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Title: The effect of dispersion forces on the interaction energies and far infrared spectra of protic ionic liquids

This communication reports the competition between hydrogen bonding and dispersion interaction in protic ionic liquids. It is shown that dispersion forces can be as strong as hydrogen bonds and that they influence vibrational frequencies in the far infrared to different extents. This information is useful to understand the subtle balance between Coulomb interaction, hydrogen bonding and dispersion forces and the effect on the properties of these Coulomb dominated systems.

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The effect of dispersion forces on the interaction energies and far infrared spectra of protic ionic liquids†

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We could show by means of dispersion-corrected DFT calculations that the interaction energy in protic ionic liquids can be dissected into Coulomb interaction, hydrogen bonding and dispersion interaction. The H-bond energy as well as the dispersion energy can be quantified to be 50 kJ mol^{-1} each representing ten percent of the overall interaction energy. The dispersion interaction could be dissected into two portions. One third could be related to the dispersion interaction within an ion-pair enhancing the H-bond strength, two thirds stem from dispersion interaction between the ion-pairs. This distribution of dispersion interaction is reflected in the far infrared (FIR) spectra. The H-bond band is shifted weaker than the low frequency band where the latter indicates diffuse cation–anion interaction and H-bond bending motions. Finally, we can dissect the different types of interaction energies indicating their characteristic influence on vibrational modes in the FIR.

Over the past decade ionic liquids (ILs) attracted much attention in science and technology. Their potential applications include novel synthesis, electrolyte devices, photochemical cells, separation, and catalysis.[1–3] The unique properties of these new liquid materials result from a subtle balance between different types of interaction energies: Coulomb interaction, hydrogen bonding and dispersion forces. These types of interaction between anions and cations differ in strength, locality and directionality, all having their characteristic influence on the transport and thermodynamic properties of ILs. Although the Coulomb forces describe the dominant intermolecular interaction, hydrogen bonding and dispersion-forces can be relevant for the structure and dynamics of ionic ILs.[4,5] It has been shown that local and directional

hydrogen bonding in aprotic ionic liquids can result in more fluid rather than more viscous liquids. Acting as defects, H-bonds may lower melting points, viscosities and enthalpies of vaporization.[6,7] It is obvious that hydrogen bonding increases by switching from aprotic to protic ILs. For some PILs we could dissect the interaction energies into parts resulting from Coulomb interaction and hydrogen bonding. H-bonds could be analysed due to their locality and directionality reflected by characteristic features in the far infrared spectra.

However, describing the role of dispersion forces in ILs is still a challenge. For this reason dispersion interaction is mainly studied by dispersion-corrected DFT methods using accurate coupled-cluster methods as benchmarks. Grimme and Kirchner reported the relevance of London dispersion interactions for the overall interaction energy in aprotic ionic liquids.[8] Izgorodina *et al.* showed that melting points and transport properties are better related to interaction energies if dispersion forces are considered.[9] Malberg *et al.* discussed the bulk and the gas phase of 1-ethyl-3-methylimidazolium ethylsulfate in the light of dispersion interaction. The probes for dispersion effects have been the cation–anion spatial distributions and the power spectra, both obtained from *ab initio* molecular dynamics simulations.[10] For long time, there was no direct experimental evidence for dispersion forces in bulk ionic liquids. Quite recently, we have studied the transition from hydrogen-bonding to dispersion dominated interaction between anions and cations in the PIL trihexylammonium triflate [(C$_6$H$_{13}$)$_3$NH][CF$_3$SO$_3$].[11] By combining far infrared spectroscopy and dispersion-corrected DFT methods, we obtained direct access to the relative strength of hydrogen bonding and dispersion forces in Coulomb-dominated liquids. This approach strongly suggested us to study the influence of dispersion forces on the interaction energies and the far infrared spectra in more detail. How do dispersion forces contribute to the overall interaction energies? How do these weak and non-directional forces shift the frequencies of vibrational bands describing the anion–cation interaction? Can changes in frequency and intensity be related characteristically to different

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types of ion motion? These questions are properly addressed in the present study.

As an example we have chosen the protic salts tetramethyl-ammonium nitrate $[(CH_3)_4N][NO_3]$ and trimethylammonium nitrate $[(CH_3)_3NH][NO_3]$. In a recent study, we already measured the far infrared spectra for these salts and dissected the overall interaction energy between the ammonium cations and the nitrate anion into Coulomb interaction and hydrogen bonding.[12] We picked up this system because the relatively small size of the NO_3^- anion compared to $CF_3SO_3^-$ or NTf_2^- anions allows us to extend the frequency calculations for clusters up to ten ion-pairs. Additionally, the dissection of the overall interaction energy was already shown for Coulomb interaction and hydrogen bonding. Herein, we significantly extend this study by increasing the cluster size of calculated PIL clusters and taking dispersion forces explicitly into account. This approach allows us to quantify dispersion interaction and to discuss their influence on different vibrational bands in the FIR spectra.

First, we calculated the interaction energies for clusters tetramethylammonium nitrate $([(CH_3)_4N][NO_3])_n$ and trimethyl-ammonium nitrate $([(CH_3)_3NH][NO_3])_n$ up to $n = 10$ at the B3LYP/6-31+G* level of theory without additional dispersion correction (see also the ESI†).[13] As noticed earlier, the binding energies do not further change for clusters from hexamers onwards.[12] In principle, the Coulomb and dispersion forces should be similar for both PILs. The main difference in energy is due to the presence of hydrogen bonding in $[(CH_3)_3NH][NO_3]$. From the energy difference of both PIL clusters we could confirm a recent result that the H-bond strength is in the range of 50 kJ mol^{-1}. In separated calculations we could show that the additional dispersion interaction due to the additional methyl group in $([(CH_3)_4N][NO_3])_n$ merely accounts for 2 kJ mol^{-1} and thus leads to only a minor reduction of the H-bond energy.

For dissecting the dispersion interaction present in the triethyl ammonium nitrate, we reoptimized the $([(CH_3)_3NH][NO_3])_n$ clusters by taking dispersion correction directly into account. For this purpose we applied Grimme's DFT-D3 method for calculating non-covalent interactions.[14,15] Again the many-body effects are saturated from the hexamer onwards. The addition of dispersion forces lowers the overall interaction energy by another 50 kJ mol^{-1} and is thus in the order of the H-bond strength. The energy gaps by adding both non-Coulomb interactions are shown in Fig. 1. For trimethyl ammonium nitrate they represent about 20% over the overall interaction. Interestingly, the dispersion contribution can be further dissected into two parts, which will be of relevance for the interpretation of the dispersion corrected FIR spectra. The overall dispersion energy of about 50 kJ mol^{-1} is the contribution per ion-pair relative to the isolated ions. Thus it takes the explicit anion–cation interaction along the H-bond as well as the interaction between formed ion-pairs into account. This situation is cartooned in Fig. 2, wherein the dispersion interaction within ion-pairs and that between ion-pairs is indicated by red and pink lines, respectively.

The dispersion interaction between ion-pairs can be obtained by calculating the overall dispersion interaction relative to an
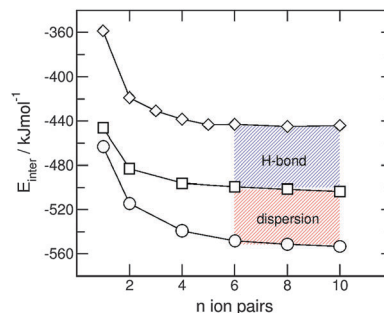

Fig. 1 DFT-calculated interaction energies per ion-pair for PIL clusters with $n = 1$–10: I. $[(CH_3)_4N][NO_3]_n$ without D3-correction (diamonds), II. $[(CH_3)_3NH][NO_3]_n$ without D3-correction (squares), and III. $[(CH_3)_3NH][NO_3]_n$ with D3 correction (circles). The energy differences between II and I represent the H-bond strength of the $^+N–H\cdots NO_3^-$ interaction in $[(CH_3)_3NH][NO_3]$.[12] The energy differences for the clusters $[(CH_3)_3NH][NO_3]_n$ calculated with (III) and without (II) D3-correction show the contribution due to dispersion forces.
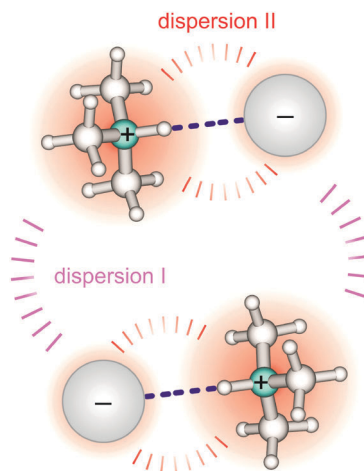

Fig. 2 Cartoon describing the overall dispersion interaction for a system including two ion-pairs. Two thirds of the dispersion interaction is described by the interaction between intact ion-pairs as indicated by the purple lines (dispersion I). The dispersion interaction within each ion-pair is shown by the red lines (dispersion II). It describes only one third of the overall dispersion energy and strengthens the hydrogen bond between the cation and the anion. It is supposed that this difference in dispersion interaction is reflected in vibrational bands in the far infrared spectra describing either motion.

isolated ion-pair. In Fig. 3 it is shown that this proportion of dispersion interaction (dispersion I) sums up to 33 kJ mol^{-1}, accounting for two thirds of the overall dispersion interaction. The remaining 17 kJ mol^{-1} energy is related to the dispersion interaction within an ion-pair along the H-bond (dispersion II) and is therefore close to 15 kJ mol^{-1} which are calculated for the dispersion within a single ion-pair as shown in Fig. 1 for $n = 1$. It can be expected that these different portions of dispersion interaction are differently reflected in the FIR spectra. This means that the vibrational bands and intensities change characteristically depending on the amount of dispersion interaction relevant for particular ion motion.
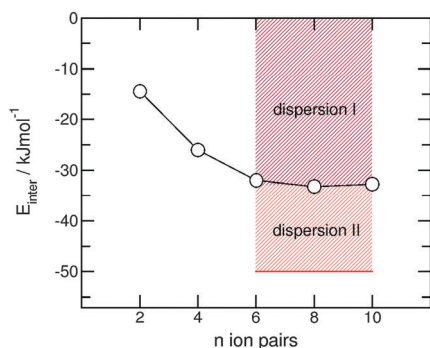
Fig. 3 The overall dispersion interaction energy of about 50 kJ mol^{-1} for PIL clusters $[(CH_3)_3NH][NO_3]_n$ with $n = 2$–10 (see also Fig. 1) can be dissected into two parts. The larger part of about 33 kJ mol^{-1} (dispersion I, purple) can be related to the dispersion interaction between intact ion-pairs. It can be obtained by calculating the dispersion interaction per isolated ion-pair within each cluster. The remaining 17 kJ mol^{-1} (dispersion II, red) describes the dispersion interaction within an ion-pair strengthening the N–H···O hydrogen bond.

Thus we analysed the influence of dispersion forces on the far infrared spectra for this PIL. First we recall the measured FIR spectra of trimethylammonium nitrate $[(CH_3)_3NH][NO_3]$ as published recently (Fig. 4).[12] The two main vibrational bands could be observed and interpreted. The low frequency contribution at around 100 cm^{-1} is generally assigned to librational and bending motions of H-bonds between cations and anions. The distinct vibrational mode at 171 cm^{-1} clearly describes the anion–cation interaction along the $^+$N–H···NO$_3^-$ hydrogen bond. This assignment could be confirmed for similar types of PILs.[12] Then, we calculated the geometries and frequencies
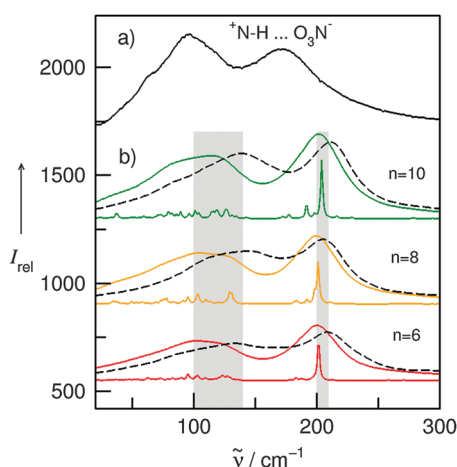

Fig. 4 (a) Far infrared (FIR) spectrum of the protic ionic liquid trimethyl-ammonium nitrate $[(CH_3)_3NH][NO_3]$ in the pellet state. The vibrational band at 171 cm^{-1} in the spectrum can be assigned to the $^+$N–H···O$_3$N$^-$ intermolecular interaction. (b) DFT-calculated low frequency infrared spectra of clusters $[(CH_3)_3NH][NO_3]_n$ with $n = 6$, 8, 10 without (straight line) and with dispersion correction (dotted lines). The calculated spectra were simulated by using a width at half maximum of 10 cm^{-1} for each vibrational mode (shown here for the non-corrected spectra). The simulated spectra reasonably reproduce the features of the measured spectrum (top), in particular the H-bond vibrational mode.

of clusters $[(CH_3)_3NH][NO_3]_n$ with $n = 6$, 8 and 10 with and without dispersion-correction (all spectra for $n = 2$–10 are shown in the ESI,† Fig. S1). The FIR spectra in Fig. 4 were simulated by applying a width at half maximum of 10 cm^{-1} for the Lorentzian functions for each vibrational mode. Throughout, the calculated frequencies are higher than the measured frequencies. However, the characteristic vibrational signatures at 100 cm^{-1} and 171 cm^{-1} are well reproduced by the DFT calculations. In this sense the calculated and measured frequencies are consistent. We then calculated the FIR spectra of all clusters by taking dispersion forces directly into account. It is observed that both major vibrational bands shift to higher wavenumbers indicating enhanced anion–cation interaction due to dispersion forces. It can be further noticed that the frequency shift is significantly higher for the vibrational band at 100 cm^{-1} compared to that at 170 cm^{-1}, respectively. On average this shift is between two and four times larger than for the latter ($\Delta\nu = 10$–40 cm^{-1} *versus* $\Delta\nu = 5$–10 cm^{-1}). These different frequency shifts can be related to the two-to-one relationship of dispersion interaction as shown before. For the vibrational mode along the $^+$N–H···NO$_3^-$ hydrogen bond, only the dispersion interaction within an ion-pair is of relevance. With the help of isotopic substitution experiments we have recently shown that a shift of about 1 cm^{-1} in frequency can be related to a change in interaction energy of about 1.7 kJ mol^{-1}.[4,16] This relationship is confirmed here. Enhancing the H-bond strength due to dispersion by 17 kJ mol^{-1} results in frequency shifts up to 10 cm^{-1} for the cation–anion stretching mode. That the other vibrational band shifts stronger to higher frequencies can be explained by a stronger influence of dispersion forces. The vibrational band at 100 cm^{-1} describes librational motions and bending mode of the H-bond. For both motions the dispersion interaction between ion-pairs rather than that within ion-pairs are of relevance. Consequently these bands are strongly shifted to higher wavenumbers in accord with enhanced interaction strength due to two thirds of the dispersion energy (for details see the ESI,† Fig. S2).

Summarizing, we could show that the interaction energy in PILs can be dissected into Coulomb interaction, hydrogen bonding and dispersion interaction. For this particular PIL both the H-bond as well as the dispersion energy can be quantified to be 50 kJ mol^{-1}, each representing 10% of the overall interaction energy. The dispersion interaction could be dissected into two portions. One third could be related to the dispersion interaction within an ion-pair enhancing the H-bond strength, and two thirds stem from dispersion interaction among the ion-pairs. This distribution of dispersion interaction is reflected in the far infrared spectra. The H-bond band is shifted weaker than the low frequency band where the latter indicates diffuse cation–anion interaction and H-bond bending motions. Finally, we can dissect the different types of interaction energies indicating their characteristic influence on vibrational modes in the FIR of PILs.

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