Rotational and Translational Dynamics and Their Relation to Hydrogen Bond Life-Times in an Ionic Liquid by Means of NMR Relaxation Time Experiments and Molecular Dynamics Simulation

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We report a concerted theoretical and experimental effort to determine the reorientational dynamics as well as hydrogen bond life-times for the doubly ionic hydrogen-bond (DIHB) \( ^{\text{17}}\text{OH} \cdots \text{O}^- \) in the ionic liquid (2-hydroxyethyl)trimethylammonium bis(tri-fluoromethylsulfonyl)imide \([\text{Ch}]\text{[NTf}_2\text{]}\) by using a combination of NMR relaxation time experiments, density functional theory (DFT) calculations, and molecular dynamics (MD) simulations. Due to fast proton exchange, the determination of rotational correlations-times is challenging. For molecular liquids, \( ^{\text{17}}\text{O} \)-enhanced proton relaxation time experiments have been used to determine the rotational correlation-times for the OH vectors in water or alcohols. As an alternative to those expensive isotopic substitution experiments, we employed a recently introduced approach, which is providing access to the rotational dynamics from a single NMR deuteron quadrupolar relaxation time experiment. Here, the deuteron quadrupole coupling constants (DQCCs) are obtained from a relation between the DQCC and the \( ^{\text{1}}\text{H} \) proton chemical shifts determined from a set of DFT calculated clusters in combination with experimentally determined proton chemical shifts. The NMR-obtained rotational correlation times were compared to those obtained from MD simulations and then related to viscosities for testing the applicability of popular hydrodynamic models. In addition, hydrogen bond life-times were derived using hydrogen-bond population correlation functions computed from MD simulations. Here, two different time-domains were observed: The short-time contributions to the hydrogen life-times and the reorientational correlation times have roughly the same size, and are located in the picosecond range, whereas the long-time contributions decays with relaxation-times in the nanosecond regime and are related to rather slow diffusion processes. The computed average hydrogen-bond life-time is dominated by the long-time process, highlighting the importance and longevity of hydrogen-bonded ion pairs in these ionic liquids.

I. INTRODUCTION

The importance of structural and thermodynamical properties of ionic liquids is well recognized and has been thoroughly investigated. However, the knowledge about the rotational motion of molecular vectors is rather scarce, particularly about those vectors which are involved in doubly ionic hydrogen bonding [1–12]. In principle, single particle correlation times can be determined by means of NMR relaxation time experiments. This has been done for molecular solutes such as benzene, or for molecular vectors of cations which are not involved in hydrogen bonding [13–18]. However, hydrogen bonding is often subject to substantial proton transfer, which is fast on the NMR time-scale. Thus, typical \( ^{\text{13}}\text{C} \)- or \( ^{\text{15}}\text{N} \)-relaxation time measurements accompanied by Nuclear Overhauser experiments for separating the dipolar relaxation with the neighboured protons, are not applicable. Some time ago Leyte et al. introduced the \( ^{\text{17}}\text{O} \)-method for the determination of rotational correlation times \( \tau_\text{OH} \) in water [19–21]. From the slope of relaxation rates for differently \( ^{\text{17}}\text{O} \)-enriched water samples, the purely intramolecular \( ^{\text{17}}\text{O} \)-\( ^{\text{1}}\text{H} \) relaxation rates could be derived and provided direct access to the rotational correlation times of the OH bonds. This procedure has been applied to water in mixtures with various solvents, and also to alcohols ranging from methanol to propanol [22–27]. For studying alcohols, the alkyl-groups had to be fully deuterated for suppressing the proton-proton interaction for undefined molecular vectors [24, 25]. Such a costly and challenging approach is hardly justifiable for ionic liquids. However, following an idea introduced by Wendt and Farrar, we recently developed an alternative approach for providing indirect access to rotational correlation times of molecular vectors being involved in doubly ionic hydrogen bonds in ionic liquids [28–31].

In the present study, we focus on the ionic liquids (IL) (2-hydroxyethyl)trimethylammonium (or cholinium) bis-(trifluoromethylsulfonyl)imide \([\text{Ch}]\text{[NTf}_2\text{]}\). Recently we could show that the far infrared (FIR) spectra...
of this particular IL shows a well distinguished vibrational feature, which could be assigned to the intermolecular vibrational mode between the hydroxyl group of the (2-hydroxyethyl)trimethylammonium cation and the oxygen of the NTf2 anion [32]. Thus we were able to provide evidence for the presence of a well-defined doubly ionic hydrogen bond \("OH\cdots O^\text{-}\"), which should have a significant influence on the interaction strength between the ions, and the rotational dynamics of the individual ions. Here we present calculated clusters using density functional theory (DFT) methods with and without considering explicit dispersion interaction. Thus, we are able to dissect the different types of interaction energies in terms of Coulomb interaction, hydrogen-bonding and dispersion forces. We then study the rotational dynamics of the hydroxyl group, which is involved in the doubly ionic hydrogen bond \("OH\cdots O^\text{-}\"), by a single NMR quadrupole relaxation time experiment. For that purpose we apply an approach for determining accurate deuteron quadrupole coupling constants (DQCCs) from simple measurements of NMR proton chemical shifts. The method relies on a reliable relation between DQCCs and proton chemical shifts based on calculations of these properties for a variety of molecular and IL-based clusters, which all possess hydroxyethyl groups. In addition, the single particle rotational correlation times are also compared to those we obtain from molecular dynamics (MD) simulations, and referred to measured viscosities for testing the applicability of the Stokes-Einstein-Debye relation. Finally, we calculated the life-times of the hydrogen bonds (H-bonds) for usual doubly ionic hydrogen bonds \("OH\cdots O^\text{-}\"). We are in particular interested to determine the relationship between the rotational relaxation times and the H-bond life-times. Recently, Zhang and Maginn [33] reported a linear relationship between the calculated self-diffusivities and ideal ionic conductivities and the inverse ion-pair life-times for a larger number of ILs. In their study, they compare transport properties with life-times of ion-pairs that were selected from a crudely structure-based definition. In our study the situation is somewhat more complicated by having a well defined ion-pair interaction via the \("OH\cdots O^\text{-}\") H-bond, and a rotational correlation time for the OH molecular vector which is directly involved in the formation of doubly ionic hydrogen bonds. However, on the upside this enables us to investigate the interplay between reorientational dynamics, diffusion, and hydrogen-bonding.

II. EXPERIMENTAL

A. Sample Preparation

[Ch][NTf2] was purchased from IOLITEC with purity degrees of > 97%. Prior to experiments, the samples were subjected to vacuum evaporation at 333 K for more than 72 hours to remove possible traces of solvents and moisture. Once purified, the sample was transferred under inert argon atmosphere ans stored in a hermetically sealed bottle. The residual water concentration in the sample was determined by Karl Fischer titration and lower than 100 ppm.

B. NMR Experiments

The 1H-NMR spectra of [Ch][NTf2] were recorded on a Bruker Avance 500 MHz spectrometer using 5mm probes. The samples were deuterated by H/D exchange in D2O and dried again. Longitudinal magnetic relaxation times \(T_1\) were measured with the same spectrometer at a resonance frequency of \(ν = ω/(2π) = 76.7\,\text{MHz}\) employing the inversion recovery (180° - τ - 90°) pulse sequence. \(T_1\) is estimated to be accurate within ±2%. Temperature calibrations were carried out using methanol and ethylene glycol NMR thermometers.

C. Viscosity Measurements

The viscosity of the pure ILs were determined as a function of temperature using a microviscosimeter (Lovis 2000 ME / Anton Paar Austria) based on the rolling ball principle. The estimated accuracy of the viscosity measurements was ±0.5%.

D. DFT calculations

DFT calculations were performed using the B3LYP exchange-correlation functional implemented in the Gaussian 09 program [34]. The spectroscopic properties were then calculated for the computed NMR proton chemical shifts, \(δ\,\text{H}\), were referenced against the of TMS (chemical shielding 32.06 ppm). The deuteron quadrupole coupling constant \(χ_D = (eQ\varepsilon_{zz}/h)\) were obtained by multiplying the main component of the calculated electric field gradients, \(\varepsilon_{zz}\), with a calibrated nuclear quadrupole moment, \(eQ\). The calibrated NQM is obtained by plotting measured gas phase quadrupole coupling constants from microwave spectroscopy versus calculated electric field gradients for small molecules such as CD4, CD3OH, HNCO etc. as described by Huber et al [38–40]. The slope gives a reasonable nuclear quadrupole moment, NQM (namely, 295.5 fm²), which can be used for calculating the deuteron quadrupole coupling constants at the
B3LYP-D3/6-31+G\(^*\) level of theory, no matter whether we investigate gas phase molecules, hydrogen bonded clusters or ionic liquid complexes [41, 42].

E. MD simulations

For the Bis(Trifluoromethyl-Sulfonyl)Imide-anion ([\(\text{NTf}_2\)]\(^-\)) anion we are using an improved version of the force field from KüdErrmann et al. [43]. The choline cation is based on a force field of Aparicio et al. [44]. The dihedral potentials and point charges on the atoms were fitted on ab initio calculations and ESP charges. Here, we are covering the temperature range between 300 K and 400 K, while employing simulation length of 50 ns for each temperature. The details about the employed forcefield are summarized in the supporting information.

The simulated ionic liquids is presented by systems composed of 512 ion pairs in a cubic simulation box using periodic boundary conditions. All molecular dynamics (MD) simulations are performed in the isobaric-isothermal (NPT) ensemble, employing Nosé-Hoover thermostats [45, 46], and Rahman-Parrinello barostats [47, 48], using coupling-times of \(\tau_T = 1 \text{ ps}\), and \(\tau_p = 2 \text{ ps}\), respectively. The electrostatic interactions are treated in the “full potential” approach by the smooth particle mesh Ewald summation [49] with a real space cutoff of 0.9 nm and a mesh spacing of approximately 0.12 nm and 4th order interpolation. The Ewald convergence factor \(\alpha\) was set to 3.38 nm\(^{-1}\) (corresponding to a relative accuracy of the Ewald sum of 10\(^{-5}\)).

A 2.0 fs timestep was used for all simulations and the constraints were solved using the LINCS procedure [50]. During the simulations all bond-length were kept fixed. All simulations reported here were carried out using the GROMACS 5.0.6 program [51, 52]. For all reported temperatures initial equilibration runs of 2 ns length were performed using the Berendsen weak coupling scheme for pressure and temperature control \(\tau_T = \tau_p = 0.5 \text{ ps}\) [53]. Production runs of 50 ns simulation-length for 303 K, 315 K, 326 K, 338 K, 349 K, 360 K, 372 K, 383 K, 396 K and 406 K were finally recorded and analyzed. All simulations are carried out at a pressure of 1 bar.

III. RESULTS AND DISCUSSION

A. Dissecting binding energies into hydrogen bond and dispersion contributions by means of DFT calculations of clusters of varying size

Although the Coulomb forces describe the dominant mode of intermolecular interaction between the ions, hydrogen bonding and dispersion forces are also of relevance for the structure and dynamics of ionic liquids [54–57]. In this study we focus on the doubly ionic hydrogen bond \(\overset{+}{\text{OH}}\cdots\overset{\cdot}{\text{O}}=\overset{\cdot}{\text{S}}\) of the ionic liquid (2-hydroxyethyl)trimethylammonium bis(trifluoromethylsulfonyl) imide [\(\text{Ch}\)[\(\text{NTf}_2\)]. We are in particular interested in estimating the strength of the hydrogen bond, and whether it is additionally strengthened or weakened by dispersion forces.

This will be realized in two steps: First we calculate the interaction energies per ion-pair at the B3LYP/6-31+G\(^*\) level of theory of clusters with sizes \(n = 1 – 4\) for (2-hydroxyethyl)trimethylammonium bis(tri-fluoromethylsulfonyl) imide [\(\text{Ch}\)[\(\text{NTf}_2\)], but also trimethyl-propylammonium bis(tri-fluoromethylsulfonyl) imide [\(\text{TMPA}\)[\(\text{NTf}_2\)], where the hydroxyl-group of [\(\text{Ch}\)[\(\text{NTf}_2\)] is replaced by a methyl-group. [20–22] The total interaction energies per ion-pair are about \(-345\) kJ mol\(^{-1}\) for [\(\text{TMPA}\)[\(\text{NTf}_2\)] and \(-380\) kJ mol\(^{-1}\) for [\(\text{Ch}\)[\(\text{NTf}_2\)]. Because both ILs experience rather similar Coulomb interactions, the energy differences of the same sized clusters should provide us with a reasonable estimate for the hydrogen bond energies. It is shown in Figure 1, that the interaction energies for both ILs do not further change for the larger clusters (\(n=3,4\)). Apparently, the cooperativity effects are saturated for trimers and tetramers. The constant energy difference can be now referred to the H-bond energy \(+\overset{\cdot}{\text{OH}}\cdots\overset{\cdot}{\text{O}}=\overset{\cdot}{\text{S}}\). The calculated value of about 35 kJ mol\(^{-1}\) can be regarded as a moderately strong H-bond. In the second step we calculate the interaction energies per ion-pair for the same clusters at the B3LYP-D3/6-31+G\(^*\) level of theory including D3 dispersion correction as introduced by Grimme et al [35–37]. We would like to emphasize that we do not simply add the dispersion contribution to the earlier calculated clusters, but have re-optimized their structure by taking the presence of dispersion interaction into account. The result is quite interesting. For both ILs the cluster energies per ion pair decrease in the order of 100 kJ mol\(^{-1}\). Thereby the H-bond energy does not change and remains almost constant as shown in Figure 1. Obviously, the overall dispersion energy is about three times as large as the H-bond energy, which itself is not influenced by this type of interaction at all. The linear and directional H-bond \(+\overset{\cdot}{\text{OH}}\cdots\overset{\cdot}{\text{O}}=\overset{\cdot}{\text{S}}\) of [\(\text{Ch}\)[\(\text{NTf}_2\)] is not further strengthened by dispersion forces, which is different from what we have recently observed for the IL trimethylammonium nitrate, where we found that about one third of the total dispersion interaction contributed to strength of the H-bond \(+\overset{\cdot}{\text{NH}}\cdots\overset{\cdot}{\text{O}}\) [58]. Regarding the structure of [\(\text{Ch}\)[\(\text{NTf}_2\)], our result can be well understood. Whereas in trimethylammonium the three methyl groups of the cation support the H-bond, this is not the case for the hydroxyethyl ammonium cation due to the hydroxyethyl group spacer.
B. Determination of deuteron quadrupole coupling constants

Recently, we could show for a large set of DFT calculated clusters of trialkylammonium-based protic ionic liquids (PILs) that a linear correlation between the calculated proton chemical shifts, $\delta^1\text{H}$, and the calculated deuteron quadrupole coupling constants, $\chi_D$, can be achieved [31]. Here, $eQ_{zz}$ is principle component of electric field gradient tensor of the OD hydroxyl groups and $eQ$ a calibrated nuclear quadrupole moment. The easily measured $\delta^1\text{H}$ then provide access to reasonable $\chi_D$ values in the liquid phase. Consequently, we apply this approach here to [CH$_3$][NTf$_2$].

First, we calculated the proton chemical shifts, $\delta^1\text{H}$, and the quadrupole coupling constants, $\chi_D$, for clusters including $n=1$-4 ion pairs. We then calculated both properties for 10 differently bound OH groups in the monomers, dimers, trimers and tetramers. Throughout, the proton chemical shifts and the electric field gradients of the deuterons were calculated at the B3LYP-D3/6-31+G$^*$ level of theory including D3 dispersion correction as introduced by Grimme et al. [35-37]. The proton chemical shifts were referenced against TMS for comparison with experiment. The $\chi_D = (eQ_{zz}/h)$ values are derived by multiplying the calculated main components of the electric field gradient tensor $eQ_{zz}$ with a calibrated nuclear quadrupole moment $eQ = 295.5$ fm$^2$. The asymmetry parameters of the electric field gradients for OD, $\eta_D = (q_{xx} - q_{yy})/q_{zz}$ are small ($\sim 0.12$) and do not have to be considered here. As shown in Figure 2, we find an almost linear behavior between the deuteron quadrupole coupling constants, $\chi_D$, and the proton chemical shifts, $\delta^1\text{H}$. From linear regression we obtain the relation

$$\chi_D = 315.07 \text{kHz} - 16.409 \cdot \delta^1\text{H kHz/ppm} \quad (1)$$

with a correlation coefficient of about 0.9953. We observe that the proton chemical shifts vary between 1.5 and 5.6 ppm depending on the strength of the “OH···O” cation-anion interaction at the different positions within the clusters. This range for the chemical shifts corresponds to deuteron quadrupole coupling constants varying from 300 down to 230 kHz. The weakly bound O-H bonds are characterized by smaller $\delta^1\text{H}$ shifts, and larger $\chi_D$ values, and vice versa. It does not matter, whether these pairs of properties are calculated for O-H/O-D in varying sized clusters or for different configurations within these clusters, they all show linear dependence. Obviously, both properties $\delta^1\text{H}$ and $\chi_D$, are similarly sensitive to local and directional interactions, such as hydrogen bonding. An ultimate test for the reliability of the linear relation between both properties in ILs is carried out by extrapolating the chemical shifts to 0 ppm, indicating the absent of intermolecular interactions. For this case we expect the calculated $\chi_D$ values to be similar to those measured for the gas phase of related molecules. And indeed, the obtained $\chi_D = 315 \text{kHz}$ is very close to the measured gas phase and calculated monomer values of water (308 kHz) and methanol (303 kHz), respectively [59, 60]. Moreover, we show that the temperature dependent proton chemical shifts of water $\delta^1\text{H}(T)$ result in slightly changing $\chi_D$ values all lying on the obtained linear relation between both properties (Equation 1). We now apply this relation for deriving the deuteron quadrupole coupling constant of the IL in the liquid phase. The measured proton chemical shifts $\delta^1\text{H}(T)$ range from 2.47 to 2.86 ppm as a function of temperature. That corresponds to deuteron quadrupole constants $\chi_D$ lying between 268 to 274.5 kHz. Obviously the DQCC is not very sensitive towards temperature. However, as we will show later the DQCC occurs as square in the relaxation rates, leading to a five per cent difference in the resulting correlation times. This should be considered by using the Bloembergen-Pound-Purcell approach for deriving correlation times and assuming a fixed coupling parameter over the entire temperature range [61, 62]. The most important result here is that the $\chi_D$ values for OD in the IL are significantly larger than expected for doubly ionic hydrogen bonds. The $\chi_D$ values lie between the liquid and the gas phase values for water indicating that the hydrogen bonds in the IL are weaker than those in water [22, 23]. However, one has to be cautious with this statement because it is only true if all O-D bonds are involved in DIHBs. From our MD simulations we have estimated that this counts only for about 60 percent of the O-D-bonds, whereas 40 percent are “quasi free”. Thus it might be that the measured DQCC of about 270 kHz is an average value, which is composed to 60 percent of $\chi_D = 250 \text{kHz}$ and to 40 per cent of $\chi_D = 300 \text{kHz}$. Then, the resulting $\chi_D$ should resemble that of water and would be in better agreement with the calculated H-bond energy.

C. Rotational correlation times from quadrupole relaxation time experiments

For the determination of the reorientational correlation time of the O-H molecular vectors, $\tau_c$, of the hydroxyl groups of the cations, we measured the deuteron relaxation times ($T_1$)$_D$ of the deuterated IL which are shown in Figure 4. Deuteron nuclear magnetic relaxation is driven by the interaction of the electrostatic quadrupole moment, $eQ$, of the deuteron nucleus with the main component of the electric field gradient tensor at the nucleus, $eQ_{zz}$, generated by the electron distribution surrounding the nucleus along the O-H bonds. The relaxation rate ($1/T_1$)$_D$ is given by [61, 62]

$$\left(\frac{1}{T_1}\right)_D = \frac{3}{10} \pi^2 \left(1 + \frac{\eta_D^2}{3}\right)^2 \left(\frac{eQ_{zz}}{h}\right)_D^2 \times \left(\frac{\tau_{OD}}{1 + \omega_0^2 \tau_{OD}^2} + \frac{4\tau_{OD}}{1 + 4\omega_0^2 \tau_{OD}^2}\right),$$

where $\chi_D = (eQ_{zz}/h)$ is the deuteron nuclear quadrupole coupling constant, $\eta_D = (q_{xx} - q_{yy})/q_{zz}$ is the related asymmetry parameter, and $\tau_{OD}$ represents...
the integral reorientational correlation time. If the relaxation process does not depend on frequency (extreme narrowing condition, $\omega \tau \ll 1$) Equation 3 simplifies to

$$\left( \frac{1}{T} \right)_D = \frac{3}{10} \pi^2 \left( 1 + \frac{\eta D}{3} \right) \chi_D \tau_{OD}$$

(3)

The $\chi_D$ values for the IL as obtained from the above described approach can be now used for the determination of the reorientational correlation time $\tau_{OD}$ (Equation 1).

The measured deuteron quadrupole relaxation times for temperatures between 303 K and 406 K are shown in Figure 4. Within this temperature range the $\tau_{OD}$ values for the IL decrease from 32.4 ps to 3.1 ps.

D. The validity of Stokes-Einstein-Debye relation

Additionally, we measured the viscosity for the temperature range between 293 K and 353 K. The most popular empirical representation for the temperature dependence is the Vogel-Fulcher-Tammann (VFT) equation (Equation 4)

$$\eta = \eta_\infty \cdot \exp \left( \frac{B}{T - T_0} \right)$$

(4)

where $T$ is temperature, and the three VFT parameters ($\eta_\infty$, $B$, and $T_0$) are obtained by fitting Equation 4 to the measured viscosity data as shown in Figure 5. In Figure 6 we plot the reorientational correlation times, $\tau_c$, versus the experimentally determined viscosities $\eta$. A linear relationship between $\tau_c$ and $\eta$ is expected from the Stokes-Einstein-Debye (SED) relation, if the volume/size of the solute is similar for all ILs [63, 64]. In the SED relation (Equation 5)

$$\tau_c = \frac{V_{eff} \eta}{k_B T}$$

(5)

$\tau_c$ is the reorientational correlation time, $\eta$ is the viscosity, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $V_{eff}$ is the effective volume. $V_{eff}$ is obtained by multiplying the volume $V$ with the friction factor for rotation $f$, as suggested by Gierer und Wirtz [65] Here we use the value for pure molecular liquids $f \approx 0.16$ assuming that the solute and the solvent molecules are of similar size ($r_s/r$). From the slope of the plot in Figure 6, we could estimate the effective volume $V_{eff}$ to be about 12.3 Å³. If we assume a spherical shape of the solute particle ($V = \frac{4}{3} \pi r^3$), we obtain an effective radius $r$ of about 1.43 Å, which is half of the radius of the Cholinium cation, which has been calculated to be 3.18 Å[63–65]. That the fitted straight line nearly goes through zero further supports the idea that the microscopic correlation times and macroscopic viscosities describe the dynamical behaviour of similar molecular species. For the high temperature values a linear correlation supporting Stokes-Einstein-Debye (SED) behaviour is observed.

However, at low temperatures the correlation times increase less than the viscosities. Apparently, the formation of clusters leads to a violation of the SED relation.

E. Self-diffusion coefficients and reorientational dynamics obtained from MD simulations

The translatory self-diffusion coefficients of the cations and anions in [Ch][NTf₂] were computed from slope of the mean square displacement of the ions obtained from the MD simulations using the Einstein relation with

$$D_t = \frac{1}{6} \lim_{t \to \infty} \frac{\partial}{\partial t} \left( \tau_c(t) - \tau_c(0) \right)^2$$

(6)

Here $\tau_c(t)$ is the position of the center of mass of either the cation or anion in the IL at time $t$, and the brackets (...) denote averaging over all times “0” as well as over all ions of the same type in the simulation. In order to avoid an influence of short-time cage-effects the self-diffusion coefficients were determined from the linear part of the mean square displacement functions over the time-window between 3 ns and 20 ns. Over the temperature range between 303 K and 406 K the self-diffusion coefficients of the cation were found to increase by almost one order of magnitude from $3.6 \times 10^{-11}$ m² s⁻¹ to $3.2 \times 10^{-10}$ m² s⁻¹. The diffusion coefficients for both, anions and cations are shown as a function of temperature in Figure 7. In contrast to ionic-liquids with weak hydrogen bonds, such as for example imidazolium-based ionic liquids, the difference between the self-diffusion coefficients between anion and cation is remarkably small. Considering that the molecular mass of the [Ch]+ cation is roughly similar or even smaller compared with short-alkane-chain substituted imidazolium-cations, this small difference is probably caused by the formation of doubly ionic hydrogen bonds.

To complement the quadrupolar relaxation experiments we computed reorientational correlation functions $R(t)$ of the O-H bond-vector according to

$$R(t) = \langle P_2 \{ \cos[\theta_{OH}(t)] \} \rangle$$

(7)

where $P_2$ is the second Legendre polynomial and

$$\cos[\theta_{OH}(t)] = \frac{\vec{r}_{OH}(0) \cdot \vec{r}_{OH}(t)}{|\vec{r}_{OH}|^2}$$

(8)

represents the angle-cosine between the OH-bond vector at times “0” and $t$ and $|\vec{r}_{OH}|$ is the OH-bond length, which is kept fixed during the simulation. The reorientational correlation times $\tau_c$ are obtained as integral over the correlation function

$$\tau_c = \int_0^\infty R(t) \, dt$$

(9)

Here, the long-time behavior is fitted to a single stretched exponential function and the total correlation time is determined by numerical integration. The obtained values
are shown in Figure 4 and are provided as tabulated data in the supporting information. The temperature dependence can be described by the following Vogel-Fulcher-Tamman (VFT) equation (Equation 10)

\[ \tau = \tau_\infty \cdot \exp \left( \frac{B}{T - T_0} \right) \]  

where \( T \) is temperature, and the three VFT parameters (\( \tau_\infty, B, \) and \( T_0 \)) are obtained by fitting Equation 10 to the calculated O-D correlation times as shown in Figure 4.

In the Stokes-Einstein relation

\[ D_t = \frac{k_B T}{6 \pi \eta r} \cdot \frac{1}{f_t} \]

\( r \) represents the radius of the solute molecule, \( D_t \) is the translatorial diffusion coefficient, \( \eta \) is the viscosity, \( k_B \) is the Boltzmann-constant, \( T \) the temperature, and \( f_t \) represents the microscopic friction factor for the translational motion as suggested by Gierer and Wirtz [65]. Accordingly, the corresponding expression for rotational diffusion is given

\[ \tau_c = \tau_2 = \frac{1}{6 \cdot D_t} \cdot \frac{4 \pi \eta r^3}{3 k_B T} \cdot f_r \]

where \( \tau_c \) is the reorientational correlation time, \( D_t \) is the rotational diffusion coefficient, and \( f_r \) the corresponding microscopic friction factor.

For pure molecular liquids the solute and the solvent molecules are assumed to be of similar size (\( r_S/r \approx 1 \)), and hence \( f_t \approx 1/2 \) and \( f_r \approx 0.16 \). By combining the expressions given for the translational and rotational diffusion, we obtain

\[ D_t \cdot \tau_c = \frac{2}{9} \cdot f_r \cdot \frac{f_r}{f_t} \cdot r^2 \]

The product value \( D_t \cdot \tau_c \) obtained from our MD simulations varies between \( 6.1 \times 10^{-22} \) m² for 303 K and \( 7.4 \times 10^{-22} \) m² for 406 K leading to an upper estimate of \( r \approx 0.1 \) nm, which represents only about one third of the quantum chemically determined average radius of the cholinium cation. Apparently, \( D_t \) and \( \tau_c \) are both linearly related to the viscosity, but the Stokes-Einstein-relation is not very well obeyed.

F. Hydrogen-bond life-times determined from MD simulations and their relation to reorientational and translational motions

The correlation time \( \tau_c \) describes the rotational motion of a specific molecular vector (here the OH-vector on the cation), whereas the self-diffusion coefficients characterize the overall translational motion of the individual ions. It is fair to assume that both modes, rotation and translation of the cation are affected by the formation and life-time of doubly ionic hydrogen-bonds in the ionic liquids and vice versa.

To further analyze the hydrogen-bond dynamics, we followed the procedure suggested by Chandler [66]. We first determined the intermolecular hydrogen-bond population function \( h(t) \) as a function of time for all possible hydrogen-bond donor/acceptor combinations with \( h(t) = 1 \) if a hydrogen-bond exists and \( h(t) = 0 \) if it doesn’t. Then we characterised the time dependence of the hydrogen-bond population fluctuations by computing the hydrogen-bond population correlation function using

\[ C(t) = \frac{\langle h(0) h(t) \rangle - \langle h \rangle^2}{\langle h^2 \rangle - \langle h \rangle^2} \]

Here the brackets \( \langle \cdots \rangle \) indicate averaging over all times “0” as well as over all possible hydrogen-bond donor/acceptor combinations. The normalized correlation function \( C(t) \) can be regarded as the fraction of hydrogen-bonds being intact after a time interval \( t \), given the hydrogen-bond was intact at time “0”. The correlation functions were computed for time-intervals \( t \) up to 20 ns for all simulated temperatures between 303 K and 406 K, and are shown in Figure 8. The often used approximation \( C(t) \approx \langle h(0)h(t) \rangle / \langle h \rangle \) using the identity \( \langle h \rangle = \langle h^2 \rangle \), and assuming \( \langle h \rangle^2 \approx 0 \) is not advised here since \( \langle h \rangle \approx 3 \times 10^{-4} \) is small but still not negligible, as indicated by the variation of \( C(t) \) over 5 orders of magnitude as shown in Figure 8. In addition, the calculated value for \( \langle h \rangle \) represents about 60 percent of the theoretical upper limit of

\[ \langle h \rangle = \frac{1}{4 \times 512} = 4.88 \times 10^{-4} \]

in case the OH-hydrogen would all the time be involved in a hydrogen-bond to one of 4 hydrogens on one of the 512 anions in the simulation. Consequently, the OH-group on the cation can be considered to be engaged in a doubly ionic hydrogen-bond about 60 percent of the times.

A remarkable feature of the computed time-correlation functions \( C(t) \) shown in Figure 8 is the presence of two clearly separated time-domains with a fast initial decay within a few picoseconds to a plateau-value of \( C(t) \approx 1.5 \times 10^{-2} \) and an apparent mono-exponential long-time tail with relaxation times in the nanosecond-range. To quantify the average hydrogen-bond life-time \( \tau_P \), we determine the integral over the correlation function with

\[ \tau_P = \int_0^\infty C(t) \, dt . \]

To separate the long-time tail from the short-time behavior, we fitted the long-time tail to a mono-exponential function according to

\[ C(t) = A \cdot \exp \left( -t / \tau'_P \right) , \]
represented by the coloured solid lines in Figure 8. Here \( \tau'_l \) denotes the fitted “relaxation-time”. The long-time contribution to the hydrogen-bond life-time is then available as

\[
\tau_{IP,l} = A_l \cdot \tau'_l ,
\]

(18)

whereas the short-time part is determined by numerically integrating the difference between the correlation functions

\[
\tau_{IP,s} = \int_0^\infty [C(t) - C_l(t)] \, dt ,
\]

(19)

leading to the total hydrogen-bond life-time of

\[
\tau_{IP} = \tau_{IP,s} + \tau_{IP,l} .
\]

(20)

Figures 9 and 10 show a comparison of the different contributions to the hydrogen-bond life-times with the reorientational correlation times and the inverse self-diffusion coefficients, respectively. In addition, the tabulated data are provided in the supporting information. It is evident that the short-time contributions to the hydrogen life-times and the reorientational correlation times have roughly a similar size, whereas the long-time contributions are about a factor between two and four times larger. This is even more remarkable, since the average pre-factor for the long-time tail is rather small with about \( A_l \approx 1.5 \times 10^{-2} \), such that the relaxation times \( \tau'_l \) vary between about 400 ps for 406 K and about 4 ns for 303 K. Given that the hydrogen-bond life-time has to be attributed between 65\% (406 K) and 81\% (303 K) to the long-time process is highlighting the importance and longevity of hydrogen-bonded ion pairs in these ionic liquids, as sketched out in Figure 11.

IV. CONCLUSION

To conclude, the structure, interaction and dynamics of the IL [Ch][NTf\(_2\)] were studied as a function of temperature by using a combination of quantum chemical calculations on clusters, NMR relaxation time experiments and MD simulations. The studied IL is characterized by a doubly ionic hydrogen bond \( ^+\text{[OH]}\ldots\text{[O]}^- \) between the anion and the cation. First, we could show that the hydrogen-bond energy is about 35 kJ mol\(^{-1}\) which not further influenced by dispersion forces. By using an approach which provides reasonable deuteron quadrupolar coupling constants, we determined the rotational correlation times of the OH molecular vectors by one single NMR quadrupolar relaxation time experiment. We find that the Stokes-Einstein-Debye relation is applicable if a friction coefficient is applied similar to what has been suggested by Gierer and Wirtz for molecular liquids. The good agreement between the measured and simulated reorientational correlation times as a function of temperature encouraged us to compute as well self-diffusion coefficients and hydrogen-bond life-times by means of MD simulation. Surprisingly, the magnitude of the self-diffusion coefficient of both, cation and anion are almost similar over the whole temperature range, suggesting that both species diffuse as hydrogen-bonded ion pairs. In addition, we discussed the relation of both, reorientational correlation times and self-diffusion coefficients to the hydrogen bond life-times computed from the MD simulations. The computed hydrogen bond population correlation function clearly consists of two separate time-domains. The short-time-part decays within the picosecond time-range showing time-constants very similar to the computed reorientational correlation times. The relaxation time of the long-time-part, however, is in the nanosecond range and is apparently attributed to exchange based on translatorial diffusion. Since the overall hydrogen bond life-times consists to about two thirds of contributions from the long-time part, it is fair to assume that long-living hydrogen bonded ion-pairs do exist in this particular ionic liquid.

V. SUPPLEMENTARY MATERIAL

In the supplementary material we provide additional information about the MD simulations and the DFT calculations: A detailed description of forcefield used in the MD simulations is given. In addition, we also provide the self-diffusion coefficients for the individual ions, the reorientational correlation times, as well as the computed hydrogen bond-lifetimes. With respect to the DFT calculations, the structures of all computed molecular and ionic clusters are provided, as well as the computed \(^1\text{H}\) chemical shifts and deuteron electric field gradients.
FIG. 1. DFT-calculated interaction energies per ion-pair for IL clusters with n=1-4: I. [Ch][NTf₂]ₙ without D3-correction (open squares), II. [TMPA][NTf₂]ₙ without D3-correction (open circles), III. [Ch][NTf₂]ₙ with D3-correction (filled squares), and IV. [TMPA][NTf₂]ₙ with D3-correction (filled circles). The energy differences between II and I and IV and II represent the H-bond strength of the $^+\text{O-H} \cdots \text{O=S}^-$ interaction in [Ch][NTf₂]. The energy differences III and I and IV and II for the clusters with and without D3-correction show the contribution due to dispersion forces.

FIG. 2. Calculated deuteron quadrupole coupling constants, $\chi_D$, plotted versus calculated proton chemical shifts, $\delta^1\text{H}$ of the O-H groups in different sized clusters of [Ch][NTf₂] including n = 1 – 4 ion pairs (B3LYP-D3/6-31+G*). The fit (dashed line) was based on properties calculated for propanol clusters (triangles). From linear regression we obtained the relation $\chi_D = 315.07 \text{kHz} - 16.409 \cdot \delta^1\text{H kHz/ppm}$ with a correlation coefficient of about 0.9953. For comparison we show the well known experimental values for the gas, the liquid and the solid phase of water and methanol [22–26, 59, 60, 67].

FIG. 3. Deuteron quadrupole relaxation rates $(1/T_1)_D$ of the OD hydroxyl groups in [Ch][NTf₂] as a function of the inverse temperature. The extreme narrowing condition ($\omega \tau \ll 1$) is fulfilled between 338 K and 406 K. These relaxation rates will be used to calculate the reorientational correlation times and to test the validity of the Stokes-Einstein-Debye relation.
FIG. 4. Reorientational correlation times $\tau_{OD}$ of the OD hydroxyl groups in [Ch][NTf$_2$] as a function of the inverse temperature from NMR deuteron quadrupolar relaxation time experiments (filled symbols) and MD simulations (open symbols). The absolute correlation times and their temperature behaviour are described reasonably well.

FIG. 5. Experimentally obtained viscosities of [Ch][NTf$_2$] as a function of the inverse temperature. The solid line represents the VFT-fit.
FIG. 6. Reorientational correlation times $\tau_c$ plotted versus $\eta/T$. For the high temperature regime between 360 K and 406 K a linear correlation is supporting Stokes-Einstein-Debye (SED) behaviour. The effective volume $V_{\text{eff}}$ obtained from the slope is close the calculated volume of the Cholinium [Ch] cation. At lower temperatures, the correlation times increase less than the viscosities.

FIG. 7. Self-diffusion coefficients $D_t$ of the cation (circles) and anion (squares) in the IL [Ch][NTf$_2$] as function of the inverse temperature obtained from MD simulations.
FIG. 8. Depiction of the hydrogen-bond population time correlation functions $C(t)$ obtained from MD-simulation for all investigated temperatures. The solid lines represent monoexponential fits to the long-time-behavior.

FIG. 9. Correlation between the reorientational correlation times $\tau_c$ and the ion-pair (IP) life-time $\tau_{IP}$ for the IL cation from MD simulations: a) the short IP life-times from the fast decay of the correlations functions (open circles); b) the long IP life-times from the long tail of the correlations functions (open squares); c) the total integral of the correlation functions including the fast and the slow components (filled squares).
FIG. 10. Correlation between the calculated average self-diffusion coefficient $D$ and the inverse of the ion-pair (IP) life-time $\tau_{IP}$ for the IL cation from MD simulations: a) the short IP life-times from the fast decay of the correlations functions (open circles); b) the long IP life-times from the long tail of the correlations functions (open squares); c) the total integral of the correlation functions including the fast and the slow components (filled squares).

FIG. 11. Cartoon illustrating the well distinguished H-bond dynamics. a) The OH group switching between two oxygen atoms of one sulfonyl group within the NTf$_2$ anion. Breaking an H-bond and formation of a new one goes fast and does not require any rearrangement of the ions within the IP. b) The OH group switching between two oxygen atoms of different sulfonyl groups within the NTf$_2$ anion. Now, the formation of a new H-bond requires significant rearrangement of the cation related to a diffusive process. Thus, the first process of the H-bond dynamics is characterized by reorientational dynamics on short time scale, whereas the second process is diffusion controlled and takes place on a longer time scale.