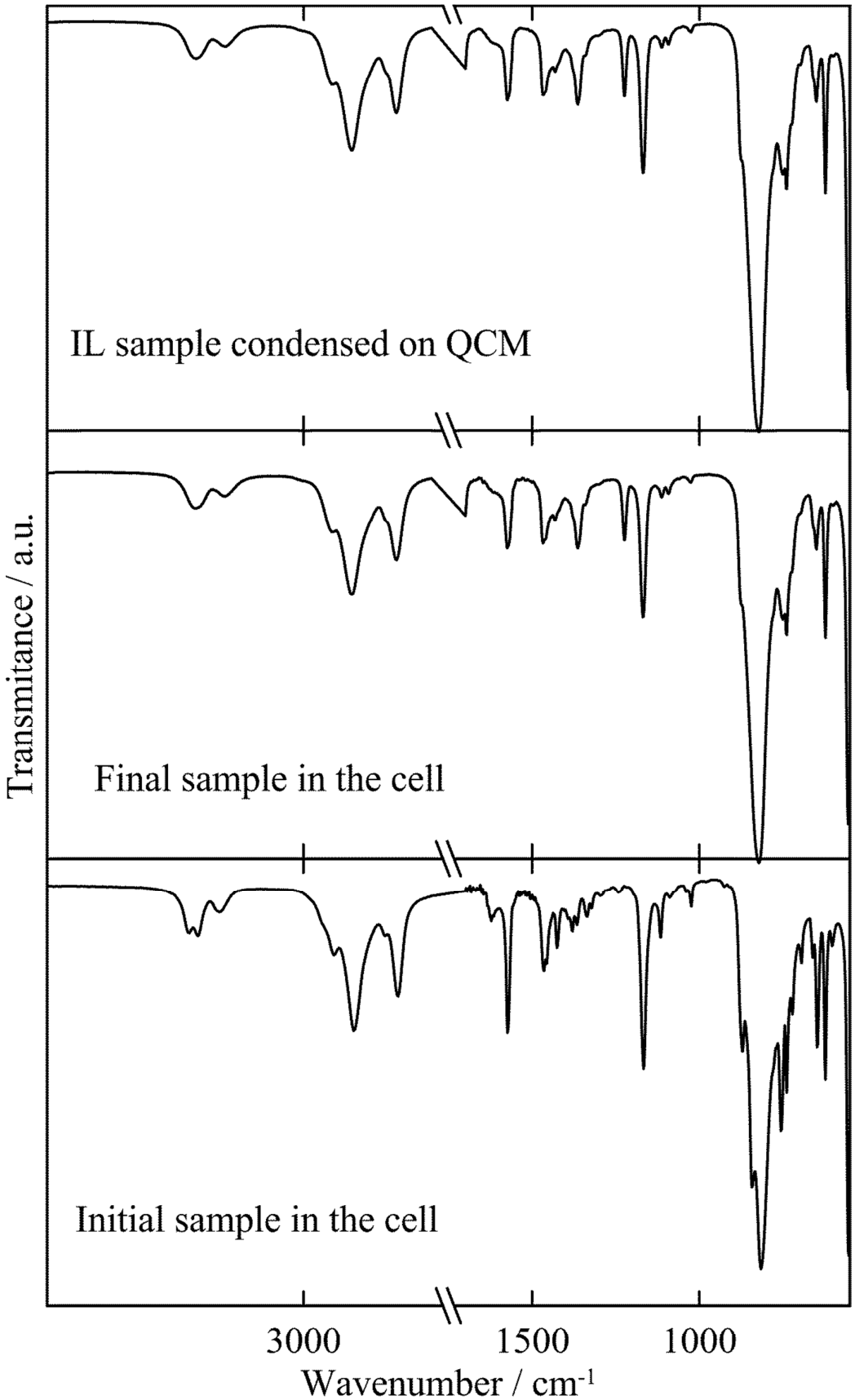

Figure S6. The IR spectra for $[C_{10}mim][PF_6]$ during enthalpy of vaporization investigation with QCM –method

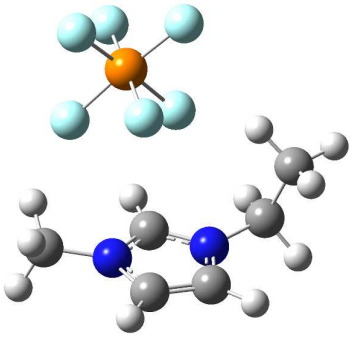

Figure S7. Conformation of [C_2mim][PF_6] with minimal energy.

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