

# Supplementary Information to Understanding the infrared spectrum of the protic ionic liquid [DEMA][TfO] by atomistic simulations

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## 1 Molecular dynamics simulations

Molecular dynamics simulations of the bulk phase of the ionic liquid [DEMA][TfO] were performed on 200 ion pairs in a simulation cell with an initial edge length of 40 Å and periodic boundary conditions. Figure S1 shows an illustration of the simulation cell. After velocities according to Langevin dynamics were assigned to the atoms, an initialisation of 10 ps was performed in the NPT ensemble with a Nosé-Hoover barostat at 1 bar and a time step of 0.1 fs. Subsequently, an equilibration of 3 ns with a Nosé-Hoover barostat and thermostat at 1 bar and 25 °C was performed using a time step of 1 fs. The calculated potential energy and density is shown in Figure S1b and c. It can be seen that both values reach equilibrium well within the equilibration run and the simulated density matches the experimental density of 1.28 g/cm<sup>3</sup> with a deviation below 4 %. This illustrates that the chosen force field can sufficiently describe the macroscopic properties of the ionic liquid. Following the equilibration, the simulated volume was fixed and a production run of 10 ns was performed in the NVT ensemble still using the thermostat at 25 °C and a time step of 1 fs.

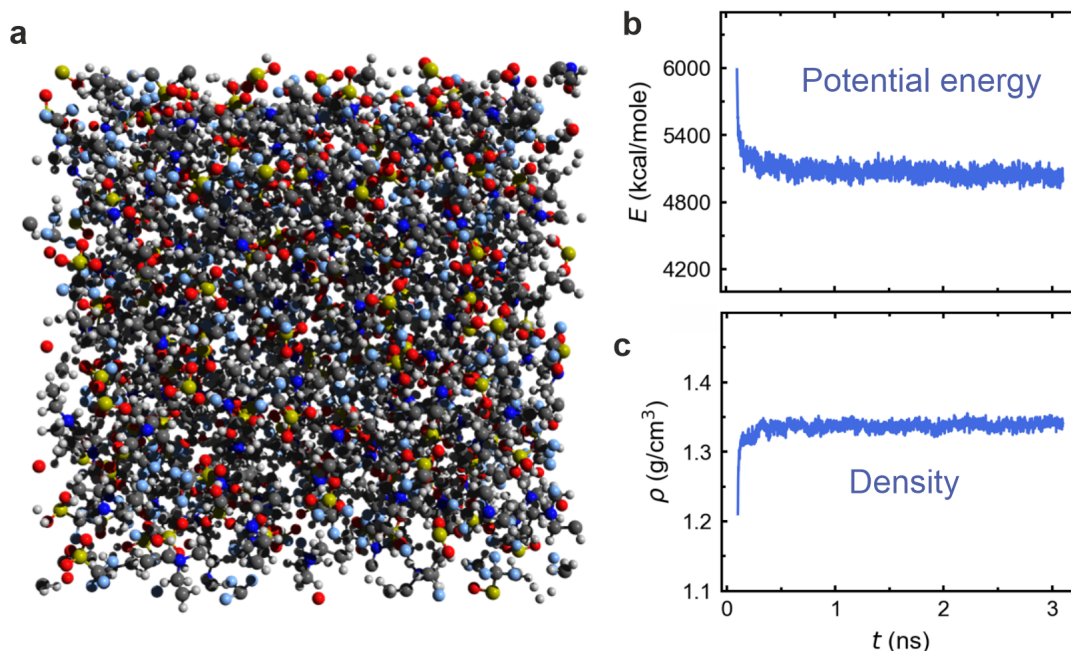


Figure S1: Molecular dynamics simulation of bulk [DEMA][TfO]. a) Illustration of the simulation cell containing 200 ion pairs; b) potential energy and c) density as function of equilibration time.

## 2 Cation conformations

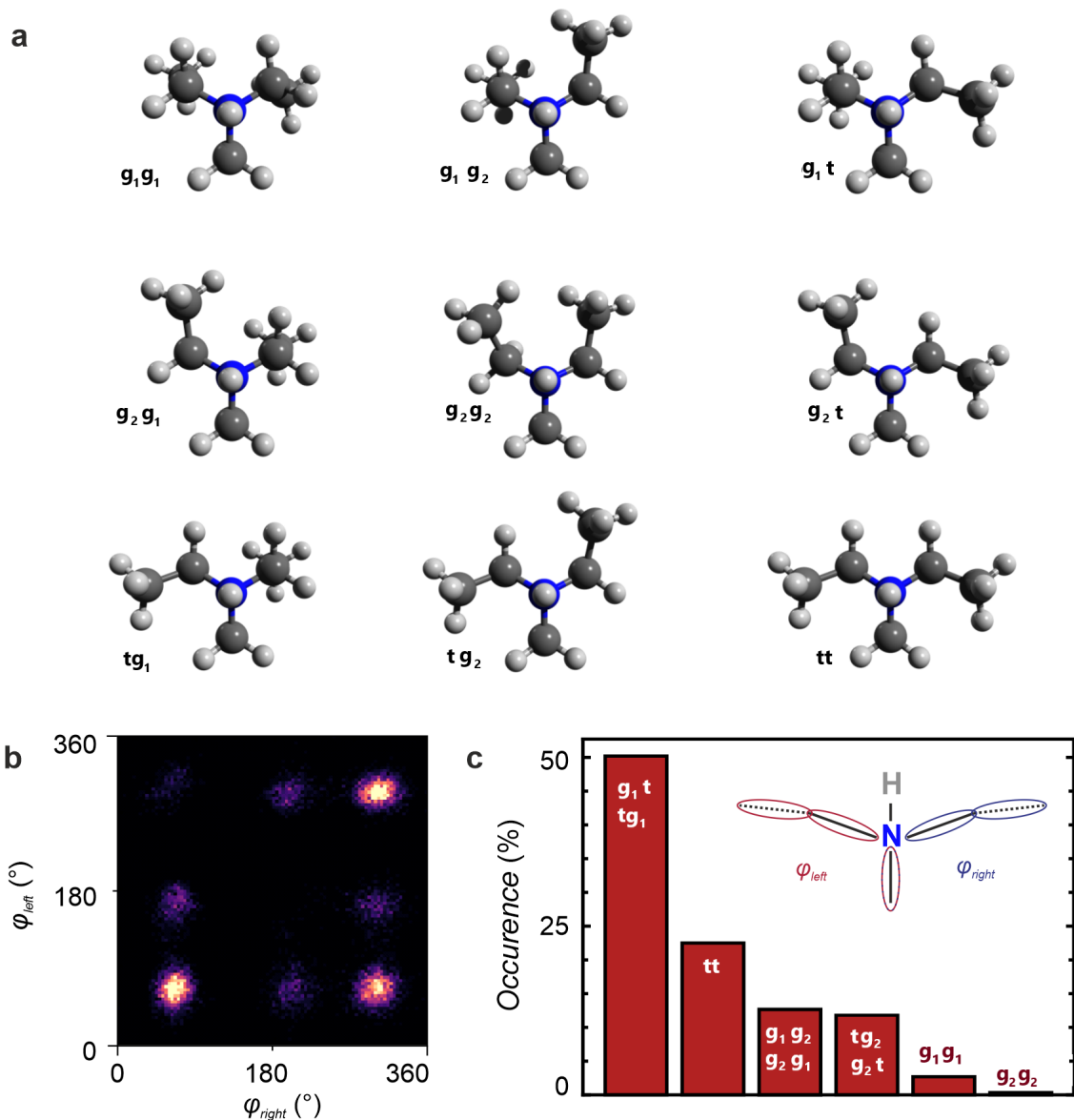


Figure S2: Analysis of cation conformations in the bulk of [DEMA][TfO]. a) Illustration of the nine main conformations; b) 2D histogram of the occurrence of the dihedral angles  $\varphi_{left}$  and  $\varphi_{right}$  being a descriptor of the conformations; c) histogram of the occurrence of conformations (the inset illustrates the definition of the dihedrals).

As the DEMa cation contains two ethyl groups, their orientation defines different conformations. Figure S2a illustrates the nine main conformations, which are theoretically possible. In order to label the different conformations, we used the abbreviation  $t$  for trans and  $g_1$  and  $g_2$  for gauche related to the orientation of the two ethyl groups with respect to the methyl group of the cation (cf. Figure S2b and Figure 2 in the main manuscript). The orientation of the ethyl groups is described by the dihedral angles between the two carbon atoms of the ethyl group, the central nitrogen atom and the carbon atom of the methyl group. In order to get an impression of the expected dihedral angles, the different cation conformations were simulated using the universal force field (UFF) [1] as implemented in the avogadro software [2] and the resulting angles  $\varphi_{left}$  for the left ethyl group and  $\varphi_{right}$  for the right ethyl group are summarized in Table 1. By comparing these values with the dihedral angles of the cations in the production run of the molecular dynamics simulation, we can thus determine, which conformations are

present in the simulated bulk phase of the ionic liquid. Figure S2b displays a 2D histogram, in which the occurrence of the dihedral angles is plotted. It can be seen that nine spots with different intensities are present representing the nine conformations. For a further analysis, it also has to be taken into account that the cation possesses a mirror symmetry and hence several conformations are energetically equivalent, e.g.,  $g_1g_2$  is equivalent to  $g_2g_1$ . Hence, in total only six characteristic conformations have to be considered. Using the expected dihedral angles from Table 1, we then converted the dihedral angles found in the simulation into a histogram for the different conformations (Figure S2c and pie chart in Figure 2 in the main manuscript).

Conformation	$\varphi_{left}$ (°)	$\varphi_{right}$ (°)
$g_1g_1$	306	65
$g_1g_2$	295	199
$g_1t$	295	297
$g_2g_1$	165	68
$g_2g_2$	167	221
$g_2t$	156	290
$tg_1$	64	66
$tg_2$	60	198
$tt$	65	295

Table 1: Dihedral angles of the different conformations of the DEMA cation.

## 2.1 IR spectra of different conformations

In order to analyze the influence of the conformations on the IR spectrum, we simulated isolated cations by DFT using the Quantum-ESPRESSO package. The input coordinates of the cations were taken from the avogadro simulation with the dihedral angles of Table 1. Exploiting the mirror symmetry, we only needed to simulate the six energetically different conformations. As described in the methods section, a relaxation was performed before the eigenfrequencies and the IR spectrum were calculated. When simulating the  $g_2g_2$  conformation, the ethyl groups moved significantly during the relaxation and ended in the  $tg_2$  conformation. This shows that the  $g_2g_2$  conformation is unstable confirming the results of the molecular dynamics simulation. Comparing the simulated IR spectra of the five remaining stable conformations presented in Figure S3, one can see that there is not much difference regarding peak positions and intensities. Only in the region between  $1200\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ , some minor differences can be recognized since the IR absorption in this wavelength range is related to the bending vibrations of the ethyl groups (cf. Figure 3 in the main text). The comparison of the IR spectra reveals that conformations do not have a large impact on the shape of the spectrum. However, the simulation of isolated molecules cannot reproduce the experimentally observed spectrum with a good agreement. In particular, the high frequency region of the simulated spectra shows distinct deviations from the experimental spectrum. For all conformations, a sharp peak related to the N-H vibration was simulated around  $3400\text{ cm}^{-1}$ , which does not match the shape of the broad “double” peak in

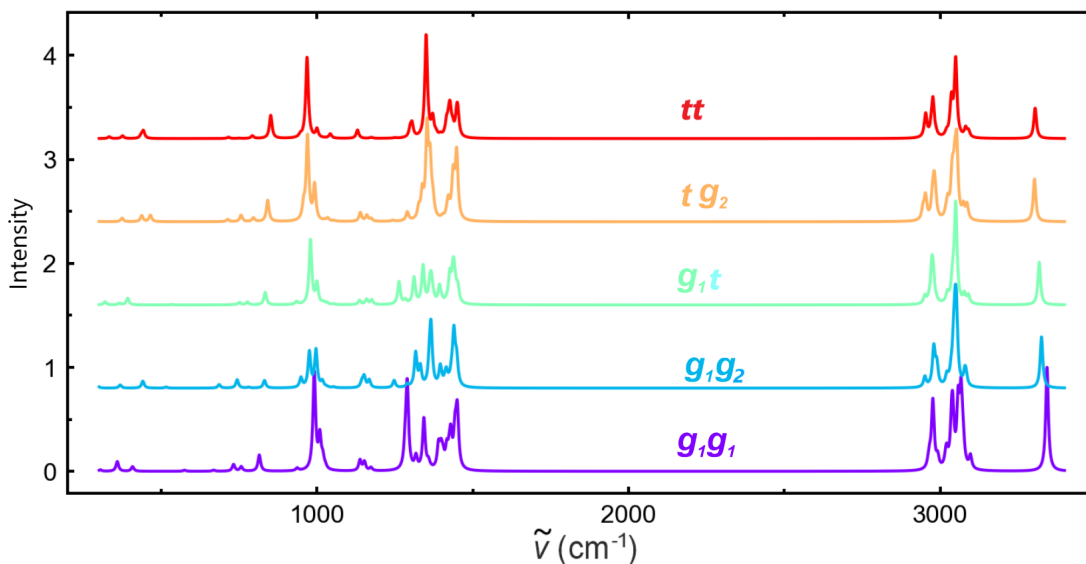


Figure S3: Infrared spectra of single DEMA cations in different conformations simulated with DFPT (see main text for details).

the experimental spectrum. This indicates that the intermolecular interactions strongly determine the molecular vibrations. Hence, the liquid bulk phase was simulated using DFT with periodic boundary condition as described in the main text.

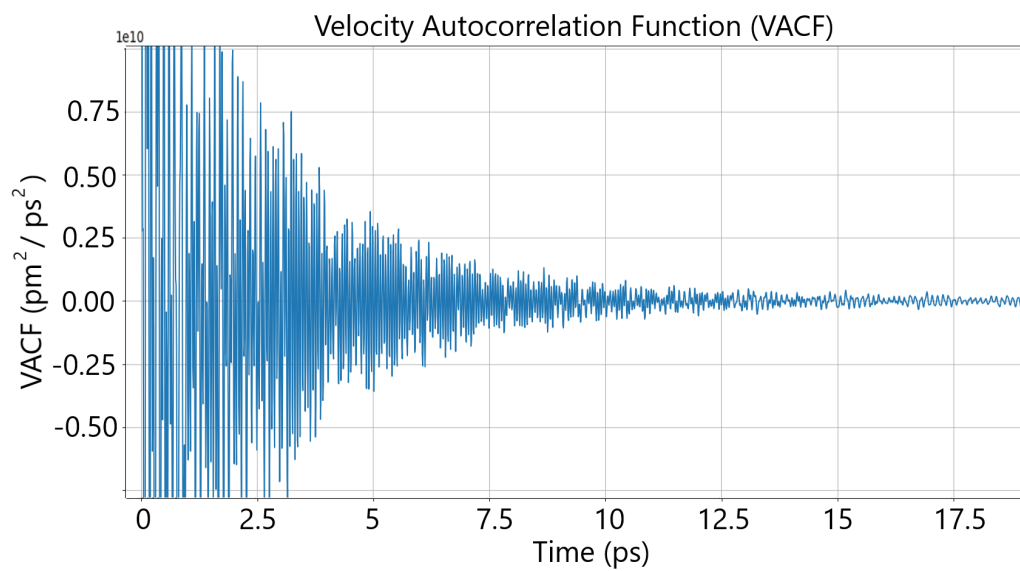
## 2.2 Investigation of the existence of ion triples

Mori et al. [3] proposed that the broad high-frequency “double” peak would be related to [DEMA]-[TfO]-[DEMA] ion triples, in which the active protons of the cations form a hydrogen bridge to the oxygen atoms of the anion. In such a system, the vibration of the two active protons could be coupled resulting in a symmetric and antisymmetric vibration mode. In order to investigate, whether this mechanism is reasonable, we analyzed the output of the classical molecular dynamics simulations of 200 ion pairs.

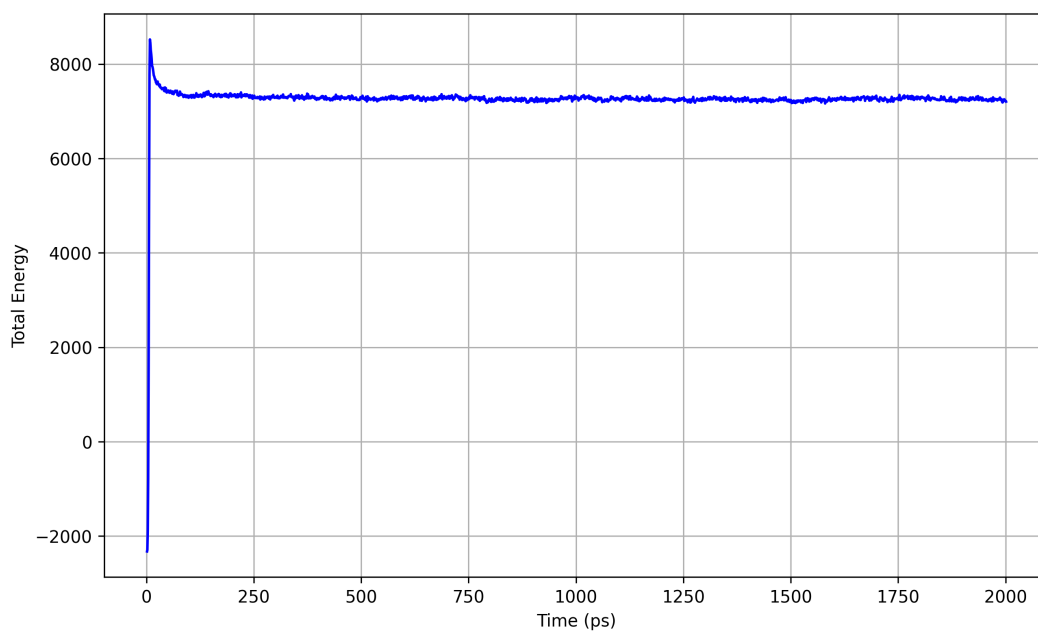
First, we checked if the equilibration time of 2 ns MD simulation was sufficient for the system to equilibrate. For this purpose, we computed the velocity auto-correlation function (VACF, Figure S4a) of DEMA cation to derive the correlation time. Fig. S4a indicates correlation time of 4 ps, which is three orders of magnitude smaller than the time of the equilibration run. The oscillations of the VACF decay to 0 ( $\text{pm}^2/\text{ps}^2$ ) after 10 ps which means that, at longer simulation time, velocities are uncorrelated with the initial configuration. The full equilibration is demonstrated by constancy of the total energy along the simulated trajectory, as illustrated in Figure S4b.

When analyzing the equilibrated system, indeed, ion triples were found as illustrated in Figure S6a. Figure S5 shows a deeper analysis of the number of triplets found during the trajectory. The plot shows that the number of triplets oscillates around a constant value of  $25 \pm 5$ . A statistical analysis revealed, however, that only 12 % of the 200 simulated DEMA cations are involved in an ion triple raising the question, if this small fraction is sufficient for the explanation of the “double” peak feature of the spectrum. Hence, we performed an experimental analysis of the existence of ion triples. At first, we recorded IR spectra of neat [DEMA][TfO] in ATR configuration at different temperatures from 25 °C up to 120 °C. As an increased temperature corresponds to a higher kinetic energy of the system, the probability for the formation of ion triples would decrease. However, the experimental spectrum of the “double” peak region only exhibits negligible changes when the temperature is increased as shown in Figure S6b. In particular, the characteristic shape of the spectrum remains intact, thus not supporting the hypothesis of the influence of ion triples.

As further test, we conducted dilution experiments. Similar as for the increase of temperature, a dilution of the ionic liquids with solvents increases the disorder thus lowering the probability of ion triples’ formation. We used the organic solvent dimethyl sulfoxide (DMSO) in the deuterated form, in



(a) Velocity autocorrelation function (VACF) of DEMA cation with respect to time in the first 20 ps of equilibration



(b) Total energy of the system with respect to time in the 2 ns of equilibration.

Figure S4: Demonstration of the equilibration of the system.

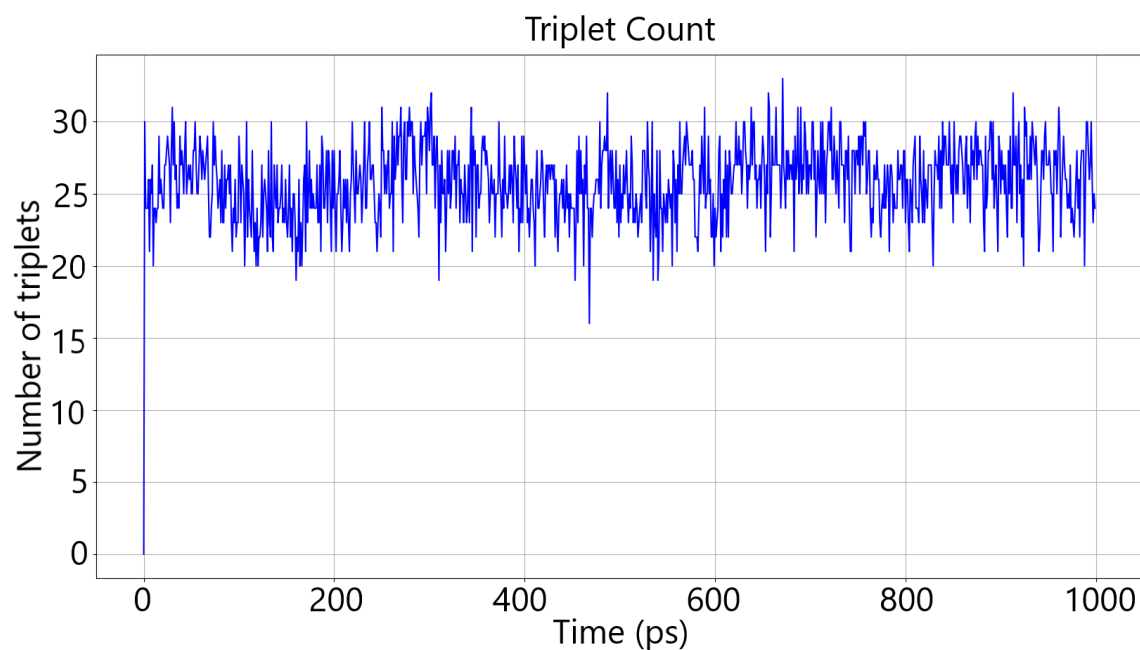


Figure S5: Number of triplets during the simulation. The number of triplets was determined by identifying the hydrogen atom bonded to the nitrogen of the DEMA cation, with a distance smaller than 1.9 Å to any of the three oxygens belonging to the same triflate. A triplet was detected, when the distance criterion was fulfilled for two DEMA connected to the same triflate.

which the hydrogen atoms are replaced by deuterium. This was done in order to avoid an overlap of IR absorption of the C-H vibrations of the solvent with that of the C-H and N-H vibration of the DEMA cations. When increasing the concentration of DMSO from 0 vol% up to 2000 vol%, the spectrum changes in a complex manner (Figure S6c). The part of the “double” peak at higher wavenumber above  $3000\text{ cm}^{-1}$  decreases rapidly even at small concentrations of added solvent. In return, the intensity of two broad peak features in the wavenumber range between  $2500\text{ cm}^{-1}$  and  $2800\text{ cm}^{-1}$  increases even at small amounts of added DMSO. At higher solvent concentrations, the intensity of all peaks decreases due to the increasing ratio between ionic liquid and solvent. In contrast to the expectation that the “double” peak would change in a “single” peak upon dilution due to the lower probability of ion triple formation we observed that the spectrum gets even more complex related to a change of the intensities of the N-H vibrations. This indicates that the IR spectrum of the high-wavenumber region is mainly determined by the surrounding of the active proton of the cation. When [DEMA][TfO] is mixed with DMSO, the chemical surrounding established by the arrangement of anions and neighbouring cations is replaced by the arrangement of DMSO molecules thus resulting in a change of vibration frequencies and intensities.

A similar conclusion can be drawn from the dilution experiment using deuterated water displayed in Figure S6d. With increasing water content, the intensity of both “double” peak features decreases simultaneously as would not be expected in the case of ion triples. Furthermore, one can identify a series of smaller peaks in the wavenumber range between  $2900\text{ cm}^{-1}$  and  $3050\text{ cm}^{-1}$  that are less affected by the increasing water content. This indicates that these peaks are related to the C-H vibrations of the cation, as the cations only exchange the active proton bonded to the nitrogen with  $\text{D}_2\text{O}$  and not the protons bonded to the carbon atoms. The positions of the remaining C-H vibrations are also in relatively good agreement with the simulations (cf. Figure S7).

In conclusion, we can state that we did not find an indication for the hypothesis that the formation of ion triples is the main reason for the observed “double” peak feature in the high-frequency region. Instead, the measurements and simulations indicate that the chemical surrounding of the cations influences the N-H vibration significantly thus causing a complex IR spectrum.



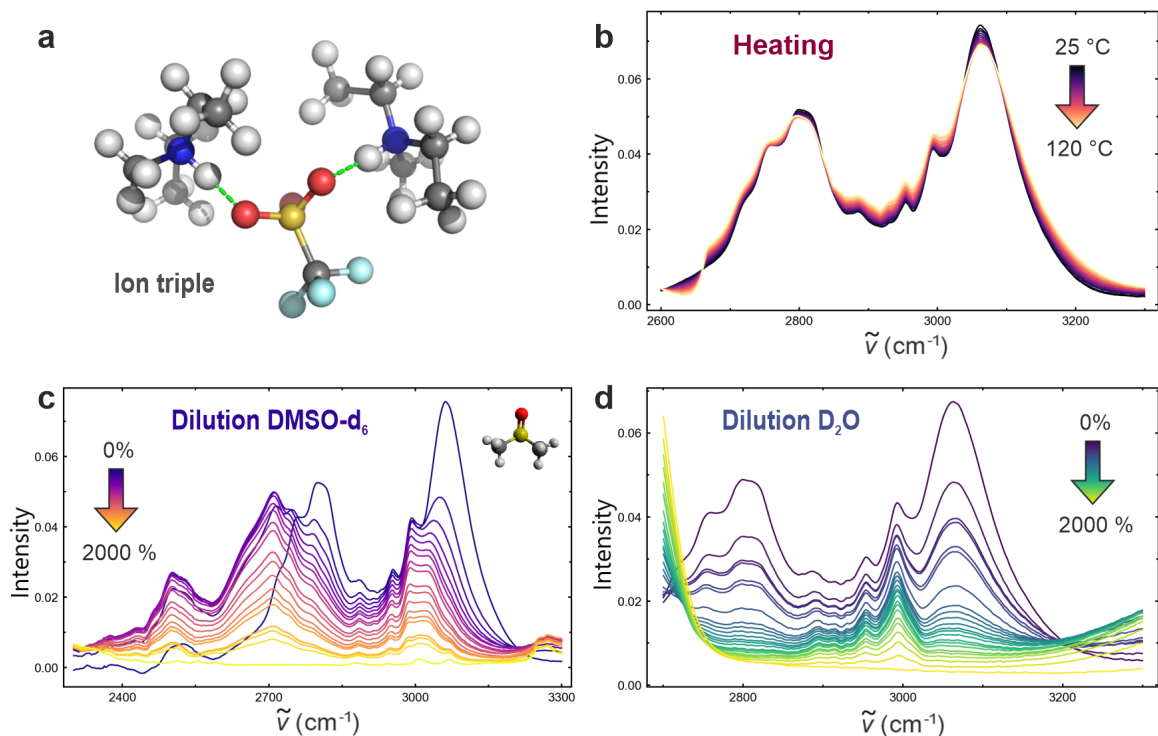


Figure S6: Experimental investigation of the existence of ion triples in bulk [DEMA][TfO]. a) Illustration of an ion triple as found in the molecular dynamics simulations; b) ATR IR spectra of neat [DEMA][TfO] as function of temperature; c) IR spectra of mixtures between [DEMA][TfO] and DMSO; d) IR spectra of mixtures of [DEMA][TfO] and D<sub>2</sub>O.

### 2.3 AIMD simulation of deuterated [DEMA][TfO]

Additional to the AIMD simulation of [DEMA][TfO] described in the main article, we performed simulations of the IR spectrum of deuterated [DEMA][TfO] in order to further elucidate the relation between the high-frequency region of the IR spectrum and the N-H vibration of the cation. Figure S7 shows a comparison of the experimental spectrum of [DEMA-d][TfO] as measured by Mori et al. [3] with the spectrum of [DEMA-d][TfO] and [DEMA-h][TfO] simulated using six ion pairs each. A good agreement between simulation and experiment is obtained, especially regarding the position of the peaks in the high-frequency region. The IR peaks representing the N-D vibration can be found in the region between  $2000\text{ cm}^{-1}$  and  $2500\text{ cm}^{-1}$  thus having a lower frequency than the N-H vibration of the nondeuterated cation due to the higher mass of deuterium. It can also be seen that the N-D vibration region does not exhibit a sharp single peak but a broad feature with at least three main peaks. One corresponds to the H<sub>c</sub> vibrations and the other two to the proton dynamic. This observation also challenges the ion triple hypothesis, which should result in the formation of only two main peaks for the symmetric and antisymmetric vibration of N-D in a [DEMA-d]-[TfO]-[DEMA-d] triple.

Since during deuteration of the DEMA cation only the active proton bonded to the central nitrogen atom is replaced by deuterium, the C-H vibrations remain the same. Hence, we can conclude that the spectral region with a main peak centered around  $3000\text{ cm}^{-1}$  of the experimental spectrum in Figure S7a corresponds to the C-H vibrations. In the simulated spectrum, this C-H region is slightly blue shifted and ranges from  $3000\text{ cm}^{-1}$  to  $3200\text{ cm}^{-1}$ . When we analyze the difference between the simulated spectra of [DEMA-d][TfO] and [DEMA-h][TfO] in Figure S7b, we find that the IR intensities belonging to the N-H are mainly responsible for the simulated intensity in the broad high-frequency region between  $2700\text{ cm}^{-1}$  and  $3300\text{ cm}^{-1}$  while the C-H vibration only contribute in the region between  $3000\text{ cm}^{-1}$  to  $3200\text{ cm}^{-1}$ . This illustrates that the AIMD simulations can successfully reproduce the experimental spectrum in terms of wavenumbers' position. However, there are still some deviations in terms of vibrational intensities indicating that the interaction of the molecules within the bulk phase is far more complex than what can be reproduced by the simulation due to the intrinsic limitations of

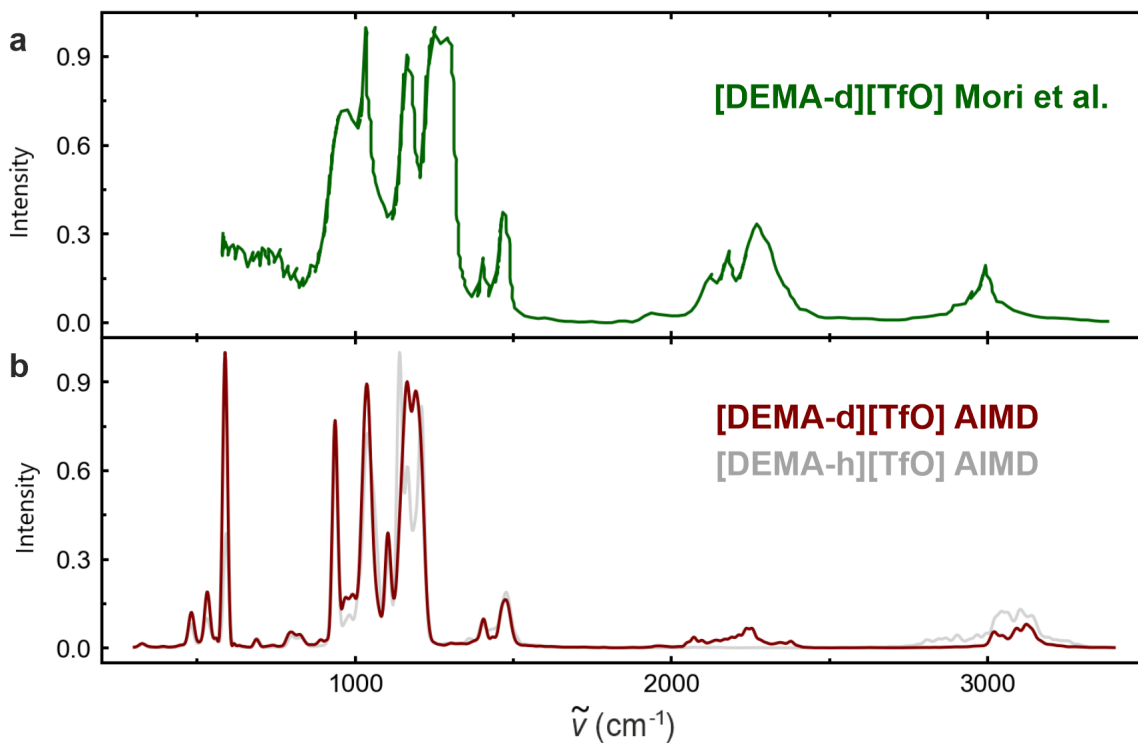


Figure S7: IR spectrum of deuterated [DEMA][TfO]. a) Experimental investigation by Mori et al. [3]; b) ATR IR spectra of neat [DEMA][TfO] as function of temperature; c) IR spectra of mixtures between [DEMA][TfO] and DMSO; d) IR spectra of mixtures between [DEMA][TfO] and D<sub>2</sub>O.

ab initio simulations.

## 2.4 Proton dynamics

In this subsection we present a detailed analysis of the active proton behaviour during the simulation. The trajectory analyzed encompasses 26 ps of AIMD for 10 ion pairs within a system of 280 atoms, performed using the CP2K software with the BLYP functional and a time step of 0.5 fs.

In Figure S8 a), the histogram of the distribution between one active proton and the nearest oxygen is shown. It can be seen that the simulation exhibits a broad range of distances, suggesting a highly dynamic environment around the active proton. The analysis focuses on a specific proton of the DEMA cation, the one attached to nitrogen, within a molecular simulation. To gather the data for the histogram, a Python script was employed to examine each time step within the trajectory file. The script identified the proton of interest and then calculated its distance from all oxygen atoms within a predefined range. At every time step, it determined the closest oxygen atom to this proton. The distances were plotted in a histogram (referred to as Figure S8), with the entire range of observed distances divided into 1000 bins. This histogram allows for an analysis of the distance variations over time, highlighting the dynamic nature of the interactions within the molecular system. Together with the high variation in time of the angles, it suggests that the anion undergoes partial rotation throughout the trajectory. This rotational movement further emphasizes the complex and dynamic environment in which these molecular interactions occur. The observed variability in both distance and angle measurements demonstrates that the surrounding of the N-H bond is constantly changing. Hence, also the frequency of the N-H vibration does not have a fixed value, but shows a broad distribution resulting in the complex high-frequency part of the infrared spectrum.



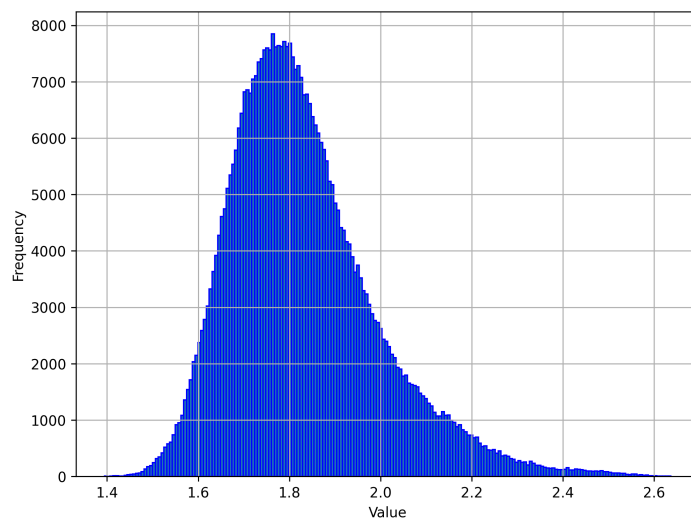


Figure S8: a) Histogram of distance between the shared hydrogen atom and the closest oxygen of the triflate. b) Histogram of the N-H-O angles distribution. The N and H atoms belong to the DEMA cation, the O atom belongs to the TfO anion.

## References

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