Understanding the Structure of the Hydrogen Bond Network and Its Influence on Vibrational Spectra in a Prototypical Aprotic Ionic Liquid

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Supporting Information

ABSTRACT: Analysis of the hydrogen bond network in aprotic ionic liquid 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide (EMIM-TFSI) has been performed based on structures obtained from ab initio or classical molecular dynamics simulations. Statistics of different donor and acceptor atoms and the amount of chelating or bifurcated bonds has been presented. Most of the hydrogen bonds in EMIM-TFSI are formed with oxygen atoms as hydrogen acceptors; and the most probable bifurcated bonds are those with a mixed pair of oxygen and nitrogen acceptors. Spectral graph analysis has shown that the cations may form hydrogen bonds with up to five different anions and the connectivity of the whole hydrogen bond network is supported mainly by H–O bonds. In the structures of the liquid simulated via force field-based dynamics, the number of hydrogen bonds is smaller and fluorine atoms are the most favored hydrogen acceptors. One-dimensional potential energy profiles for hydrogen atom displacements and corresponding vibrational frequencies have been calculated for selected C–H bonds. Individual C–H stretching frequencies vary by 200–300 cm⁻¹, indicating differences in local environment of hydrogen atoms forming C–H···O hydrogen bonds.

1. INTRODUCTION

Room-temperature ionic liquids (ILs) are salts, typically with bulky organic cations, molten at relatively low temperatures (below 100 °C). Large scientific attention gained by these systems stems from their physicochemical properties and prospective use as alternative solvents or solvents tailored for specific applications.

ILs are composed entirely of ions; therefore, strong electrostatic interactions between charged species occur in the solvent and dominate properties of ILs. Nevertheless, there is a possibility of hydrogen bond (HB) formation in ILs composed of cations with hydrogen atoms and anions with appropriate H-atom acceptors. Although HB effects are weak compared to electrostatic interactions between ions, there is no doubt that hydrogen bonding is present in ILs and its importance for the solvation properties and reactivity of ILs has been recognized.¹,²

Experimental studies on hydrogen bonding in ILs have been supported by theoretical methods. Some recent examples of quantum chemical calculations include investigations of geometries and binding energies of ion pairs,³–⁶ interaction energy decomposition via symmetry adapted perturbation theory,⁷ electrostatic potential analysis,⁸ gas-phase or solid-state calculations of vibrational frequencies and intensities for isolated ion pairs or crystals,⁹,¹⁰ natural bond orbital¹¹ or quantum theory of atoms in molecule analysis for ion pairs⁷,⁸,¹⁰,¹¹ and crystals,⁸,¹¹ and noncovalent interaction index calculations.¹⁰,¹¹ Information on the structure of the liquid, distribution of HB donor and acceptor atoms, and the number of possible HBs is obtainable from molecular dynamics (MD) simulations either employing classical force fields¹²–¹⁵ or based on ab initio methodology.¹⁶ Infrared (IR) spectra of bulk ILs can be calculated from ab initio MD (AIMD) simulations by means of Fourier transform of the autocorrelation function of the dipole moment.¹⁴,¹⁶

Combined experimental and theoretical studies have been extensively used for better understanding effects of hydrogen bonding on physicochemical properties of various aprotic ILs.¹⁸ Several recent works study the H-bonding correlations with the spectroscopic features of selected systems. Gu et al.¹⁹ discussed in details the HBs in the alpha-hydroxy carboxylic acid complexes reviewing current knowledge. Analysis of MD simulations in relation to IR spectroscopic results provides a great opportunity to gain deeper insight into physical properties of considered systems; for example, HB network effects on aggregation of water molecules in mixed solvents.²⁰

A class of commonly investigated prototypical ILs are based on imidazolium derivatives. A summary of vibrational spectroscopy studies on such systems can be found in a recent review.²¹ Interactions in the liquid, its structure, and the

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possibility of hydrogen bonding are usually analyzed based on quantum-chemical calculations for ion pairs and MD simulations.

In our recent work, we performed AIMD simulations for 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (EMIM-TFSI) liquid to study solvent effects on UV–vis and vibrational spectra. The IR spectrum of bulk EMIM-TFSI was calculated in the range of 600–3500 cm⁻¹. In this paper, we used the structures of the IL recorded in the previous study to get a better understanding of the network of HBs in EMIM-TFSI.

We produced statistics of individual bonds with different donors and acceptors and determined the connectivity of the total network of HBs. For the latter purpose, the methodology of spectral graph analysis was used. We also checked the structure of the IL for the presence of special cases of HBs, such as bifurcated or chelating bonds. AIMD simulations are computationally challenging, and despite increasing power of computational resources, classical, inexpensive, MD simulations will continue to be a method of choice for many applications. Therefore, we performed a similar analysis for EMIM-TFSI structures obtained from force field-based simulations to compare the predictions of ab initio and classical MD. Finally, using the geometries from AIMD simulations to construct the potential energy profiles, we calculated vibrational frequencies of one-dimensional (1D) quantum-mechanical oscillators modeling the effects of HBs on the IR spectra.

2. COMPUTATIONAL DETAILS

EMIM-TFSI is a prototypical aprotic IL. HBs in EMIM-TFSI are formed between cations and ions; therefore, they may be classified as doubly ionic HBs.

To test the force field-based MD for this system, we started with classical MD simulations of EMIM-TFSI using NAMD v. 2.12 simulation package. A nonpolarizable force field was based on the OPLS parameterization (including corrections for the cation from ref 30) and nonbonded terms from the Kördemann’s paper. In addition to the nonpolarizable field, we used another parameterization in which polarization effects were taken into account via Drude oscillators. In our simulations, we set the force constant of Drude oscillators to k₀ = 1000 kcal·mol⁻¹·Å⁻². Drude particles were attached to all nonhydrogen atoms. For the polarizable parameterization, polarizabilities of atoms and partial charges were adapted from the APPLLE&EP polarizable force field for liquids and electrolytes. As a test of correctness of the FF parameters, we performed additional simulations in the NPT ensemble. The calculated density of the liquid was 1.515 and 1.521 g/cm³ in nonpolarizable and polarizable FF, respectively; therefore, it deviated less than 0.01 g/cm³ from the experimental value of 1.518 g/cm³.

We performed classical MD simulations for systems of 500 EMIM-TFSI ion pairs in the NVT ensemble at T = 298 K with Langevin dynamics and a time step of 1.0 fs used to integrate the equations of motion. To assess the possible size effects, another series of simulations with 15 ion pairs in the simulation box was performed; the smaller size corresponds to the size of the systems used in ab initio computations. Periodic boundary conditions were applied to the system, with the periodic box size set to reproduce the experimental density of the neat IL. Electrostatic interactions were taken into account via particle mesh Ewald algorithm; cutoff for van der Waals interactions was set to 9 Å (this value was limited by the side length of the periodic simulation box for smaller systems). The length of classical MD simulations comprised 120–150 ns of equilibration stage, and the production part of the trajectory with frames saved every 1 ps (small systems) or 5 ps (large systems) for another 40 ns. As found during analysis of the results, differences between systems with 15 and 500 ion pairs are practically negligible, except for better statistics [smaller standard deviations, smoother radial distribution function (RDF) plots] obtained for large systems. Therefore, in the main paper, we will show only the results of classical MD simulations for 500 EMIM-TFSI pairs; selected parameters are compared for both system sizes in the Supporting Information.

The AIMD structures of the liquid obtained using CP2K v. 2.6.1 software were reused from the Born–Oppenheimer MD simulations performed in our recent paper on solvent effects in EMIM-TFSI. Density functional theory (DFT) methodology with Pade functional and molecularly optimized DZVP basis set was used in simulations; other details can be found in ref 25. In our previous work, this setup of simulations resulted in good reproduction of the experimental IR spectrum of EMIM-TFSI, suggesting that the structure of the liquid and ion–ion interaction have been properly described. For the analysis of HBs reported in this work, we used 40 ps of the AIMD trajectory with frames saved in 1 fs intervals. The results were averaged over the whole production part of the trajectory; therefore, the total number of frames used in averaging was of the same order for classical and AIMD, although the total time of classical simulations was 1000 times longer than the time of AIMD.

Selected frames of the AIMD trajectory were used in a series of single-point energy calculations at the same level of DFT methodology as applied in MD simulations. On the basis of these computations, potential energy profiles for displacements of hydrogen atoms in EMIM cations were constructed. This treatment allowed us to analyze the C–H stretching motions (for C2–H, C4–H and C5–H bonds) and their spectroscopic features in details. These studies were performed based on the 1D potential curves for protons where displacement vectors for hydrogen atoms were along the axis of the considered C–H bonds. Snapshot structures of the analyzed system were extracted every 500 MD steps (equivalent to 0.5 ps). The corresponding internal coordinate (x) was defined as the distance between the hydrogen and carbon atoms. In each scan, the position of the hydrogen atom was changed in steps of 0.05 Å in the range from 0.80 to 2.30 Å with respect to the hydrogen-donating carbon atom; positions of all other atoms in the structure were kept fixed. Each potential for proton motion was created based upon 31 single-point calculations. In each structure of the MD simulation box, five selected HBs were analyzed. Our procedure involved totally 37 200 single-point calculations. This number looks discouragingly large; however, original calculations of 40 ps AIMD trajectory with 1 fs time step required 40 000 calculations; therefore, computational effort for potential energy calculations, although significant, was not larger than that for AIMD simulations. It should be stressed that the big advantage of such a post-MD quantization methodology is the possibility of full parallelization because each single-point energy can be computed independently. This methodology was originally postulated
3. RESULTS AND DISCUSSION

3.1. Structure of the Liquid. Before investigating the HB network in simulated structures, we performed some preliminary analysis of relevant distributions of atoms. In Figure 1, we present RDFs for pairs of imidazolium hydrogen atom and oxygen or fluorine atoms from the anion. The $\text{H}_{\text{Im}}\text{−O}$ and $\text{H}_{\text{Im}}\text{−F}$ RDFs for classical simulations generally agree with the MD results reported for the EMIM-TFSI liquid. In the $\text{H}_{\text{Im}}\text{−O}$ RDFs, there is a well-pronounced peak just above 2 Å, followed by other, lower maxima above 4 Å. The position of the first peak depends slightly on the simulation protocol: in the classical, nonpolarizable simulations, the maximum is located approximately at 2.25 Å and shifts to about 2.2 Å in polarizable FF. In the structures from AIMD, the first maximum appears at about 2.15 Å. Interactions of imidazolium hydrogen atoms with TFSI oxygens in the ab initio simulations are therefore slightly stronger than those in the nonpolarizable force field-based dynamics; inclusion of polarization effects in classical simulations improves agreement with ab initio results. The main maximum in all $\text{H}_{\text{Im}}\text{−F}$ RDFs is located at about 5 Å. In classical MD simulations, there is another, weak maximum at 2 Å, indicating that the probability of finding fluorine atom close to imidazolium hydrogen in the structures obtained from force field-based simulations is larger than that in AIMD trajectories.

The possibility of formation of the X−H···Y HBs depends not only on the H−Y distance but also on the angle formed by the three atoms involved in the HB. In Figure 2, we visualized the probability of finding the Y atom at the $r_{XY}$ distance from the donor atom X, depending on the angle $\alpha_{\text{XHY}}$ between XH and XY vectors. The differences between nonpolarizable and polarizable classical MD are barely noticeable; therefore, in Figure 2, we compared only structures from AIMD and classical nonpolarizable simulations.

In AIMD structures, there is an increased probability of finding an O atom at the distance about 3 Å from the C atom of the imidazolium ring with the $\alpha_{\text{CHO}}$ angle about 30°−40°. In classical NP simulations, this probability maximum moves toward larger angles and longer distances. Finding an oxygen atom at short distance from the carbon atom of the CH$_3$ group is less probable than in the vicinity of imidazolium C atom, even in ab initio simulations; nevertheless, in AIMD structures, there are some oxygen atoms found between 3 and 3.5 Å from the CH$_3$ carbon atom and with the $\alpha_{\text{CHO}}$ angle less than 60°. Only few O atoms can be found within these limits in classical simulations.

Finding an F atom close to the imidazolium carbon atom with a small $\alpha_{\text{CHF}}$ angle is much less probable than finding an oxygen atom in similar location; this probability increases in classical NP simulations compared to AIMD (as already indicated by $\text{H}_{\text{Im}}\text{−F}$ RDFs in Figure 1). On the other hand, there is little difference between distributions of fluorine atoms around CH$_3$ groups obtained from ab initio and classical simulations.
From this part of the analysis, we can conclude that in AIMD structures, most HBs involving imidazolium or CH₃ hydrogen atoms will be formed to oxygen acceptor atom. In classical NP simulations, number of such bonds will be greatly reduced, in particular in the case of CH₃ donor atoms. Distribution of HBs from CH₃ hydrogens to fluorine atoms is expected to be much less affected by the simulation protocol, and the probability of forming a HB between imidazolium H and fluorine atoms, although small, will increase in classical MD structures.

3.2. Statistics of HBs. In order to check our simulated structures for the presence of HBs, we have to set the criteria of existence of a X−H···Y bond between donor X and acceptor atom Y. In this work, we set the following thresholds for HB detection: (1) the X−Y distance less than or equal 3.5 Å and (2) the angle \( \alpha_{XY} \) between XH and XY vectors less than or equal 40°. These values were set based on the previous analysis of HB parameters and are in agreement with geometries of EMIM-TFSI ion pairs calculated in ref 22.

As stated in ref 47, setting the angle limit as a geometrical criterion for the HB detection is problematic; therefore, we focused on the condition that the distance between the proton and the acceptor atom must be shorter than the sum of their van der Waals radii and checked whether it is fulfilled when the above thresholds are used. In Figure 3, we present histograms of H−Y distances between atom pairs selected according to our criteria; the H−O distribution was decomposed into contributions arising from different types of hydrogen atoms (from the imidazolium ring, CH₂, and CH₃ groups, respectively). Maxima for H−F and H−N distributions appear between 2.3 and 2.4 Å, and the maximum for H−O distribution is located at 2.2 Å. From its decomposition, one may note that the distances between oxygen atoms and CH₂/CH₃ hydrogen atoms (maximum at about 2.4 Å) are significantly longer than distances between O and imidazolium H atoms (maximum of the distribution around 2.1 Å), indicating larger strength of the latter bonds. The sum of H and Y Pauling radii equals 2.6, 2.55, and 2.7 Å for Y=O, F, and N, respectively. It is readily noticeable that our thresholds for the X−Y distances and the \( \alpha_{XY} \) angles lead to H−Y distances shorter than the sum of atomic radii, and therefore may serve as geometrical indicators of HBs.

We begin our analysis of the HB network in EMIM-TFSI with the statistics of HBs obtained from AIMD and classical MD simulations. In Figure 4, we show total number of HBs per pair of IL ions and its breakdown into contributions from HBs to different acceptor atoms. In AIMD structures, there are about 3.6 HBs per cation−anion pair, most of which are H−O bonds (2.6 bonds per pair). Bonds to F or N acceptors are less probable, with about 0.7 and 0.3 H−F and H−N bonds per ion pair, respectively.

As stated in ref 47, the number of HBs is significantly smaller in classical MD simulations: the total number of bonds is 1.8 and 2.0 bonds per pair in nonpolarizable and polarizable simulations, respectively. The difference to ab initio structures is mainly due to much smaller number of H−O bonds (0.8−1.0 bonds/pair). Classical simulations predict slightly more H−F bonds and less H−N bonds than AIMD. Inclusion of polarizability in classical force field via Drude oscillators has a rather limited effect on the results toward AIMD values by 0.1−0.2 bonds/ion pair.

Figure 3. Distributions of H−Y distances in H−Y pairs selected according to the geometrical thresholds. Vertical broken lines mark the sum of the van der Waals radii of H and Y atoms.

Figure 4. Average total number of HBs per cation and its breakdown according to different acceptor atoms.

In the next step, we try to analyze the relative abundance of different HBs, presenting for each X−H···Y bond a breakdown into contributions arising from different hydrogen donor atoms X: carbon atoms of the imidazolium ring, carbon atoms from CH₂ groups, and carbon atom from the CH₃ unit (Figure 5). In AIMD structures regardless of the donor atom, most HBs are formed to oxygen atoms: on average, there are 1.2, 1.0, and 0.4 bonds/pair from imidazolium, CH₂, and CH₃ carbon donor atoms, respectively. Taking into account different number of imidazolium, CH₂, and CH₃ hydrogen atoms in the cation (3, 6, and 2, respectively), we can estimate that the probability of a H atom to form a HB is the largest for imidazolium hydrogens and is about two times smaller for CH₂ or CH₃ hydrogen atoms. The average number of 1.22 HBs per imidazolium atom may be further decomposed into contributions of 0.47, 0.43, and 0.32 HBs per C2, C4, and C5 atom, respectively, in accord with expected larger acidity of the C2 atom (numbering of imidazolium atoms is shown in Figure S1 in the Supporting Information). Probability to form a HB to fluorine atom is similar for all types of hydrogen atoms in the EMIM cation; therefore, most H−F bonds (0.4 bond per pair of ions) are formed by CH₃ hydrogens.

In the structures obtained from classical nonpolarizable simulations (NP MD), practically there are no HBs between CH₃ or CH₂ hydrogen atoms and oxygen acceptor. The
number of H−O bonds from imidazolium ring hydrogens is reduced to 0.7 bonds/ion pair. Compared to AIMD results, there is a small increase in the number of H−F bonds, mainly those involving imidazolium H atoms. In classical polarizable simulations, the abundance of different types of HBs is similar to nonpolar MD; the most noticeable difference is the increase of the number of imidazolium H−O bonds by 0.2 bonds/pair to the value of 0.9 bonds/pair. Data shown in Figure 5 confirm the conclusions of the analysis of radial and spatial distribution of acceptor atoms (Figures 1 and 2) that the main difference between ab initio and classical MD is the decrease in the number of H−O bonds and the lack of H−O bonds from CH3 and CH2 groups in classical simulations.

Network of HBs in the liquid may be further complicated because of the possibility of formation of HBs with more than one hydrogen donor or acceptor, that is, chelating or bifurcated bonds.1 The presence of such bonds in EMIM-TFSI is facilitated by the fact that several atoms of EMIM cations may serve as donors, and anions of this IL contain several atoms able to act as proton acceptors. In this work, we considered two kinds of such bonds schematically depicted in Figure 6. Bifurcated HB is a pair of HBs from one X−H donor to two different acceptor atoms (from the same or different TFSI anions). The other type is the chelating bond—a pair of HBs to one acceptor atom from two hydrogen atoms within the same EMIM cation; the hydrogen atoms may be covalently bound to two different or to same donor atoms X.

Information on the number of bifurcated and chelating bonds in the structures obtained from different types of MD simulations is collected in Table 1. As expected, chelating or bifurcated bonds are much less probable than single HBs. The largest number of chelating bonds was found in AIMD structures (0.15 bonds/ion pair). In more than 90% of these bonds, the chelated acceptor Y is an oxygen atom. The number of chelating bonds is reduced to 0.02 bonds/pair in classical NP simulations, and the most probable acceptor is the F atom (66% of chelating bonds). The latter change originates from the fact that most of these bonds are formed between fluorine acceptor and two hydrogen atoms from within the same CH3 group. Polarizable classical simulations yield the ratio of O and F acceptors in chelating HBs similar to nonpolarizable MD. Unlike two other parameterizations, percentage of chelating bonds to nitrogen atom is nonnegligible only in classical polarizable simulations (13% of chelating HBs).

According to Table 1, bifurcated HBs are even less probable than chelating bonds. Although their number does not depend much on the simulation protocol (about 0.05 bonds/pair for AIMD or classical polarizable simulations), their structure significantly differs. In Figure 7, we present detailed breakdown of the number of bifurcated HBs depending on the donor atom and the pair of acceptors. With O, F, and N HB acceptor atoms present in the anion, there are five possible combinations of acceptor atoms (for steric reasons there are no HBs bifurcated to two nitrogen atoms).

In AIMD structures, the most probable is the bifurcation of a HB to the mixed pair of oxygen and nitrogen atoms as

![Figure 5](https://example.com/figure5.png)  
Figure 5. Average numbers of HBs per cation depending on the donor/acceptor atom and the type of MD used in simulations.

![Figure 6](https://example.com/figure6.png)  
Figure 6. Schematic representation of bifurcated and chelating HBs.

<table>
<thead>
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<th>n (chelating), bonds/pair</th>
<th>chelating HBs acceptors, in %</th>
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<td>classical polariz.</td>
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acceptors. There also exist bifurcated bonds to two oxygen or two fluorine atoms as well as to mixed pair of oxygen and fluorine acceptors. The bonding pattern is similar for imidazolium ring and CH$_3$ hydrogen atoms. Conversely, in classical simulations, bifurcated bonds involving O or N acceptor atom are formed only by hydrogen atoms from the imidazolium ring. Regardless of the donor atom X, most bifurcated HBs in classical MD are formed to two fluorine acceptors. Polarization in classical simulations increases the probability of ON or OO acceptor pairs for imidazolium hydrogens; nevertheless, fluorine atoms are still predominant acceptors in bifurcated bonds.

3.3. HB Network and Spectral Graph Analysis. Until now, we discussed only the average numbers of different HBs in the IL. Now, we turn our attention to the whole network of HBs and its connectivity. We start with the analysis of the number of HBs formed by an EMIM cation (Figure 8).

As seen in the top panel of Figure 8, in ab initio structures, cations can form up to 6−7 HBs. The distribution is rather flat, and the most probable are 2 or 3 bonds. Probability that there is no HB formed by the cation at the given moment is less than 10%. Looking at probability distributions of different acceptors, one can see that this result is due to wide distribution obtained for H−O bonds. The most probable is the case when each cation forms one or two HBs to oxygen atoms. On the other hand, for F or N acceptors, the probability distribution has maximum at zero, showing that only few cations form one or sometimes two HBs to fluorine or nitrogen atom.

In classical simulations, all probability distributions (the total and those for different acceptors) have maximum at zero and decay monotonically with increasing number of bonds. At a given time, about 40% of cations is not involved in hydrogen bonding at all. Distribution of bonds for O and F acceptors is similar, only up to 20% of cations forms a HB to such an acceptor atom.
Some more insight into the connectivity of HB network in simulated structures of the EMIM-TFSI liquid may be obtained by means of graph theory; such a methodology was used recently in a study of ion aggregates in salt solutions.\textsuperscript{49} For this purpose, we represent the liquid as an undirected graph consisting of a set of vertices (EMIM and TFSI ions) connected by edges (HBs). We will consider simple graphs as well as more general multigraph representation. In a simple graph, vertices are connected with single edges; thus, we encode only the fact that there is at least one HB between given ions (vertices), without information on the actual number of HBs. In a multigraph, the number of edges between vertices equals the number of HBs between corresponding ions. A schematic example of two graph representations of HBs between ions is shown in Figure 9. In this work, we analyze only HBs between EMIM\textsuperscript{+} and TFSI\textsuperscript{−} ions; therefore, our graphs are bipartite, with anions and cations forming two sets of vertices (white and black circles in Figure 9).

Connectivity of a graph with $N$ vertices is represented as its $N \times N$ adjacency matrix $A$. Diagonal elements of adjacency matrix $A_{ii}$ are equal to 0 and off-diagonal elements $A_{ij}$ equal to $n$ if there are $n$ edges between vertices $i$ and $j$; otherwise, $A_{ij} = 0$. For a simple graph representation, the off-diagonal elements of the adjacency matrix are therefore either 0 or 1. Adjacency matrices corresponding to sample graphs are shown in Figure 9.

A normalized eigenvalue spectrum of the adjacency matrix yields the spectrum of the graph. Let us recall some properties of such spectra. For a set of disconnected vertices (an edgeless graph), the spectrum has only one eigenvalue $\lambda = 0$. If there is a single isolated pair of vertices connected by a single edge, a pair of eigenvalues $\lambda = \pm 1$ appears in addition to the singularity at 0. When the number of edges in the graph increases and they start to form connected network, the eigenvalue spectrum of the connectivity matrix widens and becomes dense. We should also note that a pair of eigenvalues $\pm n$ can appear in the spectrum only if there is at least one vertex with degree (the total number of edges connecting it to other vertices) at least $\lceil n \rceil$, where $\lceil n \rceil$ is the least integer greater than or equal to $n$.

Graph spectra for the HB network in simulated IL structures treated either as simple graphs or multigraphs are displayed in Figure 10. Simple graph representation will give information on the number of the counterions linked via at least one HB to given ion, whereas multigraph representation supplements it by

![Figure 9](image1.png)

**Figure 9.** Representation of HBs in EMIM-TFSI as a simple graph or multigraph with corresponding adjacency matrices.

![Figure 10](image2.png)

**Figure 10.** Spectra of graphs formed by HBs in EMIM-TFSI (for different types of HBs and for the whole network of all bonds).
information on the actual number of bonds. We produced spectra for the graphs spanned by all HBs, as well as separate graphs constructed by different types of H–Y bonds.

As one can see from the top panels of Figure 10, the whole network of all kinds of HBs in AIMD structures yields a continuous graph spectrum spanning from −4.5 to 4.5. Therefore, there are some ions in the liquid which form HBs to five other ions. From the multigraph spectrum, we can deduce that (in agreement with Figure 8) the maximum number of HBs formed by an ion reaches 7. It is also clear that the connectivity and continuity of the HB network are provided by H–O bonds. Some ions are connected to 4 other ions via HBs to oxygen atoms. Connectivity of the network of H–F bonds is smaller. From the discrete set of eigenvalues obtained for the graph of H–N bonds, we conclude that HBs to nitrogen acceptors are isolated and do not form a continuous network.

The spectra based on the structures obtained from classical MD are narrower and with some visible gaps. The maximum number of counterions linked to given cation is reduced to 4. It may be also noted that there are much more disruptions in the network of H–O bonds and the total network of HBs is supported more-less equally by H–F and H–O bonds. The contribution of H–F bonds is larger in nonpolarizable simulations; polarizability increases a little the connectivity of the H–O bond network. The H–N HBs are in classical simulations even more isolated than in ab initio structures as seen from few isolated peaks in the eigenvalue spectrum. Graph spectral analysis supports therefore the conclusions drawn in preceding sections.

3.4. Vibrational Features of HBs. The presence of HBs in the liquid is supposed to affect its vibrational spectrum. In EMIM-TFSI, hydrogen donors are carbon atoms; therefore, the relevant part of the IR or Raman spectrum is the region of C−H stretches at about 3000 cm\(^{-1}\). In our recent work,\(^{25}\) we used AIMD simulations to reproduce the experimental IR spectrum of EMIM-TFSI liquid.\(^{22,29}\) The spectrum was calculated as the Fourier transform of the autocorrelation function of the total dipole moment of the simulated system; therefore, it corresponded to the spectrum of bulk liquid and we have not traced contributions from individual ions. In this study, we want to look at selected C−H bonds in order to assess to what extent different environments of vibrating C−H groups affect the frequencies of individual transitions and their scatter along the MD trajectory.

To this end, we constructed potential energy profiles for C−H\(_{\text{Im}}\) stretches (as described in Section 2) and then we obtained corresponding frequencies of 0–1 vibrational transitions by numerically solving Schrödinger equation for calculated 1D potentials of proton displacements. Five EMIM cations from AIMD simulations were chosen for this purpose, and only C−H stretches involving imidazolium C2, C4, and C5 carbon atoms were analyzed. An example of a proton potential for the C2−H stretch is depicted in Figure 11; all potentials calculated for one selected ion pair are presented as movie in the Supporting Information. All proton potentials have single minimum, and for small displacements their character is close to the harmonic potential. This kind of proton potentials is characteristic for typical moderate and weak HBs. No double minima potentials were observed.

The calculated individual frequencies of vibrational transitions and overall band contours for each analyzed HB involving H atom at C2 carbon atom are shown in Figure 12; similar plots for C4−H and C5−H bonds are shown in the Supporting Information. Band contours were obtained as superpositions of Gaussian functions with half width of 50 cm\(^{-1}\). As readily seen in Figure 12, the frequency of a given C2−H stretch can vary between different frames of the trajectory by 200−300 cm\(^{-1}\). These changes reflect the changes in the local environment of the EMIM cation in the timescale of MD simulation, that is, about 40 ps. We may also note that for all bonds, the highest calculated frequencies are very similar.
(about 3150 cm\(^{-1}\)), whereas the low-energy end of the interval varies much more (2700–2900 cm\(^{-1}\)). This feature is related to the shape of potentials at different snapshots of the trajectory: high frequencies are obtained in symmetric potentials, close to harmonic and this constitutes an upper limit for the vibrational frequency. On the other hand, increasing anharmonicity of the potential decreases the frequency of the vibration. Therefore, different lower limits of calculated frequencies obtained for different bonds show that the asymmetry of the potential for the C–H stretch experienced along the MD trajectory by different anions may vary quite significantly.

Frequencies for all five analyzed bonds span the range from 2700 to 3150 cm\(^{-1}\). Differences between individual C2–H vibrations are also noticeable in the simulated vibrational band. In the spectrum averaged over all considered bonds, the maximum is located at about 3075 cm\(^{-1}\) and the maxima of contributing bands appear between 3020 and 3100 cm\(^{-1}\). The bands are asymmetric with longer tail on the low-frequency side. For C4–H and C5–H stretches, the differences in frequencies calculated along the MD trajectory are smaller and the frequencies are on average shifted to slightly higher values. This can be seen in Figure 13, where we compare averaged frequencies of C–H stretches calculated from 1D potentials for three imidazolium C–H bonds.

![Figure 13. Averaged frequencies of C–H stretches calculated from 1D potentials for three imidazolium C–H bonds.](image)

spectra for all three imidazolium hydrogen atoms. Although the average over only five anions may be statistically insufficient (but even for such a small number, it was computationally demanding), the C5–H and C4–H stretches are apparently shifted to energies 15–25 cm\(^{-1}\) higher than the C2–H vibration. This indicates that the HBs formed by hydrogen atoms at C4 and C5 imidazolium carbons are weaker than those in the case of the hydrogen atom at C2, consistently with larger acidity of the C2 carbon.

In the experimental spectrum of EMIM-TFSI liquid,\(^{39}\) the C–H stretching bands of the imidazole ring are located at 3126 and 3165 cm\(^{-1}\). Our averaged band is at frequency slightly lower than experimental. To some extent, it may be related to the DFT functional used in this work, which for some C–H\(_{im}\) stretches gives frequencies lower than other functionals (cf. Table S1 in the Supporting Information). Nevertheless, in the IR spectrum of the IL calculated in ref 25 from the same AIMD trajectories, the C–H stretching frequencies were slightly underestimated; thus, the frequencies calculated for a single ion pair in the gas phase apparently are not a good measure of the effect in a bulk liquid. On the other hand, it has been shown that the 1D model of the potential underestimates the frequencies comparing to the experimental values.\(^{44}\) We conclude therefore that the possible origin of the difference between IR spectrum obtained via Fourier transform for the AIMD structures and the frequencies obtained from the model potential can be attributed to the 1D potential used here, which certainly is a rather simplified description of the real energy surface for the C–H bond involved in hydrogen bonding. Nevertheless, the approach proved its usefulness in resolving the overall spectrum into contributions arising from individual bonds and assessing the range of frequency shifts resulting form changing environment of the C–H oscillator.

4. CONCLUSIONS

We performed extensive analysis of the HB network in a typical aprotic IL, EMIM-TFSI, using quantum (AIMD) and classical MD simulations. MD results were analyzed in terms of spatial distribution of HB donor and acceptor atoms, statistics of different types of bonds, and spectral graph analysis of connectivity of HBs. In ab initio structures, most HBs are formed between hydrogen atom from the imidazolium ring or the methyl group of EMIM cation and the oxygen atom of TFSI anion. The most probable pair of acceptors in bifurcated bonds is the pair of oxygen and nitrogen atoms. EMIM cations may form HBs up to five different ions, and the connectivity of the HB network is supported by H–O bonds.

We showed that in structures of the liquid obtained from classical MD simulations, pattern of HBs is essentially different. HBs with an oxygen acceptor are formed only by hydrogen atoms from the imidazolium ring, and the probability of fluorine being an acceptor atom increases both in simple and in bifurcated bonds. Average number of HBs is reduced, and the network of HBs has more disruptions. In the polarizable force field, the number of HBs with an oxygen acceptor atom increases slightly but the results are still far from those obtained in AIMD. We conclude that the simulation protocol used in MD may affect significantly the number of HBs and the structure of their network. Appropriately parameterized classical MD simulations will continue to be useful tools in the investigations of HBs in ILs, owing to their relatively low computational cost making possible calculations for large systems and/or long timescales. Nevertheless, in the view of the results presented in this work, it is advisable to supplement such studies with AIMD simulations wherever possible, and to compare predictions of classical and ab initio approaches.

Finally, we performed a posteriori quantum chemical calculations of 1D potential energy profiles for hydrogen motions in selected HBs obtaining information on differences between individual bonds as well as on fluctuations of the potential and resulting scatter of vibrational transition energies during the simulation. Results have proven applicability of this methodology to investigate vibrational frequencies of individual bonds and to assess to which extent they may differ.

Results presented in this work provide some insights into the structure of the HB network in EMIM-TFSI liquid at atomistic resolution. We believe that methodological findings regarding the type of MD (ab initio vs classical) and usefulness of frequency calculations based on potential energy profiles extracted from the snapshots of the MD trajectory are more general and may applied to similar systems.
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.8b05839.

Numbering of EMIM+ atoms, Cn–H stretching frequencies for EMIM-TFSI pair calculated in different DFT functionals, frequencies of vibrational transitions calculated for C4–H and C5–H bond stretches from the 1D potential, animation of 1D potential curves calculated for selected C2–H bond, and comparison of data obtained for two system sizes used in classical MD simulations (PDF)

All potentials calculated for C2–H bond for one selected ion pair (AVI)

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