Intermolecular Interactions and Vibrational Perturbations within Mixtures of 1-Ethyl-3-methylimidazolium Thiocyanate and Water

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ABSTRACT

A Raman spectroscopic analysis of the room temperature ionic liquid 1-ethyl-3-methlimidazolium thiocyanate, [EMIM][SCN], has revealed that certain stretching vibrations associated with both the anion and cation shift to higher energy (or blue shift) as water is introduced to the system (by up to 15 cm^{-1} for a CH stretching mode associated with $EMIM^+$ and up to 12 cm^{-1} for the CS stretch of SCN^-). Density function theory was employed to gain molecular level insight into the origins of these spectral perturbations by computing changes in the structures, energetics and harmonic vibrational frequencies of the [EMIM][SCN] ion pair as a single explicit water molecule was added to the system. The computed harmonic vibrational frequency shifts for the low-energy structures of the ion pair and the corresponding monohydrated complex reproduce the experimentally observed trends. These results indicate that the donation of a hydrogen bond from water to the N atom of SCN^- produces the blue shifts associated with the CN and CS stretching modes. In contrast, the vibrational frequency shifts associated with CH stretches of $EMIM^+$ do not appear to require a direct interaction with the water molecule.

INTRODUCTION

Ionic liquids are a class of salts with a low melting point. Particular attention is given to room temperature ionic liquids (RTILs), which are known as so-called "designer solvents" due to the tunability of many of their physical properties. RTILs also generally have a high thermal stability, low vapor pressure, and high conductivity.[1-3] Ionic liquids experience a variety of intermolecular forces, including electrostatic interactions (charge-charge, charge-dipole, etc), hydrogen bonds, and dispersion interactions. Hydrogen bonds, in particular, play important roles in stabilizing the structures of various ionic liquids, as the direction and strength of hydrogen bonding networks has been found to have a strong impact on their structure and properties. Due to the large number of possible ionic liquids, a good understanding of their structure and intermolecular interactions is important to being able to select or design application-specific ionic liquids with tailored properties. A large number of spectroscopic, computational, and thermophysical studies have been previously performed to determine the structure and interactions of pure RTILs.[4-13]

An active area of research in RTILs is that of experimental and theoretical characterization of mixtures containing RTILs and cosolvents, which are traditional molecular solvents with water being one of the most important.[14-47] Many RTILs are very hygroscopic, and it is difficult to eliminate all traces of water from a RTIL, which means that many RTILs will contain some amount of water in most applications.[17] In addition, water can be intentionally added to a RTIL in order to create a mixture with certain desired properties. Water has been shown to have a significant impact on many of the properties of RTILs, including viscosity, conductivity, polarity, solubility and melting point.[14-16] These properties have significant effects on applications of RTILs, making understanding these changes and their underlying structural causes significant in RTIL research.

1-Ethyl-3-methylimidazolium thiocyanate [EMIM][SCN] is a RTIL that has shown promise for use in SO_2 capture,[54, 55] as an electrolyte,[56-60] and to separate a variety of compounds.[61-63] Many studies have previously characterized the properties of [EMIM][SCN].[48-74] For example, Wulf and colleagues used tetrahertz, far-infrared, and Raman spectroscopy to demonstrate that [EMIM][SCN] possesses hydrogen bonds between the anions and the hydrogen atoms on the imidazolium ring (i.e., CH···anion interactions).[52] Yamada and colleagues studied the vibrational modes of water molecules in solution with [EMIM][SCN] and other RTILs using infrared (IR) spectroscopy in order to compare variations of the anion and alkyl group length. They found that there was evidence of hydrogen bonding between the anions and water molecules.[53] Domańska and colleagues found that the density of the RTIL decreases as water is added, and that excess molar volume measurements indicate that water weakens the interactions in the solution.[69] Vataščin and colleagues studied mixtures of the RTIL and water, finding a positive excess entropy that suggests there is a less organized structure upon the addition of water.[73] Weber and Kirchner also studied this ionic liquid with *ab initio* molecular dynamics and found that SCN^- prefers to orient with the cation via π-stacking interactions with the imidazolium ring.[51] Many other studies have also characterized [EMIM][SCN],[48, 49, 64-68, 70-72] but surprisingly no studies have addressed the structure of hydrogen bond networks in mixtures of water and [EMIM][SCN] with vibrational spectroscopy.

Raman spectroscopy is a powerful tool for examining hydrogen bonded networks, as changes in the strength of hydrogen bonds alter the length of the associated covalent bond, which frequently causes a shift in a peak (or peaks) within the Raman spectrum.[75-84] Using density functional theory (DFT) to accurately predict vibrational frequency shifts within hydrogen bonded systems is quite prominent in literature.[85-90] Hydrated nitrogen containing heterocycles are of particular interest because the ring breathing modes can show progressive frequency shifts that correlate to an increase of water content within the sample.[85, 86] Pyrimidine is a very common example of this concept, where the ν_1 ring breathing mode will shift by up to +14 cm^{-1} with a mole fraction of water equaling 0.9 (χ_{H_2O} = 0.9), when compared to the non-hydrated system.[87-89] Multiple theoretical studies have shown that select density functionals, like B3LYP and M06-2X, can quantitatively predict the ν_1 frequency shift to within 1 cm^{-1}.[87-89] Since there are some structural similarities between pyrimidine and [EMIM][SCN], these density functionals were chosen to characterize this RTIL. The combination of Raman spectroscopy with computational characterization allows geometries that depict various hydrogen-bonded topologies of the cation, anion and water molecules to be examined in detail. The present study investigates the intermolecular interactions present in [EMIM][SCN] and attempts to elucidate how these interactions are affected by the addition of water molecules.

THEORETICAL METHODS

The H_2O, SCN^-, $EMIM^+$, [EMIM][SCN], and hydrated [EMIM][SCN] structures were optimized using the B3LYP[91, 92], B3LYP-D3[91-94], M06-2X[95] and ωB97XD[96] density functionals with Dunning's correlation consistent triple-ζ basis set augmented with diffuse functions on non-hydrogen atoms (cc-pVTZ for H and aug-cc-pVTZ for C, N, O and S; denoted haTZ).[97, 98] Harmonic vibrational frequencies were computed to confirm that all structures corresponds to minima on each potential energy surface. All computations were performed with the `Gaussian09` software package[99] with pure angular momentum (5d and 7f) atomic orbital basis functions and a pruned numerical integration grid having 99 radial shells and 590 angular points per shell. All electronic energies were converged to at least 1.0 x 10^{-10} E_h and the maximum Cartesian forces in the optimized structures were below 1.5 x 10^{-5} E_h a.u. $^{-1}$.

EXPERIMENTAL METHODS

1-Ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN]) was purchased from Ionic Liquids Technologies, Inc. (*io-li-tech*) and was dried under vacuum before use. The ionic liquid was transferred into a sealed cuvette inside of a glove box with a nitrogen atmosphere. Water was added to the cuvette with a microliter syringe. Raman spectra were taken of the ionic liquid-water solutions at various mole fractions of water, $\chi_{H_2O} = 0.0, 0.2, 0.4, 0.6, 0.7, 0.8, 0.9$, where $\chi_{H_2O} = \chi_{H_2O} / (\chi_{H_2O} + \chi_{[EMIM][SCN]})$. The spectra were taken over a range of 100 - 4000 cm^{-1}. The Raman spectrometer was a LabRAM HR Evolution spectrometer with 600 grooves/mm grating, and a 785 nm laser as the excitation source. All obtained spectra were normalized and smoothed.

STRUCTURES AND ENERGETICS

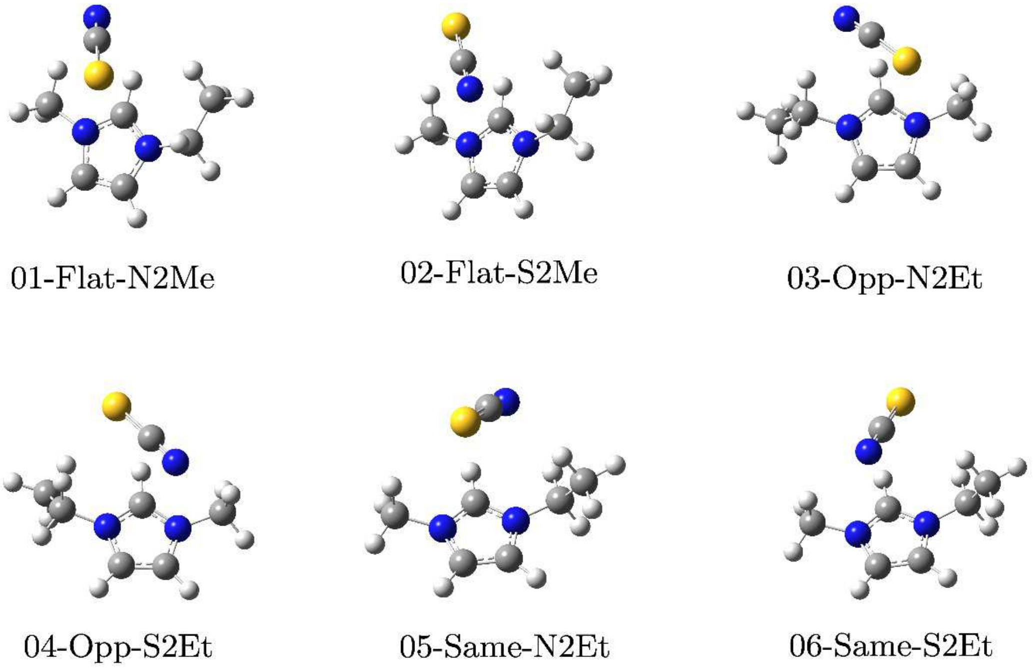
The DFT computations identified two distinct EMIM$^+$ minima that differ only by the orientation of the ethyl group relative to the ring-plane. The C_1 structure has the C-C bond of the ethyl group oriented roughly perpendicular to the imidazolium ring, and it has an electronic energy ca. 0.5 kcal mol^{-1} lower than that of the C_s conformer in which both C atoms of the ethyl chain are in the plane of the 5-membered ring.

More than 34 initial [EMIM][SCN] configurations were generated systematically by varying the orientation of the SCN$^-$ fragment about the edges and faces of the two EMIM$^+$ rotamers (C_1 and C_s). When geometry optimizations are carried out with the B3LYP-D3, M06-2X and ωB97XD functionals on these staring structures, most collapse to the six low-energy minima shown in Figure 1, in which the SCN^{-} fragment is roughly parallel to one of the faces of $EMIM^{+}$. For readers interested in the structural details of these minima, another perspective in provided in the Supporting Information (Figure S1) along with their Cartesian coordinates. The structures in Figure 1 are within 2 kcal mol^{-1} of the configuration with the lowest energy, but the Supporting Information includes data for [EMIM][SCN] structures with slightly larger relative electronic energies. When SCN^{-} interacts with the C_s $EMIM^{+}$ rotamer, both faces are equivalent, and this situation is denoted by the "Flat" label in the figures and tables. In contrast, two distinct faces are available when the ethyl group is perpendicular to the $EMIM^{+}$ ring where the SCN^{-} fragment can reside on the same or opposite face of the ring (denoted by "Same" and "Opp", respectively). An additional label is added to denote whether the N or S atom within SCN^{-} is canted towards the methyl (Me) or ethyl (Et) group (e.g., "N2Me" or "S2Et").

It should be noted that the B3LYP functional gives qualitatively different structures. When the D3 dispersion correction is omitted, B3LYP geometry optimizations only lead to minima in which the SCN^{-} essentially lies in the plane of the $EMIM^{+}$ ring, interacting via CH···anion contacts with the Me, Et, and/or the imidazolium ring. None of these B3LYP optimized structures correspond to minima with the B3LYP-D3, M06-2X and ωB97XD functionals. These results showcase how important dispersion can be for reliably describing these non-covalently bound systems. Consequently, the B3LYP results are excluded from the remainder of this study.

Motivated by the hydrogen bonding motifs observed in prior theoretical studies of SCN^{-} hydration, [100, 101] initial configurations of the monohydrated [EMIM][SCN] complex were generated by adding a single H_2O molecule in positions where it could donate a hydrogen bond to N, to S or to the π electron cloud of SCN^{-}. After B3LYP-D3, M06-2X and ωB97XD geometry optimizations most structures collapse to the six low-energy minima shown in Figure 2 that are within 2 kcal mol^{-1} of the configuration with the lowest electronic energy. The Supporting Information also reports data for other monohydrated [EMIM][SCN] minima with relative electronic energies up to 4 kcal mol^{-1}. As with the isolated ion pairs, the B3LYP-D3, M06-2X and ωB97XD optimized monohydrated [EMIM][SCN] structures are qualitatively similar. For brevity, only the B3LYP-D3 data is reported in the paper, but the corresponding M06-2X and ωB97XD results can be found in the Supporting Information. Additionally, Cartesian coordinates are provided for all structures within the Supporting Information.

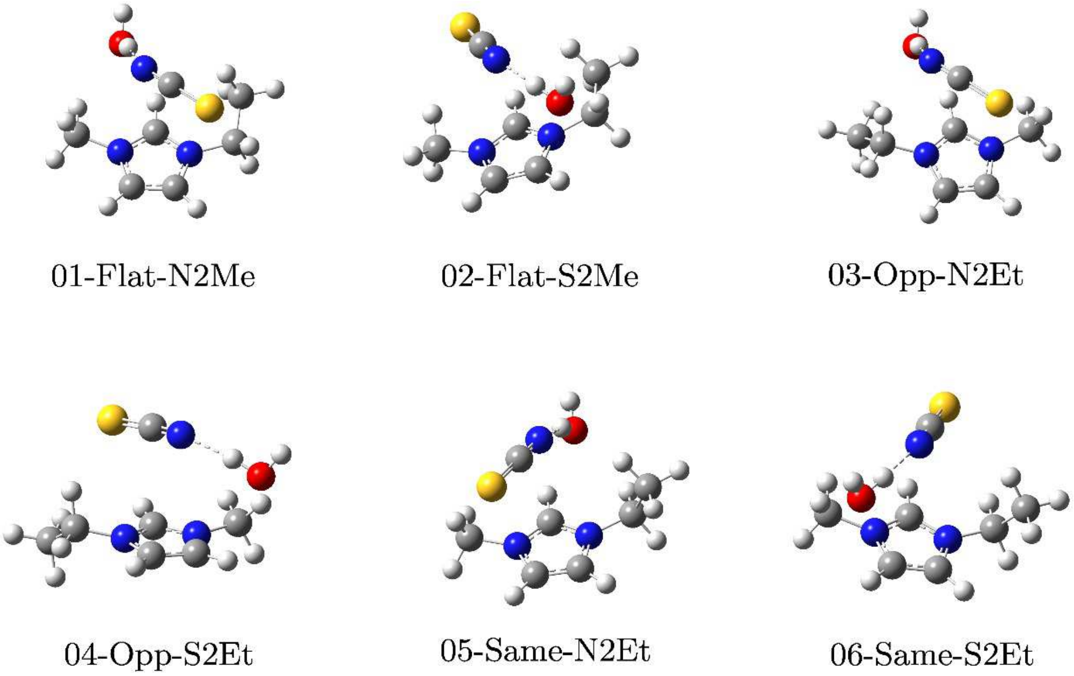
Table 1 shows the electronic and zero-point vibrational energy (ZVPE) corrected relative energies (ΔE_e and ΔE_0, respectively) for the [EMIM][SCN] structures, where the 06-Same-S2Et configuration has the lowest electronic energy with all three functionals. Table 1 also includes the relative energetics for the monohydrated [EMIM][SCN] structures. The B3LYP-D3/haTZ computations indicate that the 05-Same-N2Et configuration has the lowest electronic energy, whereas structure 06-Same-S2Et has the lowest energy after the ZPVE corrections are included. The same conclusion is reached with the ωB97XD functional, but the M06-2X computations indicate the latter structure has the lowest energy with and without the ZPVE correction. These two structures, 05-Same-N2Et and 06-Same-S2Et, are quite similar with the only difference being that either the nitrogen or the sulfur atom within SCN^{-} is canted towards to the ethyl group.



01-Flat-N2Me 02-Flat-S2Me 03-Opp-N2Et

04-Opp-S2Et 05-Same-N2Et 06-Same-S2Et

Figure 1. Low-energy [EMIM][SCN] structures.



01-Flat-N2Me 02-Flat-S2Me 03-Opp-N2Et

04-Opp-S2Et 05-Same-N2Et 06-Same-S2Et

Figure 2. Low-energy monohydrated [EMIM][SCN] structures.

Table 1. Relative electronic B3LYP-D3/haTZ energies (ΔE_e in kcal mol^{-1}) and zero-point vibrational energy corrected relative energies (ΔE_0 in kcal mol^{-1}) for the [EMIM][SCN] and [EMIM][SCN] H_2O structures.

	[EMIM][SCN]		[EMIM][SCN] H_2O	
ID Configuration	ΔE_e	ΔE_0	ΔE_e	ΔE_0
01-Flat-N2Me	+0.86	+0.95	+0.69	+0.79
02-Flat-S2Me	+0.46	+0.53	+0.60	+0.56
03-Opp-N2Et	+1.51	+1.44	+1.29	+1.28
04-Opp-S2Et	+0.97	+0.92	+0.97	+0.90
05-Same-N2Et	+0.13	+0.19	0.00	+0.12
06-Same-S2Et	0.00	0.00	+0.08	0.00

FREQUENCY ANALYSIS

Figure 3 shows the Raman spectra for all solution concentrations (χ_{H_2O} = 0.0, 0.2, 0.4, 0.6, 0.7, 0.8, 0.9) over the entire measured range (100 - 4000 cm^{-1}). Table 2 reports select stretching frequencies for the non-hydrated (χ_{H_2O} = 0.0) [EMIM][SCN] system that were experimentally, and theoretically determined within the present study and in previous Raman investigations.[27, 66, 75, 102] Additionally, this table reports experimental frequency shifts upon hydration with a mole fraction of χ_{H_2O} = 0.9 and theoretical Boltzmann weighted frequency shifts associated with the monohydrated structures depicted in Figure 2. Further information about the Boltzmann weighted frequencies are provided in the Supporting Information, along with the harmonic vibrational frequencies and Raman scattering activities for all structures.

Based on prior spectroscopic studies and our DFT computations, the prominent peak located near 2055 cm^{-1} can be assigned as the CN stretching mode within thiocyanate,[66, 102] as shown in Figure 3. This peak blue shifts by +9 cm^{-1} as the mole fraction is increased, seen in Figure 4a, and the Boltzmann weighted CN stretching frequency shift induced by a single water molecule matches the experimental value exactly (Table 2). The peak at 738 cm^{-1} can be assigned to the CS stretching mode within thiocyanate based on previous assignments of [EMIM][SCN] and the DFT harmonic vibrational frequencies computed in this study.[102] This peak, shown in Figure 4b, blue-shifts by +12 cm^{-1} as the water mole fraction is increased. The B3LYP-D3/haTZ Boltzmann weighted CS stretching frequency shift induced by a single explicit water molecule overestimated the experimental observation by 10 cm^{-1}.

Two close peaks located at approximately 2939 and 2955 cm^{-1} also blue shift by +6 and +5 cm^{-1}, respectively, as the mole fraction of water increases. These peaks are shown in Figure 4c, and the DFT computations performed in the present study suggests that they are associated with CH synchronous stretching modes of the Et and Me CH_3 groups, respectively. These assignments and frequencies are consistent with, and nearly identical to those for the closely related [EMIM][PF6] system (within 4 cm^{-1}).[75] The frequency shifts from the addition of one explicit H_2O molecule predicted by the B3LYP-D3/haTZ harmonic computations reported here are within 3 cm^{-1} of the experimental values.

The final two peaks analyzed in the spectrum are located at 3096 and 3155 cm^{-1} as shown in Figure 3. Our DFT computations indicate these peaks correspond to the CH stretching modes on the imidazolium ring. The lower energy peak is associated with the H atom at the C2 position between the N atoms whereas the latter is from the synchronous stretching of the two adjacent CH bonds at C4 and C5. These frequency assignments are within 2 cm^{-1} of a closely related experimental study of $EMIM^+$ in which it was paired with a different anion (TfO^-).[27] In this study, of these peaks blue shift as the mole fraction of water increases, shifting by +12 and +15 cm^{-1}, respectively. The Boltzmann weighted prediction dramatically overestimates the CH frequency shift at C2 by +36 cm^{-1}. In contrast, the computed Boltzmann weighted frequency shift for the other CH stretching mode is within 6 cm^{-1} of the experimental value. The larger deviation at C2 stems from an anomalously large shift (+100 cm^{-1}) associated with that mode for the 02-Flat-S2Me hydrated complex. For comparison, the shifts for the other five structures range from +11 to +44 cm^{-1}. When the outlier is omitted from the analysis, the Boltzmann weighted frequency shift moves 20 cm^{-1} closer to the experimental value.

Table 2. Select stretching modes and associated shift that were experimentally (Prior Work and This Work) and theoretically (ω) determined for the non-hydrated [EMIM][SCN] system, as well as experimental frequency shifts where χ_{H_2O} = 0.9 (Δν) and theoretical B3LYP-D3/haTZ Boltzmann weighted monohydrated frequency shifts (Δω), where all values are reported in cm^{-1}.

	Experiment			B3LYP-D3 Boltzmann	
Stretching Modes	Prior Work	This Work	Δν	ω	Δω
ν(CS)	738[a]	738	+12	746	+22
ν(CN)	2054[a,b]	2055	+9	2131	+9
ν(CH-Et)	2942[c]	2939	+6	3040	+3
ν(CH-Me)	2952[c]	2955	+5	3048	+2
ν(CH-C2)	3097[d]	3096	+12	3184	+48
ν(CH-C4/C5)	3157[d]	3155	+15	3297	+9

[a] Ref 102 [b] Ref 66 [c] Ref 75 [d] Ref 27

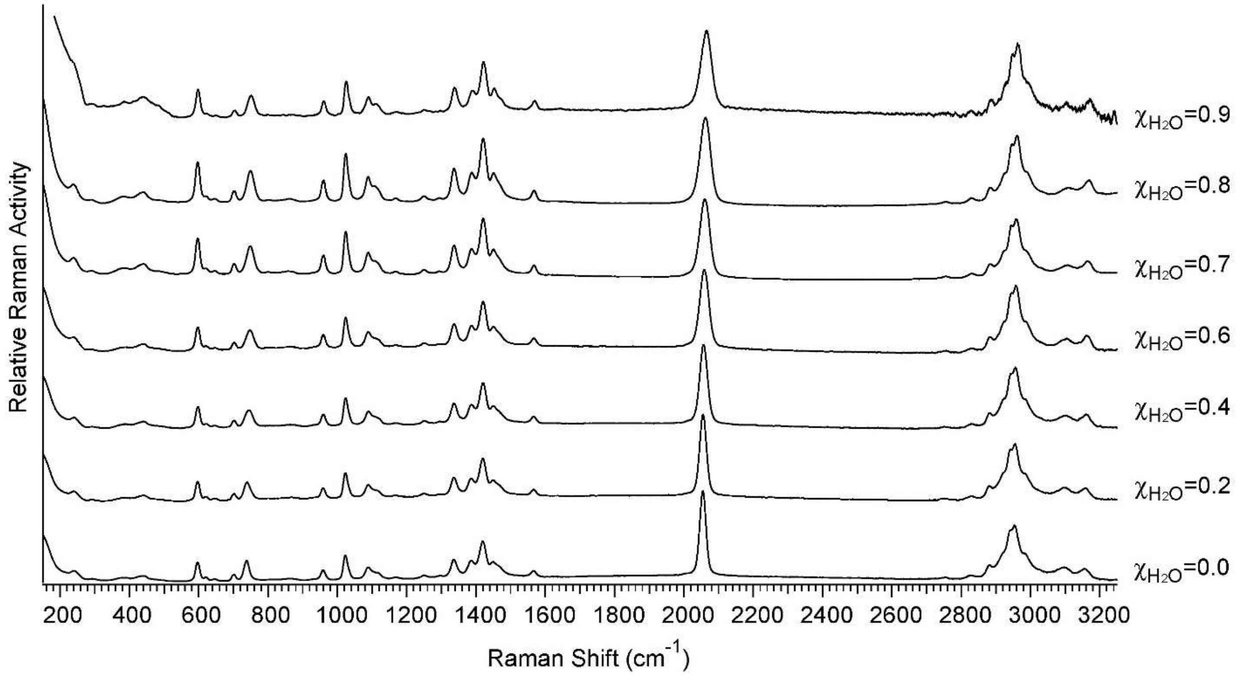


Figure 3. Experimental Raman spectra of [EMIM][SCN] and water at varying water mole fractions.

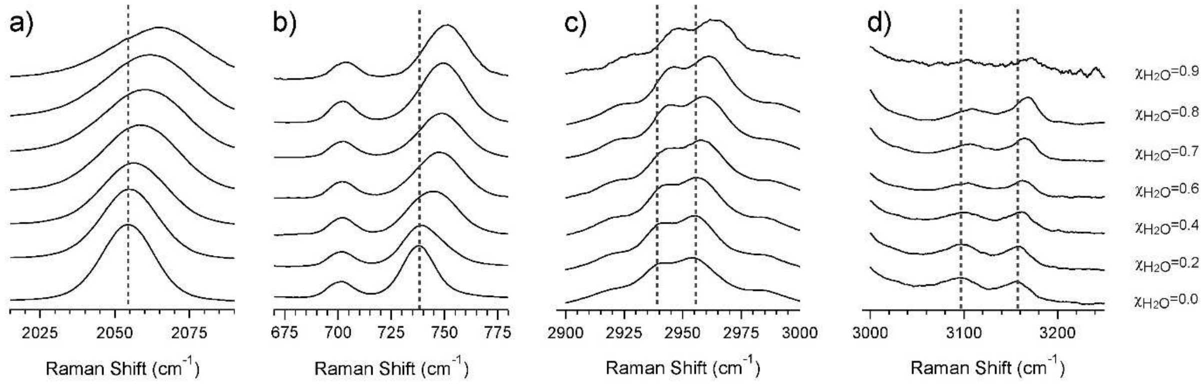


Figure 4. Experimental Raman spectra of [EMIM][SCN] and water at varying mole fractions in the region of the (a) CN stretch, (b) CS stretch, (c) Et and Me CH stretch, (d) C2 and C4/C5 CH stretch.

CONCLUSION

Raman spectroscopy and DFT computations have been used to probe the [EMIM][SCN] RTIL in order to elucidate the structural, energetic, or vibrational perturbations caused by the addition of water. The Raman spectra obtained in this work reveal that the CN and CS stretching frequencies of SCN^- gradually shift to higher energy by as much as 12 cm^{-1} as the mole fraction of water is increased. Similar behavior was also observed for the CH stretching frequencies associated with the $EMIM^+$ moiety (shifts up to +12 cm^{-1}). A variety of low-energy configurations were identified with the B3LYP-D3, M06-2X and ωB97XD methods in which the thiocyanate anion lies "above" and roughly parallel to the face of imidazolium ring, essentially forming a $\pi\cdots\pi$ type contact between the ions. In contrast, characterization of the [EMIM][SCN] ion pair with the B3LYP functional led to qualitatively different structures that could be characterized as edge-to-edge contacts which suggests London dispersion forces play an appreciable role in the intermolecular interactions of this RTIL system. Additional B3LYP-D3, M06-2X and ωB97XD computations indicate that the N atom of SCN^- is the only energetically competitive hydrogen bond acceptor when a single explicit water molecule is added to the system. The corresponding Boltzmann weighted harmonic vibrational frequency computations on the low-energy [EMIM][SCN] and [EMIM][SCN]/H_2O structures qualitatively reproduce the frequency shifts observed in the Raman spectra. Together these results indicate that the spectroscopic perturbations associated with SCN^- stem from direct interactions with the H_2O molecule whereas the shifts of the CH stretching frequencies of $EMIM^+$ are indirectly induced.

ASSOCIATED CONTENT

Supporting Information. The Boltzmann weighting, vibrational frequencies, infrared intensities, Raman activities, and Cartesian coordinated for all optimized structures and complexes are provided at all levels of theory as well as the M06-2X and ωB97XD data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

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