

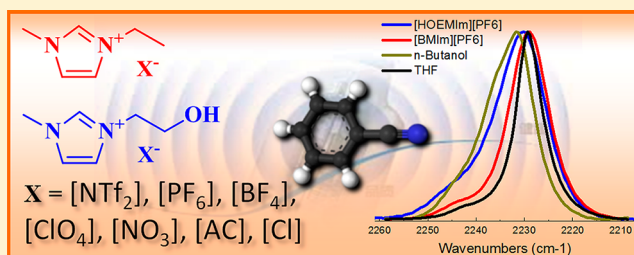
## Benzonitrile as a Probe of Local Environment in Ionic Liquids

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## S Supporting Information

**ABSTRACT:** Because of its sensitivity to chemical and electrostatic characteristics, nitrile group as an infrared (IR) probe to monitor the local structure, folding kinetics, and electrostatic environment of protein, or solvation of molecular solvents, has attracted increasing attention. Herein, by choosing benzonitrile and imidazolium ionic liquids (ILs) as the IR probe and model ILs, respectively, we report that the nitrile stretching vibration ( $\nu_{\text{CN}}$ ) could be utilized as a simple and substantial IR probe to monitor the local environment of ILs such as hydrogen bonding (H-bonding) as well as intrinsic electric field. In 1-alkyl-3-methylimidazolium-based non-hydroxyl ILs, the  $\nu_{\text{CN}}$  is in a “free” state, and is less affected by the alkyl chain, while it significantly decreases with the effective anion charge. In 1-(2-hydroxyethyl)-3-methylimidazolium-based hydroxyl ILs, however, a distinct anion-dependent  $\nu_{\text{CN}}$  forming H-bonding with the hydroxyl is also observed besides the “free”  $\nu_{\text{CN}}$  band. The “free” component of  $\nu_{\text{CN}}$  can be further employed to determine the intrinsic electric field in both non-hydroxyl (directly) and hydroxyl (indirectly by subtracting H-bonding contribution) ILs by using vibrational Stark effect. Moreover, the result suggests that benzonitrile is preferentially located in the charge domain in ILs and it could be a more suitable probe to report the ionic network rather than the nonpolar domain in ILs.



## 1. INTRODUCTION

As complex solvents, fluids, and media, ionic liquids (ILs) have attracted considerable interest in many areas of technology and science, such as organic or inorganic reactions, catalysis, separations, and electrochemical studies.<sup>1–8</sup> Since ILs are entirely composed of ions, they are indeed much more complex solvents differing significantly from common molecular solvents. A key feature of ILs is the large number of possible ion combinations,<sup>9</sup> which opens up the possibility of altering the constituent ions to tailor for some specific physical and chemical properties. Due to the large number of ion combinations and tunable structure, ILs are capable of undergoing many types of interactions, including Coulombic forces, dispersive and inductive interactions, H-bonding interactions,<sup>10–14</sup> etc., which in turn dominate their physicochemical properties and functions.<sup>9,15</sup> For example, the H-bonding in ILs was extensively studied and reported to be crucial for designing ILs as potential solvents for cellulose.<sup>16</sup> Another interesting phenomenon observed in ILs, in particular those with long cationic side chain, is that the alkyl chains are liable to aggregate and form separated nonpolar tail domains, while the cationic headgroups and anions form continuous polar networks.<sup>17–21</sup> For these reasons, the understanding of fundamental aspects of ILs, such as its microstructure, polarity, anion–cation interactions, hydrogen bonding, and solvation dynamics as well as conformation of alkyl chains, is therefore of outmost importance.

Numerous experimental and theoretical approaches, in particular photophysical experiments including Raman spec-

troscopy, neutron diffraction measurements, and X-ray scattering method, have been utilized to evaluate the fundamentals of ILs and the local structure in bulk ILs.<sup>22–25</sup> Of all methods, the response of a single molecular vibration to the local environment could be a simple and direct approach for probing both the local structural distribution and the solvation environment. Nitrile stretching vibration ( $\nu_{\text{CN}}$ ) is one of such ideal probes for a number of reasons:<sup>26–33</sup> first, the nitrile group is small, and its spectral profile and frequency are known to be highly sensitive to specific characteristics of the local solvation environment, including solvent polarity, H-bonding interaction,<sup>34</sup> and electric fields;<sup>26–30</sup> second, the  $\nu_{\text{CN}}$  band is in a region well separated from most other vibrational modes; third,  $\nu_{\text{CN}}$  is generally intense and sharp enough that small changes in frequency can be readily quantified; and finally, a normal-mode analysis of organic nitriles indicates that the nitrile stretching mode is highly localized to the nitrile bond,<sup>31</sup> minimally perturbed by the changes of the rest of the molecule. Thus, nitrile group has been widely utilized as structural and/or environmental probe to study the electrostatic environments of proteins<sup>35</sup> and ligand binding,<sup>33</sup> the microstructure and dynamic properties of various R–C≡N/solvent binary solutions,<sup>36</sup> the orientations of membrane peptides,<sup>37</sup> the properties of metal oxide and zeolite surfaces,<sup>38,39</sup> the folding kinetics of peptides,<sup>40</sup> and the Stark

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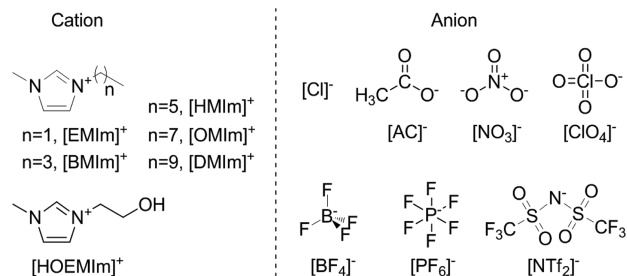
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effect in DNA.<sup>41</sup> More recently, using the special vibrational behavior of  $\nu_{\text{CN}}$  of ethyl thiocyanate (EtSCN), we have investigated the intrinsic electric fields of ILs by both vibrational Stark effect and molecular dynamic simulation.<sup>42</sup> The result demonstrated that most ILs have intrinsic electric fields slightly higher than but still comparable to those in common molecular solvents. Moreover, the intrinsic electric fields in ILs are strongly structure-dependent: it apparently decreases as the anion size increases due to the larger separation of ions, and slightly decreases with increasing alkyl chain length due to the spatial heterogeneity in ILs.

In this work, nitrile stretching vibration of benzonitrile was employed as a useful monitor in a series of imidazolium ILs with different structures to get a better understanding of the effect of anion, alkyl chain, and hydroxyl functionalization on the electric field and hydrogen-bonding behavior in these ionic media. The result demonstrated that, in common non-hydroxyl ILs, the  $\text{C}\equiv\text{N}$  is free, with stretching vibration obviously decreasing with the anionic effective anion charge. However, in hydroxyl ILs, besides the free  $\text{C}\equiv\text{N}$ , there is also hydrogen-bonded  $\text{C}\equiv\text{N}$  formed between  $\text{C}\equiv\text{N}$  and the acidic hydrogen of OH on the imidazolium ring, like the case of protic molecular solvents. The sensitive  $\text{C}\equiv\text{N}$  stretching vibration of benzonitrile in ILs is therefore expected to be useful for probing the local environment of ILs.

## 2. EXPERIMENT

**2.1. Chemicals and Synthesis of ILs.** Benzonitrile was purchased from TCI Corp. All ILs with different structures (Figure 1), namely, cations 1-ethyl-3-methylimidazolium



**Figure 1.** Structures of the cations and anions of ILs investigated.

([EMIm]), 1-butyl-3-methylimidazolium ([BMIm]), 1-hexyl-3-methylimidazolium ([HMIm]), 1-octyl-3-methylimidazolium ([OMIm]), 1-decyl-3-methylimidazolium ([DMIm]), and 1-(2-hydroxyethyl)-3-methylimidazolium ([HOEMIm]); and anions chloride ([Cl]), acetate ([AC]), nitrate ([NO<sub>3</sub>]), dicyanamide ([DCA]), perchlorate ([ClO<sub>4</sub>]), tetrafluoroborate ([BF<sub>4</sub>]), hexafluorophosphate ([PF<sub>6</sub>]), and bis-(trifluoromethanesulfonyl)amide ([NTf<sub>2</sub>]), were prepared according to the well-established procedures.<sup>43,44</sup> The above ILs can be classified into two major types: 1-alkyl-3-methylimidazolium-based non-hydroxyl ILs and 1-(2-hydroxyethyl)-3-methylimidazolium-based hydroxyl ILs. All ILs were dried in vacuum at 80 °C for 10 h prior to analysis. Benzonitrile–ILs solutions were prepared by adding weighed amounts of benzonitrile to 1 mL of ILs.

**2.2. Determination of ET(30) and Kamlet–Taft Parameters.** Polarity scales, i.e.,  $E_{\text{T}}(30)$  and Kamlet–Taft parameters of all ILs, were determined by Reichardt's dye 30,

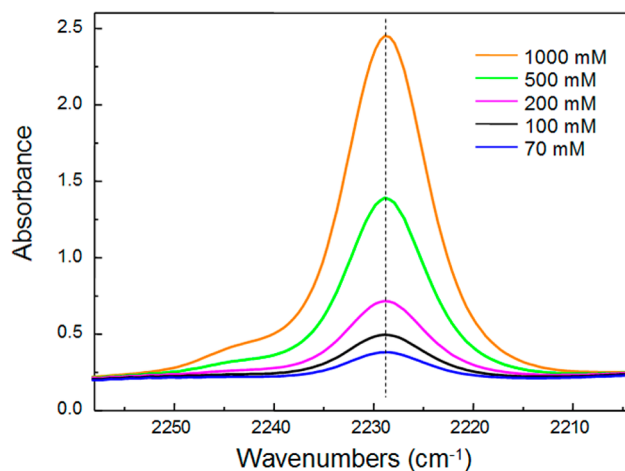
*N,N*-dimethyl-*p*-nitroaniline, and 4-nitroaniline, according to the previous procedures.<sup>45,46</sup>

**2.3. Spectroscopic Measurement.** Infrared spectra (IR) were recorded on a Thermo-Nicolet 5700 Fourier transform infrared spectrometer with 32 scanning times by taking ILs as blank. The sample cell was equipped with KBr windows separated with a Teflon spacer of 160  $\mu\text{m}$ .

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of Concentration on Central Frequency.

The frequency of  $\text{C}\equiv\text{N}$  stretching vibration in organic solvents is reported to be a function of concentration,<sup>28,47</sup> wherein the  $\nu_{\text{CN}}$  of concentrated solution is somewhat lower than that of diluted solution. The concentration-induced shift is particularly significant for the aprotic, nonpolar solvents. For example, when the concentration of benzonitrile in hexane increases from 1% (65 mM) to 10% (710 mM),  $\nu_{\text{CN}}$  red-shifts about 2  $\text{cm}^{-1}$ , which appears to be a result of a dipolar interaction between benzonitrile molecules.<sup>28,47</sup> However, this phenomenon is not observed in the case of ILs. [EMIm][BF<sub>4</sub>] as a typical example is shown in Figure 2, wherein the  $\nu_{\text{CN}}$  is fixed at

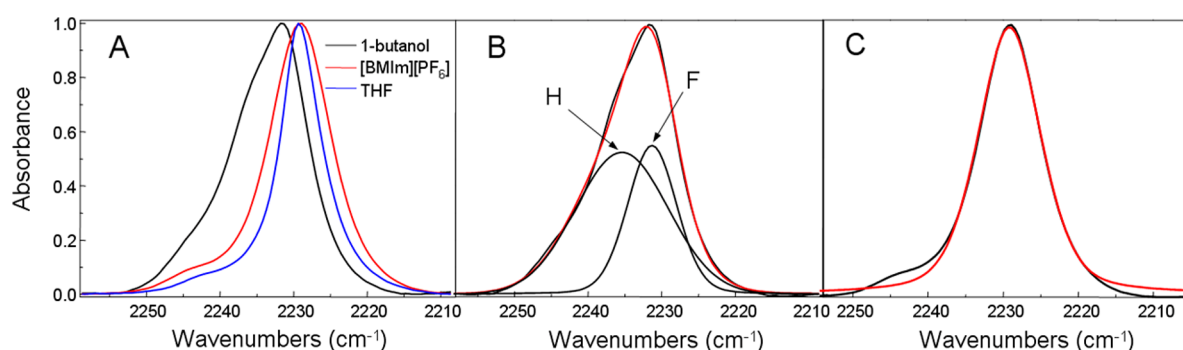


**Figure 2.**  $\text{C}\equiv\text{N}$  stretching vibration of benzonitrile in [EMIm][BF<sub>4</sub>] with variable concentration (from bottom to top: 70, 100, 200, 500, and 1000 mM).

2228.8  $\text{cm}^{-1}$ , and even the concentration increases from 70 to 1000 mM, probably because the electrostatic interaction in ILs reduces the dipolar intermolecular association of  $\text{C}\equiv\text{N}$ .

**3.2. IR Spectra of Benzonitrile in Non-hydroxyl ILs.** It is demonstrated that both the frequency and the profile of  $\text{C}\equiv\text{N}$  stretching vibration are highly sensitive to polarity and hydrogen-bonding behavior of solvent.<sup>48</sup> For example, the  $\text{C}\equiv\text{N}$  stretching vibration of benzonitrile derivative in water (2237.2  $\text{cm}^{-1}$ ) has a much broader and higher frequency  $\text{C}\equiv\text{N}$  stretching vibration as compared to that in THF (2228.5  $\text{cm}^{-1}$ ), a less-polar and non-hydrogen-bonding environment.<sup>48,49</sup> Moreover, it is well-known that the  $\nu_{\text{CN}}$  bands in aprotic solvents such as THF and DMSO are fairly symmetric; however, in protic solvents (e.g., 1-butanol) when the hydrogen-bonding donation from these solvents is possible, noticeable broadening and asymmetry is observed on the high-energy side,<sup>50</sup> as shown in Figure 3.

The broadening bands in protic solvents could be deconvolved into two components of different solvation states by using the pseudo-Voigt function;<sup>50</sup> the low-frequency one



**Figure 3.** (A) Normalized IR spectra of the C≡N stretching vibration of 100 mM benzonitrile in THF, 1-butanol and [BMIm][PF<sub>6</sub>]. (B) Fitting of the C≡N stretching vibration in 1-butanol by two pseudo-Voigt fits: F and H. (C) Fitting of C≡N stretching band in [BMIm][PF<sub>6</sub>] by one pseudo-Voigt fit. The global fit is in red.

(F) is assigned to benzonitrile molecules with free C≡N groups, and the high-frequency one (H) is assigned to those with a “linear”  $\sigma$ -type hydrogen bonding to the nitrogen species of C≡N, according to the previous result in aqueous solution.<sup>26,34,50,51</sup> In this case, the direct H-bonding interaction results in a higher C≡N bond order and thus a higher vibrational frequency.

C≡N stretching vibrations of benzonitrile in 1-alkyl-3-methylimidazolium-based non-hydroxyl ILs are given in Table 1, together with the result in molecular solvents for comparison.

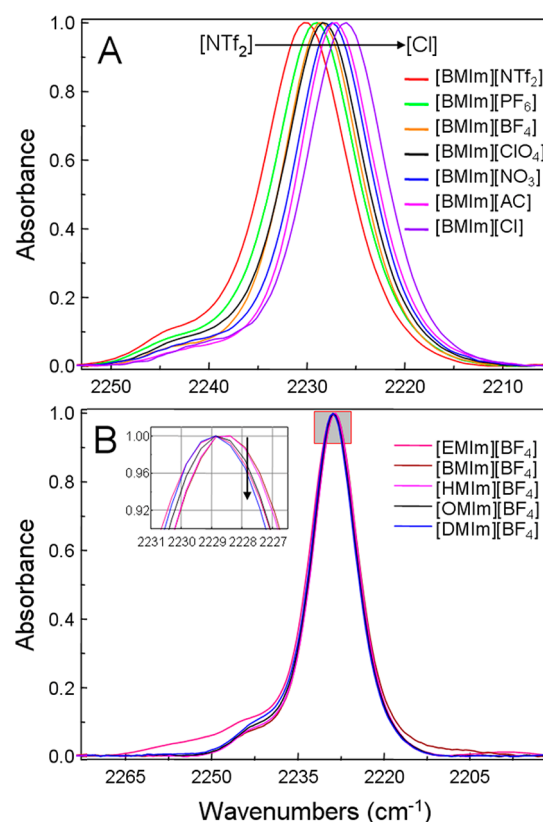
**Table 1.** C≡N Stretching Vibration of Benzonitrile in Non-hydroxyl ILs and Molecular Solvents, Together with Their Polarity and Kamlet–Taft Parameters<sup>a</sup>

ILs	$\nu_{\text{C}\equiv\text{N}}^b$	fwhm <sup>c</sup>	$E_{\text{T}}^N$	$\pi^*$	$\alpha$	$\beta$
THF	2229.3	6.6				
DMSO	2227.3	7.7				
1-butanol	2231.6					
[BMIm][NTf <sub>2</sub> ]	2230.1	10.1	0.640	0.903	0.647	0.306
[BMIm][PF <sub>6</sub> ]	2229.0	9.9	0.667	0.991	0.630	0.196
[BMIm][BF <sub>4</sub> ]	2228.6	9.4	0.669	0.991	0.643	0.407
[BMIm][ClO <sub>4</sub> ]	2228.3	9.6	0.660	1.043	0.585	0.368
[BMIm][NO <sub>3</sub> ]	2227.4	9.1	0.634	1.060	0.517	0.644
[BMIm][AC]	2227.1	9.0	0.566	0.974	0.437	1.122
[BMIm][Cl] <sup>d</sup>	2226.1	9.4	0.593	1.093	0.403	0.860
[EMIm][BF <sub>4</sub> ]	2228.8	9.6				
[HMIm][BF <sub>4</sub> ]	2228.5	9.3				
[OMIm][BF <sub>4</sub> ]	2228.7	9.3				
[DMIm][BF <sub>4</sub> ]	2228.8	9.2				

<sup>a</sup>Dipolarity/polarizability ( $\pi^*$ ), hydrogen bond donating acidity (HBD,  $\alpha$ ), hydrogen bond accepting basicity (HBA,  $\beta$ ). <sup>b</sup>In cm<sup>-1</sup>.

<sup>c</sup>Full width at half-maximum, cm<sup>-1</sup>. <sup>d</sup>Supercooled liquid.

Spectrum of [BMIm][PF<sub>6</sub>] is shown in Figure 3 as a typical example. Note that the central frequency and overall band profile are found to be reproducible within the experimental uncertainty of the instrument. The observed bands in non-hydroxyl ILs lie within a narrow region of 2226.1–2230.1 cm<sup>-1</sup>. Although dialkylimidazolium ILs are reported to be of hydrogen-bonding donors because of the acidic hydrogen atoms on imidazolium ring at C2–H, C4(5)–H ( $pK_a = 21$ –23 for the C2–H of imidazolium cation<sup>52</sup>) and the determined HBD value ( $\alpha > 0$ ),<sup>53</sup> the C≡N stretching vibrations of benzonitrile in all non-hydroxyl ILs are nearly symmetric and could be fitted to a single pseudo-Voigt function (see Figures 3 and 4, the slight asymmetry of the bands in ILs around 2242



**Figure 4.** Normalized IR spectra of C≡N stretching vibration of 100 mM benzonitrile in [BMIm]-based ILs (A) (from left to right: [NTf<sub>2</sub>], [PF<sub>6</sub>], [BF<sub>4</sub>], [ClO<sub>4</sub>], [NO<sub>3</sub>], [AC], and [Cl]) and in [BF<sub>4</sub>]-based ILs (B) (inset is the expanded region between 2227 and 2230 cm<sup>-1</sup>, from top to bottom: [BMIm], [HMIm], [OMIm], [EMIm], and [DMIm]).

cm<sup>-1</sup> is not considered in this study since it is also present in aprotic solvents), and thus the ILs seen by C≡N (a weak hydrogen bonding acceptor) are exclusively analogous to aprotic solvents, affording similar characteristics as observed in THF.<sup>50</sup> This conclusion is in agreement with the previous result demonstrating that dialkylimidazolium ILs experienced by EtSCN are analogous to aprotic solvents judging from the relation between the IR frequency ( $\nu_{\text{CN}}$ ) and the <sup>13</sup>C NMR chemical shift  $\delta(^{13}\text{C})$  of EtSCN in ILs.<sup>42</sup> Both results indicate that the H-bonding ability of acidic hydrogen on imidazolium is dependent on the target (H-bonding acceptor) in that it can form H-bonding with the basic ionic probe such as Reichardt’s dye<sup>53</sup> but is indeed inert to the neutral C≡N occurred here.



Moreover, it was reported by Londergan and co-workers that the  $\text{C}\equiv\text{N}$  line shape is sensitive to solvent dynamics, wherein its fwhm increases with the average solvation time.<sup>30</sup> The much higher fwhm of  $\text{C}\equiv\text{N}$  stretching vibration of benzonitrile in non-hydroxyl ILs ( $9.0\text{--}10.1\text{ cm}^{-1}$ ) than what is measured in conventional solvents ( $6.6\text{ cm}^{-1}$  in THF and  $7.7\text{ cm}^{-1}$  in DMSO) thus identified ILs as solvents with slow solvation dynamics. Indeed, several early studies, which were done by investigating time-resolved fluorescence behaviors of dipolar solutes in ILs, suggested that slow dynamics is a common feature in ILs.<sup>54,55</sup> Notation is that, although the average solvation time in ILs is found to be 3 orders higher than that in conventional solvents,<sup>55,56</sup> the resulting difference in fwhm observed in this study is only about  $3\text{ cm}^{-1}$ . This observation that the line shape appears to be less sensitive to the differences between the “slow” solvents is also observed in conventional solvents using of methyl thiocyanate as probe,<sup>30</sup> but is more significant in ILs. It means that certainly some other factors, for example, inhomogeneous microenvironment of ILs, may also contribute to the line width.<sup>21,57</sup>

**3.3. Effect of Anion on  $\nu_{\text{CN}}$ .** More recently, Aschaffenburg et al. reported that  $\nu_{\text{CN}}$  of benzonitrile in aprotic molecular solvents decreases linearly with increasing solvent polarity ( $E_{\text{T}}\text{N}$ ,  $R^2 = 0.94$ ) or the dipolarity/polarizability ( $\pi^*$ ,  $R^2 = 0.99$ ).<sup>50</sup> However, when the “aprotic solvent”-like ILs are included in the regression analysis, none of the polarity and Kamlet–Taft parameter scales could provide a strong quantitative correlation with the  $\text{C}\equiv\text{N}$  stretching frequency for the non-hydroxyl ILs ( $R^2 < 0.87$ , Figure S1 in the Supporting Information). In addition to this,  $\nu_{\text{CN}}$  in [BMIm]-based ILs is found to increase roughly with  $E_{\text{T}}\text{N}$ , opposite to that in aprotic molecular solvents.<sup>50</sup>

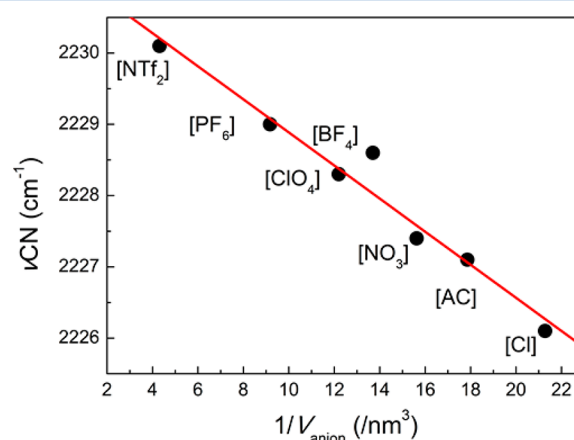
In fact, besides the polarity-induced  $\nu_{\text{CN}}$  as reported above, another possible correlation is the vibrational Stark effect (VSE) spectroscopy, where the  $\text{C}\equiv\text{N}$  frequency shift is assumed to be linearly proportional to the electric field component  $E_{\parallel}$  parallel to the  $\text{C}\equiv\text{N}$  bond.<sup>58,59</sup> In VSE spectroscopy, the intrinsic response of a probe vibrational oscillator to its local electrostatic environment is measured spectroscopically and is used to quantitate the magnitude and direction of the local electric field to which the probe is exposed,<sup>35,58–60</sup> using the following equation:

$$\Delta E \rightarrow = -\Delta\nu_{\text{CN}}^{\text{obs}}/(\Delta\mu_{\text{CN}}^{\rightarrow}/hc) \quad (1)$$

where  $h$  is Planck's constant,  $c$  is the speed of light,  $\Delta E \rightarrow$  (in MV/cm) is the change of protein electrostatic field,  $\Delta\nu_{\text{CN}}^{\text{obs}}$  (in  $\text{cm}^{-1}$ ) is the observed frequency shifts of the probe (e.g., nitrile), and  $\Delta\mu_{\text{CN}}^{\rightarrow}/hc$  (in  $\text{cm}^{-1}/(\text{MV}/\text{cm})$ ) is the characteristic linear Stark tuning rate of the probe,<sup>35</sup> a quantitative calibration of the sensitivity of the probe to electric fields. By using VSE spectroscopy, the  $\text{C}\equiv\text{N}$  probe had been widely used to determine the electrostatic field of ordered systems such as protein or polymer matrix.<sup>35,41,61–67</sup> Recently, Boxer et al. has successfully applied this method to homogeneous molecular solvents.<sup>68</sup> They demonstrated that the IR vibrational band shifts of the nitrile probe in common aprotic molecular solvents arise principally from changes in the local electrostatic field. However, in protic solvents, it could be decomposed into both the electrostatic effect and the hydrogen-bonding contribution. Inspired by Boxer's work, we have successfully determined the intrinsic electric field in ILs by using ethyl thiocyanate (EtSCN) as a VSE probe.<sup>42</sup> In this study, considering the aprotic

solvents-like nature of the non-hydroxyl ILs experienced by benzonitrile, which is rather similar to what observed for EtSCN,<sup>42</sup> we further investigate the possibility of using benzonitrile as a probe to determine the intrinsic electric field by VSE, and the obtained result is compared with that of EtSCN.

It can be clearly seen from Figure 5 that the  $\nu_{\text{CN}}$  in [BMIm]-based ILs with various anions monotonously blue



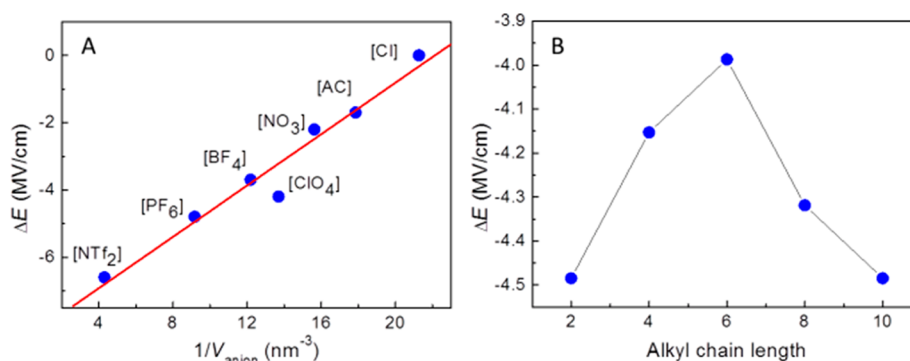
**Figure 5.** Plot of  $\nu_{\text{CN}}$  in [BMIm]-based ILs vs the effective anion charge ( $1/V_{\text{anion}}$ ).

shifts in the following order:  $[\text{Cl}] < [\text{AC}] < [\text{NO}_3] < [\text{ClO}_4] < [\text{BF}_4] < [\text{PF}_6] < [\text{NTf}_2]$ . Considering that the charge on all of the anions investigated is delocalized over the whole surface (or volume) of the ion, and which results in a dramatic reduce in charge density, herein we can define the value of anion charge/anion volume as effective anion charge ( $1/V_{\text{anion}}$ , Table 2). The frequency of  $\nu_{\text{CN}}$  in [BMIm]-based ILs is interestingly found to decrease linearly with  $1/V_{\text{anion}}$ , as shown in Figure 6, strongly suggesting that the  $\text{C}\equiv\text{N}$  stretching vibration of benzonitrile in non-hydroxyl ILs is controlled by the electrostatic interaction and therefore this method could be useful for probing the

**Table 2.** Effective Anion Charge ( $1/V_{\text{anion}}$ ) of Anion of [BMIm]-Based ILs and Relative Electric Field Determined by VSE Method

ILs	$V_{\text{anion}}^{\text{a}}$ (nm <sup>3</sup> ) <sup>a</sup>	$1/V_{\text{anion}}^{\text{a}}$ (nm <sup>-3</sup> )	$\Delta E$ (MV/cm) <sup>d</sup>	$\Delta E$ (MV/cm) <sup>e</sup>
[BMIm]	0.232 <sup>b</sup>	4.310	−6.6	−8.3
[BMIm][NTf <sub>2</sub> ]				
[BMIm][PF <sub>6</sub> ]	0.109	9.174	−4.8	−6.8
[BMIm][BF <sub>4</sub> ]	0.073	12.195	−4.2	−5.8
[BMIm][ClO <sub>4</sub> ]	0.082	13.699	−3.7	−5.0
[BMIm][NO <sub>3</sub> ]	0.064	15.625	−2.2	−3.5
[BMIm][AC]	0.056 <sup>c</sup>	17.857	−1.7	NA <sup>f</sup>
[BMIm][Cl]	0.047	21.277	0	0
[EMIm][BF <sub>4</sub> ]			−4.5	−5.8
[HMIm][BF <sub>4</sub> ]			−4.0	−6.0
[OMIm][BF <sub>4</sub> ]			−4.3	−6.4
[DMIm][BF <sub>4</sub> ]			−4.5	−6.7

<sup>a</sup>Data from ref 69. <sup>b</sup>Data from ref 70. <sup>c</sup>The volume of  $[\text{HCO}_2]$  was used instead of that of  $[\text{AC}]$  in view that the unit negative charge is centered on the carboxyl moiety. <sup>d</sup>Determined by benzonitrile. <sup>e</sup>Determined by EtSCN.<sup>42</sup> <sup>f</sup>Unavailable due to the reaction of EtSCN with [BMIm][AC].



**Figure 6.** Relative VSE electric fields of non-hydroxyl ILs as a function of anion in [BMIm][X] (left) and alkyl chain length in [C<sub>n</sub>MIm][BF<sub>4</sub>] ILs (right) determined by benzonitrile. The fitting line is in red ( $\Delta E \rightarrow (\text{MV/cm}) = -8.45002 + 0.38189(1/V_{\text{anion}}) \text{ (nm}^{-3}\text{)}$ ).

electric field of ILs, wherein a strong electric field causes a red-shifted  $\nu\text{CN}$ .

Based on a Stark tuning rate ( $\Delta\mu \rightarrow \text{CN}/hc$ ) of 0.0361 D/f,<sup>71</sup> i.e., 0.602  $\text{cm}^{-1}/(\text{MV/cm})$ , the relative electric fields of ILs were calculated by VSE equation (eq 1) with [BMIm][Cl] as a reference (Table 2), and compared with the previous result derived from EtSCN.<sup>42</sup>

As can be seen from Table 2, the electric fields of [BMIm]-based ILs obviously increase with  $1/V_{\text{anion}}$  (from [NTf<sub>2</sub>] to [Cl]), and both the value and the changing trend are rather similar to what observed for EtSCN.<sup>42</sup>  $\nu\text{CN}$  of benzonitrile in [BMIm][Cl] (2226.1  $\text{cm}^{-1}$ ), to our knowledge, could be the lowest frequency in solvents reported to date,<sup>47,50,72</sup> which could be due to the highest  $1/V_{\text{anion}}$  of [Cl]. [BMIm][Cl] exhibits a VSE electric field about 6.6 MV/cm higher than [BMIm][NTf<sub>2</sub>]. It was recently found that, irrespective of the nature of anion, [BMIm]-based ILs with various anions show comparable polarities ( $E_{\text{T}}(30) = 50.5\text{--}52.9$  kcal/mol),<sup>45</sup> while in this case they show obviously anion-dependent electric fields. This discrepancy could be due to that the polarity probe (usually Reichardt's dye) preferably interacts with cation moiety, while VSE spectroscopy is demonstrated by both the cation and the anion.

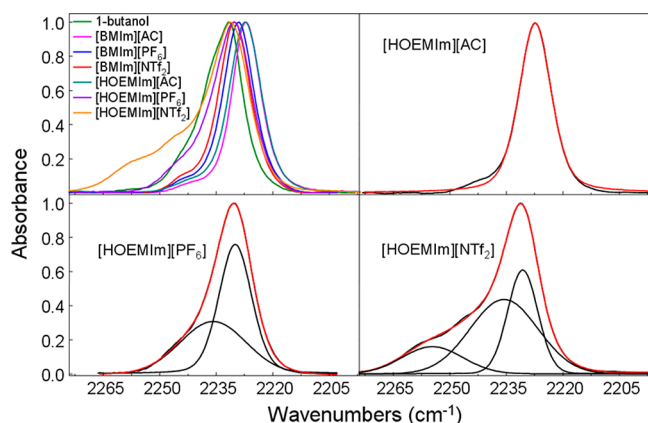
**3.4. Effect of Alkyl Chain Length on  $\nu\text{CN}$ .** With lengthening the alkyl chain from ethyl to decyl, the  $\text{C}\equiv\text{N}$  stretching vibration in all [C<sub>n</sub>MIm][BF<sub>4</sub>]-based ILs lie in the range of 2228.5–2228.8  $\text{cm}^{-1}$ , much narrower (0.3  $\text{cm}^{-1}$ ) than that of [BMIm]-based ILs with various anions (4  $\text{cm}^{-1}$ ), thus leading to comparable electric field determined by VSE. It is demonstrated by molecular dynamics simulations and experiments that imidazolium ILs possess nanostructured characteristics dramatically different from homogeneous media.<sup>21,73</sup> Usually, two specific regions coexist within the bulk of ILs, in particular for ILs with long alkyl chain: a nonpolar domain due to aggregation of alkyl chains and a polar domain due to the three dimensional  $\pi$ -stacking and mutual association of the charged imidazolium ring and anions. The aforementioned result in [BF<sub>4</sub>]-based ILs thus suggests that  $\text{C}\equiv\text{N}$  is less affected by the nonpolar domain, but preferably locates itself well in the charge domain. The driving force may be the electrostatic interaction between the polar  $\text{C}\equiv\text{N}$  group and ions, and/or the  $\pi$ - $\pi$  stacking between benzene and imidazolium moieties such as in ILs–aromatic mixtures.<sup>74</sup> This conclusion is further supported by the observation of concentration-independent  $\nu\text{CN}$  in ILs as discussed above. A careful look at the narrow region of  $\text{C}\equiv\text{N}$  stretching vibration found that the  $\nu\text{CN}$  does not monotonously red shift with

lengthening the alkyl chain. Interestingly, it first blue-shifts ([EMIm][BF<sub>4</sub>] > [BMIm][BF<sub>4</sub>] > [HMIm][BF<sub>4</sub>]) and then red-shifts ([HMIm][BF<sub>4</sub>] < [OMIm][BF<sub>4</sub>] > [DMIm][BF<sub>4</sub>]) to even its initial value. This result reinforces the view of ILs as structured media composed of nonpolar domain and ionic network. First lengthening the alkyl chain from ethyl to hexyl results in a large steric hindrance thus reduces the interaction between  $\text{C}\equiv\text{N}$  and polar domain, while further lengthening the alkyl chain to decyl, much larger and more nonpolar domains in ILs are liable to form due to increased aggregation of long alkyl chain,<sup>57</sup> and ILs appear to be more inhomogeneous at the microstructure level, leading to a similarity between the charge domain in [DMIm][BF<sub>4</sub>] and [EMIm][BF<sub>4</sub>]. It is known from theoretical and experimental works that, due to the microscopically inhomogeneity, solutes dissolved in ILs, depending on their chemical nature, tend to reside in varied environments of an ILs.<sup>75–77</sup> Generally, solute molecules at low concentrations are found in the domains for which the affinity is the greatest. For example, as indicated by molecular dynamics simulations, nonpolar molecules tend to reside in the nonpolar domains because of the cohesive energy of the charged groups, whereas polar solutes reside mainly in the ionic networks.<sup>76,77</sup> Although this work shows that benzonitrile is sensitive to the local environment in ILs, its preferential location in the charge domain suggests that it could not be a suitable probe molecular to report the nonpolar domain in ILs. To address this issue, a nonpolar molecule probe is required.<sup>75</sup>

As shown in Table 2, although the VSE electric fields determined by benzonitrile are somewhat less than that determined by EtSCN, the changing trend along with anion or alkyl chain length is same each other. Note that in some cases benzonitrile may be a better probe since EtSCN is chemically reactive to the [AC]-based ILs as observed in our experiment.

### 3.5. IR Spectra of Benzonitrile in Hydroxyl ILs.

Different from non-hydroxyl ILs,  $\text{C}\equiv\text{N}$  stretching vibration in 1-(2-hydroxyethyl)-3-methylimidazolium-based hydroxyl ILs show an anion-dependent asymmetry and in most cases an attempt to fitting the band into a single component is unsuccessful. Figure 7 shows the deconvoluted spectra of  $\text{C}\equiv\text{N}$  stretching vibration in three typical hydroxyl ILs, i.e., [HOEMIm][AC], [HOEMIm][PF<sub>6</sub>], and [HOEMIm][NTf<sub>2</sub>]. Table 3 lists the experimentally determined and fitted parameters. These results mean that the hydroxyl ILs indeed behave as not aprotic but protic solvents toward  $\text{C}\equiv\text{N}$  of benzonitrile, which is due to the presence of OH, a better



**Figure 7.** Normalized IR spectra of C≡N stretching vibration of 100 mM benzonitrile in hydroxyl ILs, and fitting spectra of [HOEMIm][AC], [HOEMIm][PF<sub>6</sub>], and [HOEMIm][NTf<sub>2</sub>]. The global fit is in red. For the deconvolution of other hydroxyl ILs, see Figure S2 in the Supporting Information.

hydrogen-bonding donor in the imidazolium cation than C2–H.<sup>45,78</sup> More specifically, all hydroxyl ILs can be classified into three groups according to their spectral profiles. (I) The C≡N stretching vibration in [HOEMIm][AC] is nearly constant in position but slightly wider than that in non-hydroxyl ILs ([BMIm][AC]). (II) The observed bands in [HOEMIm][NO<sub>3</sub>], [HOEMIm][ClO<sub>4</sub>], [HOEMIm][BF<sub>4</sub>], and [HOEMIm][PF<sub>6</sub>] can be deconvoluted into two compositions; one is intense and anion-dependent with frequency less than 2230 cm<sup>−1</sup>, and the other is weak and is nearly constant at 2236 cm<sup>−1</sup>. (III) For [HOEMIm][NTf<sub>2</sub>], in addition to the above two components, another wide composition around 2255 cm<sup>−1</sup> is observed. According to the previous result in alcohol,<sup>26,34,50</sup> the low-frequency component (<2230 cm<sup>−1</sup>) in all hydroxyl ILs could be ascribed to “free” benzonitrile (F), while the second one could be ascribed to benzonitrile with  $\sigma$ -type hydrogen bond (H). The unexpected high-frequency component in [HOEMIm][NTf<sub>2</sub>] is speculated to be C≡N groups forming either two or more (clusters) hydrogen bonds as observed in acetonitrile– or benzonitrile–water mixtures.<sup>51,79</sup>

Boxer et al. reported that, for protic molecular solvents,<sup>68</sup>  $\nu$ CN can be decomposed into both electrostatic and H-bonding contributions, and the corresponding electric field can be

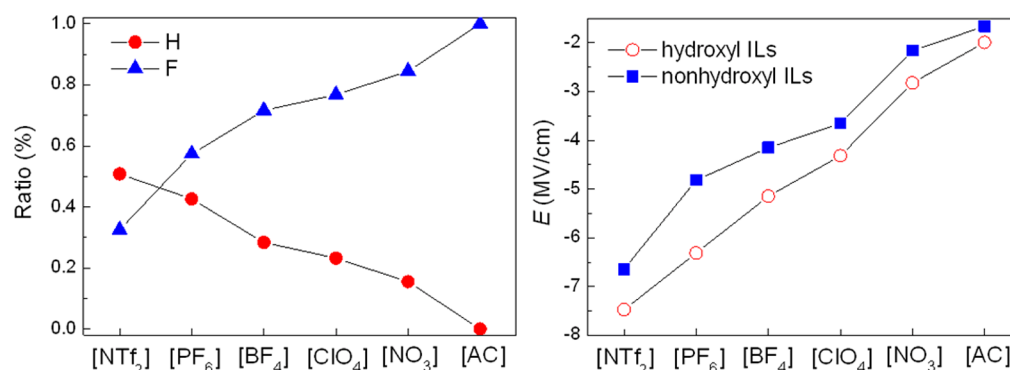
determined by VSE through subtracting the H-bonding contribution. Analogous to the conclusion from non-hydroxyl ILs, in the case of hydroxyl ILs, the electric fields thus can be determined by using the “free” component (F) of  $\nu$ CN as a sensitive probe. As shown in Table 3 and Figure 8, the peak position, fwhm and changing trend of F are consistent with that in non-hydroxyl ILs, indicating that the local environment of “free” benzonitrile molecules and intrinsic electric fields in the hydroxyl ILs are less affected by hydroxyl functionalization. The small quantitative difference in the electric field between non-hydroxyl and hydroxyl ILs, ca. 0.6–1.5 MV/cm, might come from the different substitution (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>– versus HO–(CH<sub>2</sub>)<sub>2</sub>–).

As for the H component, in addition to its high frequency, the fwhm (ca. 20 cm<sup>−1</sup>) is obviously much higher than those of non-hydroxyl ILs and F. It was reported by Samanta et al. that the solvation dynamics of hydroxyl ILs are substantially slower than that of non-hydroxyl ILs because of the hydrogen-bonding interaction between the probe molecule and hydroxyl,<sup>78</sup> which may account for this wide line width. Its composition monotonously increases in the following order: [AC] < [NO<sub>3</sub>] < [ClO<sub>4</sub>] < [BF<sub>4</sub>] < [PF<sub>6</sub>] < [NTf<sub>2</sub>], as shown in Figure 8. Such changing trend is opposite to that of F (Figure 8) but similar to the case of  $E_T^N$  and  $\alpha$  of the hydroxyl ILs (Table 3). Our previous work also demonstrated that the polarity of hydroxyl ILs with various anions increases in the same trend, although their corresponding non-hydroxyl ILs possesses comparable polarity.<sup>45</sup> The anion-dependent ratio of H component in hydroxyl ILs is thus due presumably to the differentiating effect of hydroxyl on the H-bonding formed between hydroxyl and anions (expressed as OH $\cdots$ X),<sup>45</sup> which further results in the difference in H-bonding between lone pair electrons on the nitrile group and proton of the OH (C $\equiv$ N $\cdots$ H(O) $\cdots$ X as shown in Figure 9), and gives rise to several distinct solvation states (hydrogen of different freedom and acidity) and the subtle difference in the local environments experienced by the nitrile group. It should be noted that the H component is nearly constant in central frequency (ca. 2235.7 cm<sup>−1</sup>), and the H-bonding contribution ( $\nu$ H– $\nu$ F) to  $\nu$ CN in all hydroxyl ILs is ca. 5–8 cm<sup>−1</sup>, less than the cases in water (10 cm<sup>−1</sup>) and trifluoroethanol (18 cm<sup>−1</sup>) measured by EtSCN.<sup>68</sup>

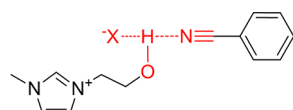
**Table 3.** C≡N Stretching Vibration of Benzonitrile in Hydroxyl ILs and Molecular Solvents, Together with Their Polarity and Kamlet–Taft Parameters<sup>a</sup>

ILs	$\nu$ CN <sup>b</sup>	fwhm <sup>b</sup>	ratio (%) <sup>c</sup>	$E_T^{N_d}$	$\pi^*{}^d$	$\alpha^d$	$\beta^d$	$\Delta E$ (MV/cm)
[NTf <sub>2</sub> ]	2230.6	9.4	32.5	0.929	1.03	1.17	0.34	−7.5
	2235.6	21.2	50.8					
	2254.6	19.0	16.7					
[PF <sub>6</sub> ]	2229.9	10.3	57.4	0.957	1.11	1.17	0.15	−6.3
	2235.8	20.5	42.6					
[BF <sub>4</sub> ]	2229.2	9.9	71.6	0.920 <sup>e</sup>	1.16 <sup>e</sup>	1.05 <sup>e</sup>	0.22 <sup>e</sup>	−5.1
	2235.8	20.0	28.4					
[ClO <sub>4</sub> ]	2228.7	10.4	76.8	0.914	1.13	1.06	0.16	−4.3
	2235.6	19.3	23.2					
[NO <sub>3</sub> ]	2227.8	10.0	84.5	0.769	1.11	0.77	0.65	−2.8
	2235.7	19.8	15.5					
[AC]	2227.3	10.1	100.0	0.633	1.04	0.53	0.90	

<sup>a</sup>Data of [HOEMIm][Cl] is unavailable due to its solid state at room temperature. <sup>b</sup>In cm<sup>−1</sup>. <sup>c</sup>The composition calculated by the area of each component. <sup>d</sup>Data from ref 45. <sup>e</sup>Data from ref 46.



**Figure 8.** F and H compositions of  $\nu$ CN in hydroxyl ILs (left) and electric field in non-hydroxyl and hydroxyl ILs (right) as a function of anions.



**Figure 9.** Cartoon illustrating plausible interaction between anion, hydroxyl group, and benzonitrile. The dotted lines indicate hydrogen bonds.

#### 4. CONCLUSION

In summary, the  $\text{C}\equiv\text{N}$  stretching vibration of benzonitrile in a series of imidazolium-based non-hydroxyl and hydroxyl ILs is investigated in detail. All non-hydroxyl ILs are aprotic solvent-like toward benzonitrile, wherein  $\text{C}\equiv\text{N}$  exists as a free state. The  $\nu$ CN decreases obviously with increasing the effective anion charge while is less affected by the alkyl chain, indicating that the nitrile in ILs is buried in the charge domain. The  $\nu$ CN can thus be principally ascribed to the intrinsic electric field, which can be directly determined by the VSE method. In hydroxyl ILs, in addition to the free  $\text{C}\equiv\text{N}$  as observed in non-hydroxyl ILs, there is still anion-dependent hydrogen-bonded  $\text{C}\equiv\text{N}$  resulting from acidic hydrogen of OH. Moreover, the composition of hydrogen-bonded  $\text{C}\equiv\text{N}$  in hydroxyl ILs is anion-dependent, and is dependent on the HBA ability of OH. The sensitivity of  $\text{C}\equiv\text{N}$  stretching vibration in ILs does indeed provide a simple method to probe the local solvent environment of ILs. Notation is that due to its polar nature and preferential location in the charge domain, benzonitrile could not be a versatile probe for the whole microheterogeneous ILs.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The  $[\text{C}\equiv\text{N}]$  stretching vibration vs the  $E_{\text{T}}\text{N}$ ,  $\pi^*$ , HBD ( $\alpha$ ), and HBA ( $\beta$ ) scales of [BMIm]-based ILs, deconvolution of  $\text{C}\equiv\text{N}$  stretching vibration in [HOEMIm][ $\text{NO}_3$ ], [HOEMIm][ $\text{ClO}_4$ ], and [HOEMIm][ $\text{BF}_4$ ]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Notes

The authors declare no competing financial interest.

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