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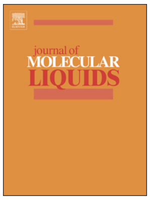

A network approach to unravel correlated ion pair dynamics in protic ionic liquids. The case of triethylammonium nitrate

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ABSTRACT

The intermolecular interactions in the title compound are investigated using self-consistent charge density functional based tight binding molecular dynamics. Emphasis is put on the analysis of correlated motions of ion pairs using ideas of network theory. At equilibrium such correlations are not very pronounced on average. However, there exist sizable local correlations for cases where two cations share the same anion via two NHO-hydrogen bonds. The effect of an external perturbation, which artificially introduces a sudden local heating of an NH-bond, is investigated using nonequilibrium molecular dynamics. Here, it is found that the average N—H bond vibrational relaxation time is about 5.3 ps. This energy redistribution is rather nonspecific with respect to the ion pairs and does not lead to long-range correlations spreading from the initially excited ion pair.

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1. Introduction

Ionic liquids (ILs) are promising candidates for a wide variety of applications, most importantly as solvents [1]. To exploit the exceptional physico-chemical properties in novel applications, the influence of intermolecular interactions must be understood in great detail. The ionic character of the molecules leads to strong Coulomb interactions, but there are also dispersion forces [2] and Hydrogen bond (HB) interactions of rather different strengths [3]. Understanding the properties and role of HBs in ILs is prerequisite, for instance, for engineering new solvents. HBs may link ions of opposite charge into networks. Here, protic ILs are of particular interest due to their rather strong HBs. Further, these systems allow for proton transfer from the cation to the anion such as to create a neutral molecular pair.

The strong Coulomb interactions lead to a long range ordering, which can be seen, for example, in the radial distribution function [4,5]. Furthermore, the polar and nonpolar groups can segregate and form spatial heterogeneities in the liquid [6]. For example, Canongia Lopes and co-workers analyzed the mesoscopic segregation of imidazolium-based ILs depending on the alkyl chain lengths [7,8]. However, the substructure of the polar regions is still not solved and the concept of ion pairing and long-lived neutral subunits is much debated [9]. Important in this context is the charge transfer between anion and cation, leading to absolute ion charges below one *e* [10]. Zhang and Maginn showed that the ion pair lifetimes can be linked to transport properties [11].

The effects of noncovalent intermolecular forces can be quantified by quantum chemical simulations on small systems down to the atomic resolution [12]. Experimentally, these interactions can be probed by NMR chemical shift measurements; see, for example, the study of the effect of mixtures on HB interactions in Ref. [13]. The intermolecular interactions give rise to signatures in infrared absorption and Raman spectra [14]. Both dispersion and HB interactions show spectral signs in the far infrared region [15–18], where HB forces manifest themselves in a blue-shift with respect to the dispersion dominated band position. In the region of CH– and NH-stretching vibrations, the H-bonded vibrational modes appear red-shifted with respect to the non-H-bonding modes. Furthermore, nonlinear spectroscopy has been employed to investigate the influence of H-bonding on the dephasing dynamics of the CH-stretching vibrations [19].

Computer simulations are a useful tool to investigate properties of liquids [20,21] and various methods, ranging from coarse grained molecular dynamics (MD) [22] to quantum chemical calculations, have been applied to ILs (for an overview, see Refs. [23,24]). Systems consisting of hundred thousands of atoms are routinely simulated with various force fields [25]. Furthermore, atomic polarization effects can be incorporated to improve the agreement with experiment, but at a high computational cost [26–28]. A yet more realistic description is provided by *ab initio* MD simulations, which were performed for a few selected small systems. For example, the ion pair and HB dynamics of methylammonium nitrate was investigated by Zahn et al. [29], finding that only 1.8 out of 3 possible HB sites are H-bonded and that preferred angles with respect to other HB exist. The ion pairs are long-

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lived, however, the lifetime of the individual conformations can be short, a behavior that is called ion cage rattling [30]. Power spectra calculated from the velocity autocorrelation functions of *ab initio* MD simulations can be employed to get insights into the dynamics at a microscopic level [31]. The experimental spectra of imidazolium-based ILs could be reproduced for clusters of 8 monomers and 10 ps trajectory length, suggesting a locality in time and space that is consistent with the ion cage interpretation. A computationally less demanding approach is provided by the self-consistent charge density functional based tight-binding method (DFTB) [32–34]. DFTB works without empirical input and provides self-consistent Mulliken charges, which account for polarization effects. As far as ILs are concerned, it has been shown, for instance, that the structure extracted from DFTB simulations matches the predicted structures of various protic ILs obtained from diffraction experiments, including alkylammonium nitrates [35].

In the present contribution we use DFTB to explore the dynamics of protic ILs. As a particular example, triethylammoniun nitrate (tEAN) has been chosen, where each isolated ion pair is capable of forming a single N—H—O HB, cf. Fig. 1 (upper panel). The focus is on the quantification of correlated motions caused by intermolecular interactions. To this end, ideas from network theory are introduced [36,37]. The ion pairs are considered as nodes of a network graph, which are connected by edges. The correlation between the pairs is quantified by the weight of the respective edge. These weights are introduced such as to relate to different types of motions, from the proton stretching vibration to the ion pair's hindered rotation. A particular role is played by disruption and formation of ion pairs. Two situations are considered. First, the equilibrium case, i.e. the system performs only thermal fluctuations within a canonical ensemble at a given temperature. Second, a proton transfer reaction is triggered by artificially raising the energy of the proton within the HB. This way we mimic infrared excitation, whose conditions are such as to promote proton transfer and thus formation of a pair of neutral molecules. This situation corresponds to a rather drastic disturbance of the system and correlations might appear in the subsequent relaxation back to equilibrium.

The paper is organized as follows. In Section 2 we start with a discussion of the MD simulation setup. Next, we provide some details concerning the generation of nonequilibrium initial conditions. We conclude this section by introducing the correlation measures used to analyze the results. Simulation results are presented in Section 3 for both, equilibrium and nonequilibrium cases. Finally, a summary is provided in Section 4.

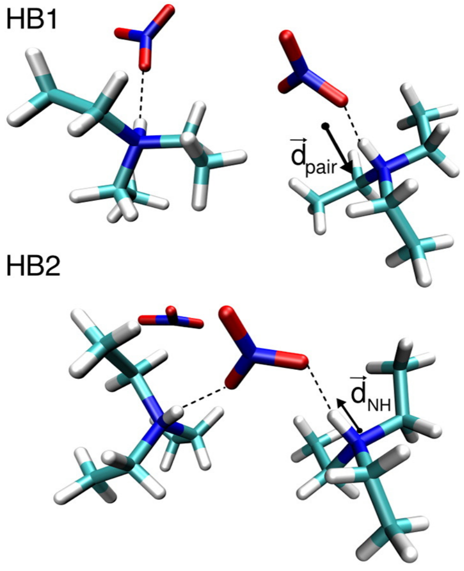

Fig. 1. Two ion pairs of triethylammonium nitrate,$[C_6H_{15}]^+[NO_3]^-$ (tEAN) with indicated HBs. The upper and lower panel show the single and double HB configuration, respectively. Correlations are quantified on the basis of the dipole moments of the NH-bonds (arrow in lower panel) and the ion pairs (arrow in the upper panel). The average absolute dipole moments for a representative case are 0.05 D (NH) and 0.67 D (pair).

2. Theoretical methods

2.1. Molecular dynamics

Molecular dynamics simulations are performed for a box consisting of 32 tEAN ion pairs with periodic boundary conditions. To simulate the liquid phase the temperature is set to 177 °C, well above the melting point of 113–114 °C [38], at a density of $\rho_{\mathrm{tEAN}} = 1.048 \mathrm{g/cm}^3$. To obtain equilibrated starting structures, first classical MD is performed, which is followed by production runs with the DFTB method. For equilibration the box is simulated with Gromacs 4.5.5 [39] with force field parameters taken from OPLS-AA [40] and its extension to ILs (especially partial charges were recalculated) by Pádua and coworkers [41,42]. Long-range Coulomb forces are evaluated using the particle mesh Ewald summation, long-range cut-off radii of 0.9 nm and a time step of 0.5 fs are used.

Production run DFTB simulations have been done with the DFTB+ code [43] including the 3rd order correction [44] and employing the corresponding Slater-Koster parameters 3ob [45]. Van der Waals dispersion forces are included a posteriori in the DFTB calculations, with parameters taken from the Universal Force Field [46]. All runs are performed at the Γ-point only. The equilibrated structure obtained from the force field was used to start a canonical ensemble simulation in DFTB. From the respective trajectory five starting structures for a microcanonical trajectory are sampled randomly. These DFTB production runs are simulated up to a length of 25 ps using a time step of 0.5 fs. The microcanonical ensemble was chosen in order to have the system free from external perturbations. This way the observed response of the system to the excitation of the NH-bond is only due to the perturbation of the bond and not from the random forces of a thermostat or barostat.

Each of the five starting structures is propagated in the equilibrium and nonequilibrium setup. In the nonequilibrium setup a single selected NH-bond in the box is excited by repositioning the respective proton as described below in Section 2.2. All other positions and momenta are equal to the initial conditions of the equilibrium setup. In the analysis particular attention is paid to HB configurations. Here, we apply a (N…O) distance criterium to distinguish between motifs with single and double HBs. A single HB is formed between the anion and the closest cation (see, Fig. 1 (upper panel). In the simulation box, on average about 18% of the cations are involved in double HB motifs, which have an anion that is H-bonded to two cations, i.e. the distance to the original cation of the ion pair is larger than that to the cation of a neighboring pair (cf. Fig. 1 (lower panel)). This suggests that for these cases different types of correlations between ion pairs may be present. To account for these particular structural motifs, we have selected two nonequilibrium starting geometries from each of the equilibrium trajectory snapshots. These are the cases with a single and with a double HB, which yields three 25 ps trajectories for each starting geometry to be used for the correlation analysis. The configurations with a single HB between anion and cation are called HB1, whereas those having an anion H-bonded to two cations are labeled as HB2.

2.2. Modeling the local excitation

A typical potential energy curve for the displacement of the proton in an N—H—O HB is shown in Fig. 2 (bottom panel), where it has been assumed that all other atoms are fixed. The solutions of the vibrational Schrödinger equation for this potential are shown as well. They have been obtained using the standard Fourier Grid Hamiltonian method [47]. To have the possibility of a transfer and to create a pair of neutral molecules, the probability density of the vibrationally excited state

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