# Raman and Infrared Spectra and ab Initio Calculations of $C_{2-4}MIM$ Imidazolium Hexafluorophosphate Ionic Liquids

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The Raman and infrared spectra of a series of 1-alkyl-3-methylimidazolium hexafluorophosphate ( $[C_{2-4}MIM]PF_6$ ) ionic liquids have been recorded and analyzed using density functional theory (DFT) and RHF methods at the 6-311+G(2d,p) computational level. The DFT calculations reproduce the vibrational spectra of 1-ethyl-3-methyl imidazolium hexafluorophosphate [EMIM]PF<sub>6</sub>, 1-propyl-3-methyl imidazolium hexafluorophosphate [PMIM]PF<sub>6</sub>, and 1-butyl-3-methyl imidazolium hexafluorophosphate [BMIM]PF<sub>6</sub> using correction factors of 0.964-0.967 with correlation coefficients  $R^2$  of 0.999. The vibrational spectra calculated at the RHF/6-311+G-(2d,p) level require a correction factor of 0.89 and a correlation coefficient  $R^2$  of 0.999 using the fully optimized structures. The 1-alkyl-3-methyl hexafluorophosphate ionic liquids have common Raman C-H stretching frequencies that may serve as possible probes in studies of ionic liquid interactions. The DFT (B3LYP) and RHF gas-phase molecular structures of the [C<sub>2-4</sub>MIM]PF<sub>6</sub> ion pairs indicate hydrogen bonding interactions between the fluorine atoms of the PF<sub>6</sub><sup>-</sup> anion and the C2 hydrogen on the imidazolium ring. Additional interactions are observed between PF<sub>6</sub><sup>-</sup> and the H atoms on the adjacent alkyl side chains.

#### Introduction

Over the past several years, room temperature ionic liquids have generated considerable excitement as they consist entirely of ions and possess minimal vapor pressure. 1-5 Consequently, ionic liquids can be recycled, thus making synthetic processes less expensive and potentially more efficient and environmentally friendly. Considerable progress has been made using ionic liquids as solvents in the areas of monophasic and biphasic catalysis (homogeneous and heterogeneous). 2,3,5 The ionic liquids investigated herein provide real practical advantages over earlier molten salt systems because of their relative insensitivity to air and water.<sup>2-5</sup> At present, little is known about the fundamental physical chemistry of these solvent systems. In this study, information is provided that may assist in an understanding at molecular level of the general interactions that exist in ionic liquids. Investigators have previously reported a limited albeit rapidly increasing number of reports covering X-ray crystallography,<sup>6–10</sup> theory,<sup>11–16</sup> viscosity,<sup>17–22</sup> NMR relaxation,<sup>23–30</sup> NMR diffusion,<sup>23–25</sup> NMR H,H-NOESY,<sup>31</sup> conductivity, 17,32 phase studies, 33 and gas solubilities in ionic liquids. 34

In the present study we report the gas-phase structures and theoretical vibrational spectra of three  $PF_6^-$ -containing ionic liquids, in which the imidazolium side chain at the C3 position varies from butyl ([BMIM]PF<sub>6</sub>) to propyl ([PMIM]PF<sub>6</sub>) to ethyl ([EMIM]PF<sub>6</sub>). The infrared (IR) and Raman spectra of each ionic liquid have been measured, and the results were correlated with those obtained from the theoretical calculations.

## Methods

**Preparation and Measurements.** The ionic liquids were prepared as described previously.<sup>8,35</sup> Only [BMIM]PF<sub>6</sub> is a liquid

at 30 °C. [EMIM]PF<sub>6</sub> and [PMIM]PF<sub>6</sub> melt at 68–70 and 37–39 °C, respectively. The ionic liquids were prepared in an inert atmosphere, and water content was checked by an indirect method. The ionic liquids were dissolved in D<sub>2</sub>O, and the previously determined HDO peak was monitored for possible increase. No apparent increase in the HDO peak (4.8 ppm) was observed, allowing for dilution of the D<sub>2</sub>O by the ionic liquid. No halide analysis was determined. Other impurities were less than detection limits by <sup>1</sup>H and <sup>13</sup>C NMR at 400 MHz. All samples were placed in sealed tubes for Raman analysis immediately after preparation.

The vibrational spectra were recorded with a Nicolet Nexus 870 Raman and a Nicolet model 360 FTIR spectrometer operating at 2 cm<sup>-1</sup> resolution. The vibrational spectra of [EMIM]PF<sub>6</sub> and [PMIM]PF<sub>6</sub> were obtained at temperatures several degrees above their melting points.

**Frequency Correlations.** The correlations between calculated and experimental spectra were based primarily on peak intensities and secondarily on peak frequencies (cm<sup>-1</sup>) for both Raman and infrared. In cases where adjacent experimental infrared frequencies overlapped such that assignment was questionable, both frequencies (two separate points) were included in the frequency correlation diagram.

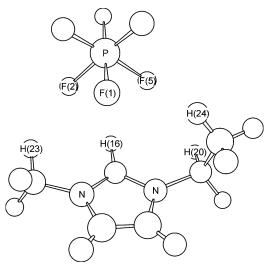
Computational Methods. The ab initio and B3LYP calculations using a 6-311+G(2d,p) basis set were obtained with GAUSSIAN 98.<sup>36</sup> The vibrational analyses on all structures revealed a lack of imaginary frequencies, ensuring the presence of a true minimum. The eigenvectors for each normal mode were displayed on the computer, and the normal modes assigned to specific group vibrations.

**Molecular Structures.** The molecular structures of [BMIM]-PF<sub>6</sub>, [PMIM]PF<sub>6</sub>, and [EMIM]PF<sub>6</sub> determined at the B3LYP/6-311+G(2d,p) level of computation are shown in Figures 1–3. Similar structures were obtained using the RHF/6-311+G(2d,p) method of computation. In ionic liquids, intermolecular inter-

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**Figure 1.** Molecular structure of [EMIM]PF<sub>6</sub> (B3LYP/6311+G(2d,p)). Hydrogen bonds include F2-H23, 2.256 Å; F2-H16, 2.078 Å; F1-H16, 2.524 Å; F5-H16, 2.146 Å; F5-H20, 2.545 Å; F5-H24, 2.546 Å

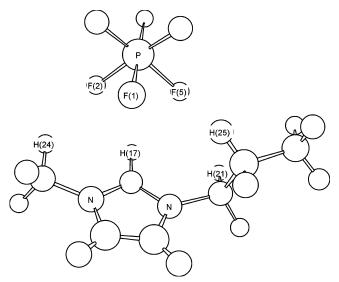
actions include dispersion forces, and DFT theory lacks this term. Theory is usually quite successful in predicting accurate molecular structure and vibrational spectra.

#### **Results and Discussion**

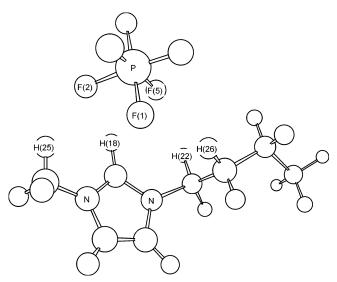
Gas-Phase Structures. The B3LYP structure of [EMIM]PF<sub>6</sub> in Figure 1 indicates nonbonded interactions between three F atoms of PF<sub>6</sub><sup>-</sup> and the imidazolium C2 hydrogen. This is consistent with a recent molecular dynamics (MD) simulation study of [BMIM]PF<sub>6</sub> that supports a strong interaction between the C2 hydrogen and the fluorine atoms in PF<sub>6</sub>.<sup>15</sup> In addition, one observes H  $\cdots$  F distances between the F atoms of  $PF_6$  and the hydrogens on both alkyl side chains that are shorter than the van der Waals H···F distance of 2.67 Å.43 There are minimal differences between the RHF and B3LYP structures using the 6-311+G(2d,p) basis set. The distances for nonbonded interactions that are observed for the B3LYP [EMIM]PF6 structure (Figure 1) are slightly shorter on the average than those from the RHF structure. The solid-state structure of [EMIM]PF<sub>6</sub> contains C2-H···F distances of the order of van der Waals distances between three F atoms of  $PF_6^-$  and the imidazolium C2 hydrogen (2.559, 2.678 and 2.697 Å).8 It is likely that the liquid-state structure of [EMIM]PF<sub>6</sub> contains C2-H···F distances that lie between the gas- and solid-phase distances.

Similar results are obtained for the B3LYP/6-311+G(2d,p) structure of [PMIM]PF<sub>6</sub> shown in Figure 2. The lengthening of the alkyl side chain from two to three carbon atoms has little effect on the interactions between  $PF_6^-$  and the H atoms on the alkyl side chains (Figure 2). As is the case with [EMIM]BF<sub>4</sub>, the hydrogen bonds in the B3LYP/6-311+G(2d,p) structure (Figure 2) are somewhat shorter than those calculated for the RHF/6-311+G(2d,p) structure (not shown).

Finally, the lengthening of the alkyl side chain to a butyl group to form [BMIM]PF<sub>6</sub> produces results similar to those obtained for [EMIM]PF<sub>6</sub> and [PMIM]PF<sub>6</sub> with the exception of the B3LYP/6-311+G(2d,p) structure of [BMIM]PF<sub>6</sub>, in which an additional hydrogen bond is formed between the methylene group containing H26 (Figure 3) and PF<sub>6</sub><sup>-</sup>. All three ion pair gas-phase structures contain hydrogen bonds between each of three F atoms and the C2 hydrogen on the imidazolium ring. The methyl group provides an additional H···F hydrogen bond,



**Figure 2.** Molecular structure of [PMIM]PF<sub>6</sub> (B3LYP/6311+G(2d,p)). Hydrogen bonds include F2-H24, 2.266 Å; F2-H17, 2.090 Å; F1-H17, 2.517 Å; F5-H17, 2.143 Å; F5-H21, 2.519 Å; F1-H25, 2.663 Å; F5-H25, 2.586 Å.



**Figure 3.** Molecular structure of [BMIM]PF<sub>6</sub> (B3LYP/6311+G(2d,p)). Hydrogen bonds include F2-H25, 2.286 Å; F2-H18, 2.089 Å; F1-H18, 2.509 Å; F5-H18, 2.121 Å; F5-H22, 2.450 Å, F1-H26, 2.493 Å; F5-H26, 2.700 Å.

as do single H atoms on each of the two CH<sub>2</sub> groups closest to the imidazolium ring.

Vibrational Spectra and Spectral Assignments. Tables 1–3 contain the theoretical and experimental vibrations for the three ion pairs, [BMIM]PF<sub>6</sub>, [PMIM]PF<sub>6</sub>, and [EMIM]PF<sub>6</sub>. Example Raman spectra are shown in Figures 4 and 5 for [BMIM]PF<sub>6</sub>. Similar Raman spectra (not shown) were obtained for [PMIM]-PF<sub>6</sub> and [EMIM]PF<sub>6</sub>.

[BMIM]PF<sub>6</sub>. Table 3 contains the calculated and experimental data for the [BMIM]PF<sub>6</sub> ion pair. The strongest region of the Raman spectrum of [BMIM]PF<sub>6</sub> is the CH stretching region between 2700 and 3200 cm<sup>-1</sup> as shown in Figures 4 and 5. There are at least four discernible strong vibrations in the 2878–2970 cm<sup>-1</sup> region of the [BMIM]PF<sub>6</sub> Raman spectrum. These Raman vibrations related to calculated vibrations in the 3011–3082 cm<sup>-1</sup> region and are assigned to theoretical B3LYP methyl and butyl CH stretching vibrations. The weak Raman bands observed at 3116 and 3179 cm<sup>-1</sup> are assigned to B3LYP vibrations associated with methyl CH, and ring H–C–

TABLE 1: B3LYP/(6-311+G(2d,p)) Vibrational Assignments  $^a$  (cm  $^{-1})$  of [BMIM]PF  $_6$ 

$ u_{\mathrm{calc}} $	assignmen	IR, Raman	calc i.r., I <sub>rel</sub>	i.r. $\nu_{\rm exp}$ , $I_{\rm rel}$	Raman $\nu_{\rm exp}(I_{\rm rel})$
18	Cat-An tors	IR	0.005	схр, -тег	
28	Cat-An tors	IR IR	0.003		
38	Cat-An bend	IR,R(w)dp	0.007		
55	Cat-An bend	IR	< 0.001		
67	Cat-An bend	IR	0.005		
73	Cat-An bend	IR	0.007		
82	Cat-An bend	IR,R(w)p	0.01		
96	Cat-An bend	IR,R(w)p	0.017		
119	CH <sub>3</sub> (N) twist	IR	< 0.001		
132	CCCC bend	IR	0.011		
148	CCCC bend	IR,R(w)p	0.034		
210	terminal CH <sub>3</sub> twist	IR	0.001		
237	CH <sub>3</sub> (N) bend, terminal CH <sub>3</sub> twist	IR,R(w)p	0.004		
279	CH <sub>3</sub> (N) bend, CCCC bend	IR	0.004		
287	PF <sub>6</sub> scissors	IR	< 0.001		
294	PF <sub>6</sub> scissors	IR ID	< 0.001		
298	PF <sub>6</sub> scissors	IR	< 0.001		
299	CH <sub>3</sub> (N) bend, CH <sub>2</sub> (N) bend, CCCC bend	IR	< 0.001		
357	CH <sub>3</sub> (N) bend, CH <sub>2</sub> (N) bend, CCCC bend	IR,R(w)p	0.003		
412	CH <sub>3</sub> (N) bend, CH <sub>2</sub> (N) bend, CCCC bend	IR	0.005 0.004		
440 444	CH <sub>3</sub> (N) bend, CH <sub>2</sub> (N) bend, CCCC bend	IR,R(w)p	< 0.004		
444	PF <sub>6</sub> scissors PF <sub>6</sub> scissors	IR,R(w)dp	0.001		
452	PF <sub>6</sub> scissors	IR,R(w)dp IR,R(w)dp	0.003		470(0.07)
516	PF <sub>6</sub> sym str	IR,R(w)dp IR,R(w)dp	0.014		470(0.07)
526	PF <sub>6</sub> asym str	IR,R(w)up IR	0.004		470(0.07)
533	PF <sub>6</sub> asym bend	IR IR	0.004		
535	PF <sub>6</sub> asym str	IR IR	0.101	558(0.54)	
535	PF <sub>6</sub> sym str, asym bend	IR IR	0.091	330(0.34)	
633	CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str, ring op bend	IR,R(w)p	0.001		600(0.05)
648	CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str, ring op bend	IR,R(w)p IR,R(w)p	0.047	624(0.13)	622(0.04)
677	CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str, ring op bend	IR,R(w)p	0.18	651(0.05)	022(0.0.1)
684	$PF_6$ sym str	IR,R(w)p	0.105	001(0.00)	
730	CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str, CCCC bend	IR,R(w)p	0.015		
732	ring HCCH sym bend, NC(H)N bend	IR,R(w)p	0.08		741(0.33)
766	CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str, CCCC str	IR,R(w)p	0.043	752(0.09)	, ,
801	CCCCH bend	IR,R(w)p	0.034		
836	ring HCCH asym bend	IR	0.195	839(0.86)	
837	PF <sub>6</sub> asym str, ring HCCH asym bend	IR	0.787	842(1.00)	
846	PF <sub>6</sub> asym str, NC(H)N bend, CCCCH bend	IR	0.944	847(1.00)	
858	PF <sub>6</sub> asym str	IR	1		
881	CCCC str	IR,R(w)p	0.006		
952	NC(H)N CH bend	IR	0.019		
961	CCCC str	IR,R(w)dp	< 0.001		
978	CCCC str	IR,R(w)p	0.004		1005(0.04)
1041	ring ip sym str	IR,R(w)p	0.004	1040(0.00)	1025(0.04)
1044	ring ip asym str	IR,R(w)p	0.026	1040(0.02)	
1072	CCCC str	IR,R(w)dp	0.002		
1111	ring HCCH sym bend, ring ip asym str	IR,R(w)p	0.03		
1122 1125	ring HCCH sym bend, ring ip asym str CCCC str	IR,R(w)p	0.006 0.006		
1123	CCCC str, ring ip asym str	IR,R(w)p	0.000		
1162	CH <sub>3</sub> (N) bend	IR,R(w)p IR,R(w)p	0.026	1114(0.03)	
1179	$CH_3(N)$ bend $CH_3(N)$ str, $CH_2(N)$ str, ring ip asym str	IR,R(w)p IR,R(w)p	0.312	1170(0.24)	
1230	CCCC str, ring ip asym str	IR,R(w)p IR,R(w)p	0.008	1170(0.24)	
1296	CCCC str, ring ip asym str	IR,R(w)p IR,R(w)p	< 0.001		
1308	CCCC str, ring ip asym str	IR,R(w)p IR,R(w)p	0.006		
1331	CCCC str, ring ip asym str	IR,R(w)p IR,R(w)p	0.005		
1347	CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str, ring ip sym str	IR,R(m)p	0.025	1340(0.06)	1340(0.05)
1361	CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str, ring ip sym str, CCCC str	IR,R(w)p	0.003	13 10(0.00)	13 10(0.03)
1384	CCCC str	IR,R(w)p	0.017	1387(0.07)	1386(0.04)
1402	CCCC str, CH <sub>2</sub> (N) str, ring ip asym str	IR,R(w)p	< 0.001	()	()
1414	CCCC str, CH <sub>2</sub> (N) str, ring ip asym str	IR,R(w)p	0.022		
1423	CCCC str	IR,R(w)p	0.003		
1451	ring ip asym str, CH <sub>3</sub> (N) str	IR,R(m)p	0.011		1420(0.13)
1468	ring ip asym str, CH <sub>3</sub> (N) str	IR,R(w)p	0.026	1432(0.09)	1432(0.06)
1492	butyl HCH sym bend	IR,R(m)p	0.018		1456(0.06)
1495	butyl HCH sym bend	IR,R(m)dp	0.008		
1503	CH <sub>3</sub> (N) HCH bend	IR,R(w)p	0.035	1468(0.08)	
1506	butyl HCH sym bend	IR,R(w)p	< 0.001		
1509	butyl HCH sym bend	IR	0.02		
1511	butyl HCH sym bend	IR,R(w)p	0.031		
1512	CH <sub>3</sub> (N) HCH bend, ring ip asym str	IR,R(m)dp	0.026		4.5.000 ***
1598	CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str, ring ip asym str	IR,R(w)p	0.143	1576(0.13)	1568(0.06)

TABLE 1 (Continued)

$ u_{ m calc}$	assigment	IR, Raman	calc i.r., $I_{\rm rel}$	i.r. $\nu_{\mathrm{exp}}, I_{\mathrm{rel}}$	Raman $\nu_{\rm exp}(I_{\rm rel})$
1606	CH <sub>3</sub> (N) str, ring ip asym str	IR,R(w)p	0.049		
3011	CH <sub>2</sub> C(N) HCH sym str	IR,R(s)p	0.055	2878(0.05)	2878(0.61)
3018	terminal CH <sub>3</sub> HCH sym str	IR,R(vs)p	0.057	2878(0.05)	2878(0.61)
3035	propyl HCH sym str	IR,R(s)p	0.062		
3055	Et HCH asym str	IR,R(s)p	0.001		2917(0.69)
3060	CH <sub>3</sub> (N) HCH sym str	IR,R(vs)p	0.07	2939(0.07)	2942(0.76)
3070	CH <sub>2</sub> (N) HCH sym str	IR,R(vs)p	0.05		
3082	propyl HCH asym str	IR,R(m)p	0.154	2966(0.09)	2970(1.00)
3088	terminal CH <sub>3</sub> HCH asym str	IR,R(vs)p	0.097		
3101	CH <sub>2</sub> C(N) HCH asym str	IR,R(m)p	0.002		
3136	CH <sub>2</sub> CH <sub>2</sub> (N) HCH asym str	IR,R(m)p	0.006		
3136	CH <sub>3</sub> (N) HCH asym str	IR,R(s)dp	0.013		
3160	CH <sub>3</sub> (N) HCH asym str	IR,R(m)dp	0.021		3116(0.11)
3270	NC(H)N CH str	IR,R(m)p	0.458	3125(0.05)	
3277	ring HCCH asym str	IR,R(m)p	0.018	3172(0.10)	
3294	ring HCCH sym str, NC(H)N CH str	IR,R(vs)p	0.001		3179(0.14)

<sup>&</sup>lt;sup>a</sup> Note that ip and op are in-plane and out-of-plane and that Cat-An are vibrations in which the imidazolium cation oscillates around the anion.

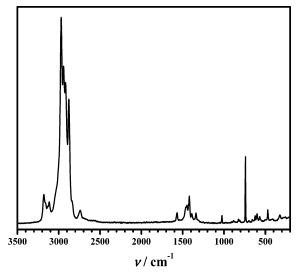
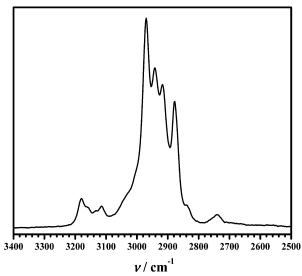
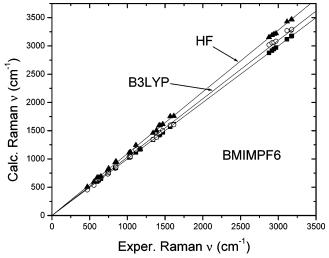


Figure 4. Raman spectrum of [BMIM]PF<sub>6</sub> at 2 cm<sup>-1</sup> resolution



**Figure 5.** Raman spectrum (C-H stretch region) of [BMIM]PF $_6$  at 2 cm $^{-1}$  resolution.

C-H and N-(C-H)-N C-H stretches. Unfortunately the observed Raman spectrum is very weak in this region, making peak identification and, correspondingly, peak assignment difficult at best.



**Figure 6.** Correlation diagram for the vibrational spectrum of [BMIM]-PF<sub>6</sub>; experimental versus calculated IR and Raman transition frequencies. Scaling factors = 0.964 (B3LYP) and 0.914 (RHF) with corelation coefficients = 0.999: ( $\blacktriangle$ ) RHF calculated values, ( $\bigcirc$ ) B3LYP calculated values, ( $\blacksquare$ ) theoretical correlation of 1.00.

The only other strong Raman band is located at 741 cm<sup>-1</sup>. This band is assigned (B3LYP) to a ring H-C-C-H symmetric bend. There is also an easily observable band at 1421 cm<sup>-1</sup> that is assigned to a ring in-plane asymmetric stretch.

Figure 6 contains a plot of the combined experimental vs theoretical (6-311+G(2d,p)) vibrational frequencies using the B3LYP and RHF methods for [BMIM]PF<sub>6</sub> and a baseline whose slope is 1.00. The [BMIM]PF<sub>6</sub> ion pair requires a scale factor of only 0.964 (DFT) to reproduce the experimental frequencies from the calculated values. As shown in Figure 6, the RHF method overestimates the vibrational frequencies to a greater degree than the B3LYP method and requires a scale factor of 0.914 to reproduce the experimental frequencies. Similar theoretical results have been obtained for a wide range of molecules.<sup>42</sup> It should be pointed out that our experimental IR vibrational frequencies are similar to those obtained for [BMIM]-PF<sub>6</sub> in the gas phase.<sup>44</sup>

**[PMIM]PF<sub>6</sub>.** Table 2 contains the theoretical and experimental vibrational frequencies for the [PMIM]PF<sub>6</sub> ion pair. The Raman spectrum of [PMIM]PF<sub>6</sub> is contained in Supporting Information. The intense Raman bands observed between 2883 and 2970 cm<sup>-1</sup> are assigned to DFT calculated vibrations between 3024 and 3106 cm<sup>-1</sup>. The broad (and weak) Raman bands at 3117 and 3178 are assigned to theoretical (B3LYP)

TABLE 2: B3LYP/(6-311+G(2d,p)) Vibrational Assignments  $^a$  (cm $^{-1}$ ) of [PMIM]PF $_6$ 

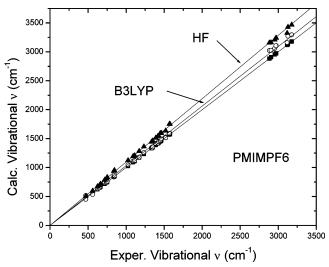
IABLE 2:	B3L 1 P/(0-311+G(20,p)) Vibrational Assignmen				
$ u_{\mathrm{calc}} $	assigment	IR, Raman	calc i.r., I <sub>rel</sub>	i.r. $\nu_{\rm exp}$ , $I_{\rm rel}$	Raman $\nu_{\rm exp}(I_{\rm rel})$
10	Cat-An tors	IR	0.003		
34	Cat-An bend	IR,R(w)dp	0.007		
44 62	Cat-An bend	IR IR	0.004 0.004		
70	Cat-An bend Cat-An bend, CH <sub>2</sub> (N) bend	IR,R(w)dp	0.004		
88	Cat-An bend, $CH_2(N)$ bend	IR,R(w)up IR	0.004		
95	Cat-An bend, CH <sub>2</sub> (N) bend	IR	0.014		
103	Cat-An bend, CH <sub>2</sub> (N) bend, CH <sub>3</sub> (N) twist	IR	0.012		
112	$CH_3(N)$ twist	IR	0.004		
150	Cat-An tors	IR,R(w)p	0.039		
232	terminal CH <sub>3</sub> twist, CH <sub>3</sub> (N) bend	IR,R(w)dp	0.004		
239	terminal CH <sub>3</sub> twist, CH <sub>3</sub> (N) bend	IR	< 0.001		
286	PF <sub>6</sub> scissors, CH <sub>2</sub> (N) bend, CH <sub>3</sub> (N) bend	IR	< 0.001		
289	PF <sub>6</sub> scissors, CH <sub>2</sub> (N) bend, CH <sub>3</sub> (N) bend	IR	0.004		
295	PF <sub>6</sub> scissors, CCC bend	IR	< 0.001		
298	PF <sub>6</sub> scissors, CH <sub>3</sub> (N) bend	IR ID	< 0.001		
304 372	CCC bend	IR ID D(vv)	< 0.001		
424	$CH_2(N)$ bend, $CH_3(N)$ bend $CH_2(N)$ bend, $CH_3(N)$ bend	IR,R(w)p IR,R(w)p	0.005 0.006		
445	PF <sub>6</sub> scissors	IR,R(w)dp	< 0.001		
447	PF <sub>6</sub> scissors	IR,R(w)dp	0.001		
451	PF <sub>6</sub> scissors	IR,R(w)dp	0.002		470(0.08)
516	FPF asym str	IR,R(w)dp	0.012		470(0.08)
526	FPF asym str	IR	0.005		()
533	FPF sym bend	IR	0.098		
535	FPF sym bend	IR	0.101	560(0.36)	
536	FPF sym str, FPF sym bend	IR	0.088		
632	ring op bend, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(w)p	0.001	623(0.35)	624(0.05)
649	ring op bend, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(w)p	0.057		
677	ring op bend, CH <sub>3</sub> (N) str	IR,R(w)p	0.194	649(0.21)	
684	FPF sym str	IR,R(w)p	0.09		
732	ring HCCH sym bend	IR	0.082	741(0.20)	741(0.41)
742	ring HCCH asym bend, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(w)dp	0.028	741(0.29)	741(0.41)
760	propyl HCH bend,	IR ID	0.035	751(0.34)	
836	FPF asym str, ring HCCH asym bend	IR ID D(vv)	0.518		
837 846	FPF asym str, ring HCCH asym bend	IR,R(w)p IR	0.459 0.909	840(0.51)	
858	FPF asym str, NC(H)N CH bend FPF asym str	IR IR	0.909	840(0.51)	
894	propyl HCH bend, CCC bend	IR IR	0.01	040(0.51)	
905	CCC str	IR,R(w)p	0.015	884(1.00)	
944	NC(H)N CH bend	IR,R(w)p IR	0.013	004(1.00)	
1033	ring asym ip bend, CCC str	IR,R(w)dp	0.004		
1041	ring sym str, CH <sub>3</sub> (N) str	IR,R(w)p	0.005		
1047	ring asym str, CH <sub>2</sub> (N) str	IR,R(w)p	0.017	1025(0.06)	
1111	ring asym str, CH <sub>3</sub> (N) bend, ring HCCH sym bend	IR,R(w)p	0.034	1092(0.12)	
1121	ring sym str, CH <sub>3</sub> (N) bend, ring HCCH sym bend	IR,R(w)p	0.009		
1126	CCC str	IR,R(w)p	0.003		
1153	CCC str, CCC bend	IR,R(w)p	0.003		
1163	CH <sub>3</sub> (N) bend	IR,R(w)p	0.024		
1180	ring asym str, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(w)p	0.308	1172(0.99)	
1257	ring asym str, CCCH bend	IR,R(w)p	0.006		
1310	ring asym str, CCCH bend, ring HCCH sym bend	IR,R(w)dp	0.001		
1336	ring sym str, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(w)p	0.003		
1339	CCCH bend, $CH_3(N)$ str, $CH_2(N)$ str	IR,R(w)p	0.017		
1357	ring sym str, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(m)p	0.007		1333(0.06)
1399	ring asym str, CCC str, CH <sub>2</sub> (N) str	IR,R(w)p	0.005	1240(0.12)	1343(0.06)
1414	ring asym str, CCC str	IR,R(w)p	0.01	1349(0.13)	1200(0.00)
1422 1450	CCC str	IR,R(w)p	0.016	1391(0.17)	1389(0.06)
	ring asym str, $CH_3(N)$ str, $CH_2(N)$ bend	IR,R(m)p	0.012 0.024	1/29(0.15)	1417(0.15)
1467 1494	ring asym str, $CH_3(N)$ str CCCH bend	IR,R(w)p IR,R(m)p	0.024	1428(0.15)	1428(0.11)
1494	CCCH bend	IR,R(m)p IR,R(w)p	0.001		1451(0.10)
1502	CH <sub>3</sub> (N) HCH bend	IR,R(w)p IR,R(w)p	0.034	1464(0.27)	1461(0.10)
1505	CCCH bend	IR,R(w)dp	0.034	1404(0.27)	1401(0.10)
1511	ring asym str, CH <sub>3</sub> (N) HCH bend	IR,R(m)dp	0.025		
1514	CCC str, CCCH bend	IR,R(w)p	0.028		
1599	ring asym str, $CH_3(N)$ str, $CH_2(N)$ str	IR,R(w)p	0.134	1577(0.40)	1571(0.06)
1607	ring asym str, $CH_3(N)$ str, $CH_2(N)$ str	R,R(w)p	0.054	1577(0.40)	()
3024	Et HCH sym str	IR,R(vs)p	0.057	2885(0.13)	2883(0.46)
3026	terminal CH <sub>3</sub> HCH sym str	IR,R(s)p	0.088	(/	2906(0.41)
3059	CH <sub>2</sub> (N) sym HCH str	IR,R(vs)p	0.074	2944(0.16)	2945(0.71)
3060	CH <sub>3</sub> (N) HCH sym str	IR,R(vs)p	0.064	, ,	
3082	Et asym HCH str	IR,R(s)p	0.039		
3106	propyl asym HCH str	IR,R(m)p	0.024		2970(1.00)
3106	propyl asym HCH str	IR,R(s)p	0.042	2976(0.29)	
3135	Et asym HCH str	IR,R(m)p	0.008		
3136	CH <sub>3</sub> (N) HCH asym str	IR,R(s)dp	0.012		
2160	CH <sub>3</sub> (N) HCH asym str	IR,R(m)dp	0.022		3117(0.13)
3160					
3271	ring NC(H)N CH str	IR,R(m)p	0.421	3128(0.26)	
	ring NC(H)N CH str ring HCCH asym str ring HCCH sym str, NC(H)N str	IR,R(m)p IR,R(m)p IR,R(vs)p	0.421 0.019 0.002	3128(0.26) 3175(0.49)	3178(0.13)

<sup>&</sup>lt;sup>a</sup> Note that ip and op are in-plane and out-of-plane and that Cat-An are vibrations in which the imidazolium cation oscillates around the anion.

TABLE 3: B3LYP/(6-311+G(2d,p)) Vibrational Assignments  $^a$  (cm $^{-1}$ ) of [EMIM]PF $_6$ 

$ u_{ m calc}$	assigment	IR, Raman	calc i.r., $I_{\rm rel}$	i.r. $\nu_{\rm exp}$ , $I_{\rm rel}$	Raman $\nu_{\rm exp}(I_{\rm rel})$
16	Cat-An tors	IR,R(w)p	0.001		
40	Cat-An bend	IR,R(w)p	0.007		
60	Cat-An bend	IR IR	< 0.001		
70	Cat-An bend	IR ID	0.006		
79	Cat-An bend, CH <sub>2</sub> (N) bend	IR ID	0.012		
96	Cat-An bend, CH <sub>2</sub> (N) bend	IR	0.007		
108	CH <sub>3</sub> (N) twist	IR	0.005		
125	CH <sub>3</sub> (N) twist	IR	0.031		
164 207	CH <sub>2</sub> (N) bend	IR,R(w)p	0.012 <0.001		
245	terminal CH3 twist CH3(N) bend	IR IR,R(w)dp	0.001		
287	PF <sub>6</sub> scissors	IR,R(w)up IR	0.003		
295	PF <sub>6</sub> scissors	IR IR	< 0.001		
299	PF <sub>6</sub> scissors	IR	< 0.001		
301	CCH bend, CH <sub>3</sub> (N) bend	IR	< 0.001		
395	CCH bend, CH <sub>3</sub> (N) bend	IR,R(w)p	0.003		
427	CCH bend, CH <sub>3</sub> (N) bend	IR	0.002		
445	PF <sub>6</sub> scissors	IR	< 0.001		
448	PF <sub>6</sub> scissors	IR,R(w)p	< 0.001		
452	PF <sub>6</sub> scissors	IR,R(w)p	0.003		469(0.08)
515	FPF sym str	IR	< 0.001		469(0.08)
527	FPF sym str	IR	0.039		
533	FPF sym bend	IR	0.114		
535	FPF sym bend	IR	0.114		
537	FPF sym bend	IR	0.058	559(0.54)	
600	ring ip sym bend	IR,R(w)p	0.004	559(0.54)	598(0.09)
643	ring op asym bend	IR,R(w)dp	0.045	625(0.13)	
676	ring op asym bend	IR,R(w)p	0.096	649(0.05)	
684	FPF sym str, ring op bend	IR,R(w)p	0.036		
705	ring ip bend, $CH_3(N)$ bend, $CH_2(N)$ bend	IR,R(w)p	0.127		
733	ring HCCH sym bend	IR,R(w)p	0.078	741(0.09)	741(0.19)
807	CCH bend	IR	0.016		
837	ring HCCH asym bend	IR	0.907	836(0.80)	
838	FPF asym str, ring HCCH asym bend	IR	0.888	838(0.86)	
847	FPF asym str, ring NC(H)N bend, CCH bend	IR IR	1	847(1.00)	
859	FPF asym str	IR ID	< 0.001		
949	ring NC(H)N bend	IR	0.008		
961	CC str	IR,R(w)p	0.011		
1042 1046	ring ip sym str	IR,R(w)p IR,R(w)dp	0.004 0.018	1033(0.02)	
1105	ring sym str, $CH_3(N)$ str, $CH_2(N)$ str CC str, ring ip sym str	IR,R(w)ap IR,R(w)p	0.018	1033(0.02)	
1114	ring HCCH sym bend, ring ip sym str	IR,R(w)p IR,R(w)dp	0.018	1007(0.01)	
1114	ring HCCH sym bend, ring ip sym str	IR,R(w)p	0.003		
1141	CC str	IR,R(w)p IR,R(w)p	0.008	1114(0.03)	
1164	CH <sub>3</sub> (N) HCH bend	IR,R(w)p IR,R(w)p	0.001	1114(0.03)	
1181	ring sym str, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(w)p IR,R(w)p	0.393	1172(0.24)	
1274	ring ip asym str, CC bend	IR,R(w)p IR,R(w)p	0.017	1172(0.24)	
1317	ring ip asym str, $CH_3(N)$ str	IR,R(W)P	0.002		
1350	ring ip sym str, CH <sub>2</sub> (N) str	IR,R(m)p	0.03	1340(0.02)	1340(0.06)
1383	ring ip sym str, $CH_2(N)$ str, $CH_3(N)$ str	IR,R(w)p	0.023	()	()
1410	ring ip asym str, $CH_2(N)$ bend	IR,R(w)p	0.032	1387(0.02)	
1426	CC str	IR,R(w)p	0.027	,	
1452	ring ip asym str	IR.R(m)p	0.027		1421(0.11)
1470	ring ip asym str, CH <sub>3</sub> (N) str	IR.R(w)p	0.039	1432(0.02)	, ,
1490	CCH HCH sym bend, CH <sub>3</sub> (N) HCH sym bend	IR.R(m)p	0.005	, ,	1452(0.08)
1497	CCH HCH asym bend, CH <sub>3</sub> (N) HCH sym bend	IR,R(w)dp	0.03	1468(0.08)	
1503	CH <sub>3</sub> (N) asym bend	IR,R(w)p	0.019		
1510	CC HCH bend	IR,R(w)p	0.023		
1512	CH <sub>3</sub> (N) HCH sym bend	IR.R(m)p	0.043		
1598	ring ip sym str, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(w)p	0.189	1575(0.12)	1572(0.06)
1608	ring ip asym str, CH <sub>3</sub> (N) str, CH <sub>2</sub> (N) str	IR,R(w)p	0.106	1575(0.12)	1572(0.06)
3042	terminal CH <sub>3</sub> HCH sym str	IR,R(s)dp	0.045	2878(0.05)	2878(0.31)
3061	CH <sub>3</sub> (N) HCH sym str	IR,R(s)p	0.064		2917(0.70)
3068	CH <sub>2</sub> HCH sym str	IR,R(s)p	0.057		2942(0.71)
3103	terminal CH <sub>3</sub> HCH asym str	IR,R(s)p	0.062	2952(0.05)	
3132	CH <sub>2</sub> HCH asym str	IR,R(m)p	0.011		2970(1.00)
3137	CH <sub>3</sub> (N) HCH asym str	IR,R(m)dp	0.021		
3145	CC HCH asym str	R,R(w)p	0.013		
3163	CH <sub>3</sub> (N) HCH asym str	IR,R(m)dp	0.004		3115(0.11)
2260	ring NC(H)N CH str	IR,R(m)p	0.016	3134(0.05)	
3268				<b>-</b>	
3276 3294	ring HCCH asym str ring HCCH sym str, ring NC(H)N CH str	IR,R(m)dp IR,R(vs)p	0.012 0.201	3168(0.21) 3179(0.29)	3180(0.14)

<sup>&</sup>lt;sup>a</sup> Note that ip and op are in-plane and out-of-plane and that Cat-An are vibrations in which the imidazolium cation oscillates around the anion.



**Figure 7.** Correlation diagram for the vibrational spectrum of [PMIM]-PF<sub>6</sub>, experimental versus calculated IR and Raman transition frequencies. Scaling factors = 0.965 (B3LYP) and 0.914 (RHF) with correlation coefficients = 0.999: (▲) RHF calculated values, (○) B3LYP calculated values, (■) theoretical correlation of 1.00.

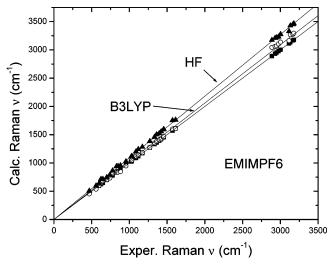
vibrations at 3160 (ring methyl H–C–H asymmetric stretch) and 3294 cm<sup>-1</sup> (ring H–C–C–H symmetric stretch and ring NC(H)N C–H stretch). The IR spectrum of [PMIM]PF<sub>6</sub> shows two broad bands centered at 3128 and 3176 cm<sup>-1</sup>. It is likely that these weak IR bands consist of multiple vibrations, although no attempt was made to deconvolute them due to their weak absorbance.

Another strong Raman band is located at 741 cm $^{-1}$ . This band is assigned (B3LYP) to a ring H-C-C-H asymmetric bend and to C-N stretches between ring nitrogens and the attached methyl and methylene groups. There is also an easily observable band at 1417 cm $^{-1}$  that is assigned to a ring in-plane asymmetric stretch, a ring methyl C-N stretch and a CH $_2$  C-N bend.

Figure 7 contains a plot of the combined experimental vs theoretical (6-311+G(2d,p) basis set) vibrational frequencies using the B3LYP and RHF methods for [PMIM]PF<sub>6</sub>. The [PMIM]PF<sub>6</sub> ion pair requires a scale factor of only 0.965 (DFT) to reproduce the experimental frequencies from the calculated values. As shown in Figure 7, the RHF method overestimates the vibrational frequencies to a greater degree than the B3LYP method and requires a scale factor of 0.914 to reproduce the experimental frequencies.

[EMIM]PF<sub>6</sub>. The Raman spectrum (see Supporting Information) of [EMIM]PF<sub>6</sub> is similar to those of [BMIM]PF<sub>6</sub> and [PMIM]PF<sub>6</sub> and contains at least four intense bands between 2878 and 2970 cm<sup>-1</sup>. The theoretical (B3LYP) vibrations assigned to these peaks include terminal CH<sub>3</sub> symmetric H–C–H stretch (3042 cm<sup>-1</sup>), the ring CH<sub>3</sub> symmetric H–C–H stretch (3061 cm<sup>-1</sup>), CH<sub>2</sub> symmetric H–C–H stretch (3132 cm<sup>-1</sup>). There are weak Raman bands at 3115 and 3180 cm<sup>-1</sup> assigned to B3LYP calculated vibrations at 3163 and 3294 cm<sup>-1</sup>. The calculated vibrations include a ring methyl HCH asymmetric stretch (3163 cm<sup>-1</sup>) and a mixture of a ring H–C–C–H symmetric stretch and a ring N(CH)N C–H stretch (3294 cm<sup>-1</sup>). The latter weak Raman band would most likely be affected by the loss or gain of hydrogen bonding.

As is the case for the other ionic liquids in this series, a strong Raman band is located at 741 cm<sup>-1</sup>. This band is assigned (B3LYP) to a ring H-C-C-H symmetric bend. There is also an easily observable band at 1421 cm<sup>-1</sup> that is assigned to a ring in-plane asymmetric stretch.



**Figure 8.** Correlation diagram for the vibrational spectrum of [EMIM]-PF<sub>6</sub>, experimental versus calculated IR and Raman transition frequencies. Scaling factors = 0.967 (B3LYP) and 0.915 (RHF) with correlation coefficients = 0.999: (▲) RHF calculated values, (○) B3LYP calculated values, (■) theoretical correlation of 1.00.

Figure 8 is a plot of the combined experimental vs theoretical (6-311+G(2d,p)) vibrational frequencies using the B3LYP and RHF methods for [EMIM]PF<sub>6</sub>. The [EMIM]PF<sub>6</sub> ion pair requires a scale factor of only 0.965 (DFT) to reproduce the experimental frequencies from the calculated values. As shown in Figure 7, the RHF method overestimates the vibrational frequencies to a greater degree than the B3LYP method and requires a scale factor of 0.914 to reproduce the experimental frequencies.

**Potential Spectroscopic Probes.** The Raman bands in the C–H stretching region may prove useful as potential spectroscopic probes for studies of molecular interactions in these ionic liquids. The Raman band in the vicinity of 3179 cm<sup>-1</sup> has some potential for studies of hydrogen bonding involving the imidazolium cation, despite its relative weakness in intensity. In addition to the Raman bands in the C–H stretching region, the Raman band at 741 cm<sup>-1</sup> contains either ring H–C–C–H symmetric or asymmetric bending character and may also prove useful as a hydrogen bonding probe in future work.

#### **Conclusions**

A comprehensive series of vibrational band assignments has been developed for a series of three imidazolium ionic liquids containing  $PF_6^-$  as the anion. The vibrational band assignments have been accomplished using a combination of experimental infrared and Raman spectra compared with results obtained from ab initio calculations. In particular, the vibrational spectra of  $[BMIM]PF_6$ ,  $[PMIM]PF_6$ , and  $[EMIM]PF_6$  calculated at the B3LYP/6-311+G(2d,p) level are in good agreement with the experimental infrared and Raman spectra. The scaling factors of 0.964, 0.965, and 0.967 for  $[BMIM]PF_6$ ,  $[PMIM]PF_6$ , and  $[EMIM]PF_6$  calculated vibrational spectra yield  $R^2$  correlation factors of 0.999 for the three ionic liquids. The gas-phase molecular structures suggest the presence of hydrogen bonding in all three corresponding ion pairs calculated at both the HF/6311+G(2d,p) and B3LYP/6311+G(2d,p) levels.

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**Supporting Information Available:** Raman spectra of [PMIM]PF<sub>6</sub> and [EMIM]PF<sub>6</sub>. This material is available free of charge via the Internet at http://pubs.acs.org.

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