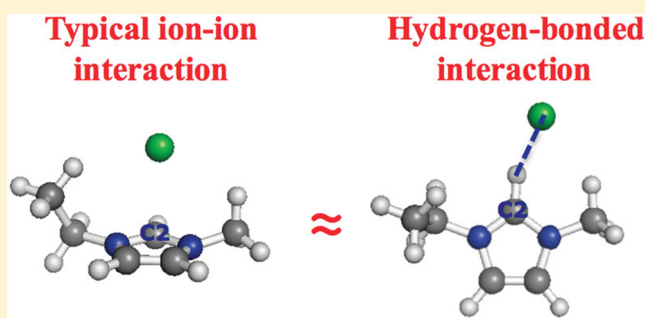


Nature of Hydrogen Bonding in Charged Hydrogen-Bonded Complexes and Imidazolium-Based Ionic Liquids

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ABSTRACT: The nature of hydrogen bonding was compared in neutral complexes and negatively charged complexes consisting of either the HF molecule or the halide anion (fluoride and chloride) and the C–H bond in the methane molecule with a varying degree of fluorination (such as CH₄, CH₂F₂, and CHF₃). Both linear (C_{3v} symmetry) and nonlinear (C_{2v} symmetry) hydrogen-bonded complexes were studied. Symmetry-adapted perturbation theory was used to decompose interaction energies into fundamental components such as Coulomb, repulsion, induction and dispersion to analyze the interplay among these forces in stabilizing hydrogen bonding. In the linear charged complexes, both Coulomb attraction and induction significantly contributed to the stabilization of hydrogen bonding. In the nonlinear charged complexes, mainly Coulomb attraction contributed to the HB complex stabilization, with the inductive forces playing a less important role. Contrary to the neutral complexes, dispersion forces played only a marginal role in the charged complexes. Interplay between the fundamental forces was also investigated in the ion pairs of the imidazolium-based ionic liquid, [C₂mim]Cl, that were categorized as either (1) typical ion–ion interaction, with the anion interacting from above or below the imidazolium plane; or (2) hydrogen-bonding interaction, with the anion interacting with the C2–H bond of the imidazolium cation. Both types of interactions were found to induce similar charge transfers, and the analysis of the energetic components revealed only a slight difference in the ion pairs studied: (1) both interactions were electrostatically driven, between 86% and 88% of the overall attractive energy, with the electrostatic component being slightly lower in the hydrogen-bonded ion pairs by $\sim 8 \text{ kJ mol}^{-1}$; and (2) dispersion forces were found to be stronger in the typical ion–ion interactions by $\sim 15 \text{ kJ mol}^{-1}$ and could be possible only due to the fact that the anion was able to move closer to the cation with no steric hindrance. From the experimental point of view, a vibrational red shift is expected in the hydrogen-bonded complexes of imidazolium-based ionic liquids, whereas the ion–ion interactions are more likely to produce a slight blue shift.



INTRODUCTION

Hydrogen bonding (HB) is an extensively researched topic in chemistry and biology because of its ubiquitous influence on a myriad of chemical and biological systems.^{1,2} Nonetheless, the nature of hydrogen bonding still represents an intriguing issue in charged complexes and systems consisting of ions because its classification appears to be rather difficult. Hydrogen bonding is normally referred to as a mainly electrostatic interaction, whereas its dispersion character arising from electron correlation effects cannot be neglected. The chemical structure of individual species in a hydrogen-bonded complex appears to dictate its nature. By definition, hydrogen bonding describes a directional X–H···Y interaction, where X and Y are electronegative atoms and $R(X\cdots Y)$ is less than the sum of the van der Waals radii of X and Y. This implies an orbital overlap between the orbitals on both atoms that results in a net transfer of charge transfer between the electronegative atoms.

The hydrogen-bonded complexes have one distinct orbital (usually the HOMO) with contributions from atomic orbitals of both electronegative atoms. There are three main contributions that determine the strength of this interaction: Coulomb and induction forces due to the dipole–dipole interaction and dispersion

forces due to electron correlation effects. The interplay among these three forces also determines the nature of hydrogen bonding. It is obvious that the Coulomb and induction interactions dominate the system, for which the dipole moments of the bonds involved are non-negligible.¹ For example, in the water dimer, (H₂O)₂, the Coulomb attraction contributes >50% to the final interaction energy.² In the CH₄···H₂O complex, where the C–H bond is much less polar than the O–H bond, the Coulomb force contribution is significantly smaller, and because of the increased repulsion, the overall interaction becomes only weakly attractive.² Overall, all three attractive forces (electrostatic, induction, and dispersion) are relatively weak in neutral systems, and therefore, the hydrogen bonding strength falls in a relatively narrow range from -1 to -40 kJ mol^{-1} .

The situation becomes different when hydrogen bonding occurs in ionic systems (e.g., between a neutral molecule and a charged species) because the leading interaction becomes that of the ion–dipole (or induced dipole) type.² Dispersion forces can

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play a role only at short distances between species because these decay very fast with distance ($\sim R^{-6}$), whereas Coulomb and induction forces are much stronger and are classed as long-range interactions because they change much more slowly with distance. For example, ion-dipole interactions decay as R^{-2} with increasing distance; dipole-dipole interactions, as R^{-3} ; and ion-induced dipole, as R^{-4} .

One of the strongest hydrogen bonding interactions in neutral systems is that in the $\text{HF} \cdots \text{OH}_2$ complex³, as it appears on the higher end of the interaction energy range at -35 kJ mol^{-1} . When the neutral HF molecule becomes a negatively charged fluoride anion,^{4,5} then the interaction energy in $\text{H}_2\text{O} \cdots \text{F}^-$ increases to as much as $-107.6 \text{ kJ mol}^{-1}$. The reasons for the increase in energy are 2-fold: the Coulomb attraction and induction forces between the ion and the water dipole are much stronger, and the dispersion interaction is also increased as a result of the fact that the electronegative atoms are drawn closer together.

Ionic liquids represent a third scenario, in which both species are charged from the outset. It has been shown before by various research groups that Coulomb forces dominate interactions in ionic liquids.^{6–14} Interionic interaction is one of the strongest intermolecular interactions observed in chemical systems and is responsible for formation of strong ionic lattices in inorganic salts such as NaCl, resulting in a high melting point of the salt. Imidazolium-based ionic liquids are of particular interest due to their low viscosity, which is a driving factor behind various applications in lithium ion batteries and fuel and solar cells.^{15–18} As opposed to ammonium- and pyrrolidinium-based cations, the imidazolium-based cation consists of multiple sites around the ring for interactions with anions, with typical interionic interactions occurring from above and below the ring.

Kirchner et al. analyzed charges in ion pairs of $[\text{NH}_4][\text{BF}_4]$, $[\text{C}_2\text{NH}_3][\text{BF}_4]$, and *N*-ethyl, *N*-methyl imidazolium chloride, $[\text{C}_2\text{mim}]\text{Cl}$, ionic liquids and their potential energy surfaces with respect to the interionic distance.¹⁹ In the case of imidazolium-based ionic liquids, the $\text{C}_2\text{—H}$ bond of the imidazolium ring is known to have an acidic character, thus encouraging formation of hydrogen bonding with anions. Elongation of the donor-proton bond, be it N—H or $\text{C}_2\text{—H}$, was observed in the ion pairs of all three ILs, with the maximum elongation exceeding that of a typical hydrogen bond. The conclusion from Kirchner's work was that regular hydrogen bonding was possible in ionic liquids as a result of a substantial charge transfer and an orbital overlap between the HOMO-1 and HOMO-2 orbitals.

Schlegel et al. identified that a subtle balance between attractive and repulsive forces governed hydrogen bonds, resulting in either elongation (red shift) or shortening (blue shift) of the X—H bond in the $\text{X—H} \cdots \text{Y}$ hydrogen-bonded complex.²⁰ The orbital interaction was found to be the main cause of the X—H bond elongation in regular hydrogen-bonded complexes, such as $\text{FH} \cdots \text{OH}_2$, whereas repulsive forces were behind the X—H bond shortening in systems such as $\text{F}_3\text{CH} \cdots \text{FH}$. Recent ab initio calculations of ionic liquid ion pairs showed no significant energetic difference between typical ion-ion and hydrogen-bonding interactions.^{10,19} The main question still remains unanswered: whether there is a distinct difference in the ratio between the three main energetic components: Coulomb (electrostatic), induction and dispersion among these two types of interactions in ionic liquids.

A supermolecular approach is the most widely used approach for predicting interaction energies in hydrogen-bonded systems

and consists of performing energy calculations of the complex and its individual fragments. Although very popular, the approach suffers from two limitations: (1) lack of formulation of individual energy components, such as polarization, dispersion, charge-transfer and induction; and (2) basis set superposition error that is manifested through mixing of molecular orbitals of individual fragments, thus resulting in an artificial lowering of the energy. Various levels of ab initio theory have been applied to study hydrogen-bonded complexes, with spin-component scaled MP2 (SCS-MP2) and methods of coupled cluster theory leading the race in terms of their accuracy.^{21,22} Symmetry adapted perturbation theory (SAPT) is by far the more sophisticated approach to decompose interaction energies into fundamental components in noncovalently bonded complexes of two interacting species (i.e., monomers), such as Coulomb, induction, exchange (Pauli repulsion), and dispersion.²³

In this study, the SAPT approach was employed to investigate the nature of interaction in charged model systems consisting of the halide anion (fluoride and chloride) and the C—H bond in the methane molecule with a varying degree of fluorination (such as CH_4 , CH_2F_2 , and CHF_3) to mimic fully ionic systems by increasing a positive charge on the central carbon atom. Two types of complexes were considered: (1) linear hydrogen-bonded complexes, in which the C—H bond and the halide anion are collinear (with the classical angle of 180°); and (2) nonlinear hydrogen-bonded complexes, in which the halide anion interacts equally with two C—H bonds, forming an angle below 180° . The latter type represents a case that is more likely to be observed in ionic liquids due to the organic nature of the ions. The individual components of interaction energies were calculated using SAPT and MP2. The ratio of the electrostatic energy to the sum of the attractive forces served as a benchmark for judging the importance of electrostatics in negatively charged hydrogen-bonded complexes. For the sake of comparison, the nature of hydrogen bonding in analogous neutral complexes with the HF molecule instead of the halide anion was also investigated.

In addition to these model systems, SAPT was applied to ion pairs of the much-studied $[\text{C}_2\text{mim}]\text{Cl}$ ionic liquid. All possible configurations of the chloride anion around the imidazolium ring were studied and categorized as either (1) typical ion-ion interaction, with the anion interacting from above or below the imidazolium ring plane; or (2) hydrogen-bonding interaction that corresponds to the anion located in the same plane as the $\text{C}_2\text{—H}$ bond of the imidazolium cation, with a hydrogen atom separating the two ions. Components of the total electrostatic and dispersion energies were calculated with the view of identifying the main difference between the two types of interactions (typical ion-ion and hydrogen bonding) that would serve as a guide for designing ionic liquids with tuned properties.

Theoretical Procedures. Standard ab initio molecular orbital theory calculations were carried out using the Gaussian 09 set of programs.²⁴ All geometry optimizations of the model systems were performed using the MP2/6-311+G(3df2p) level of theory. For linear hydrogen-bonded systems, C_{3v} symmetry was used, with the $\text{CH}_2\text{F}_2 \cdots \text{F}^-$ complex being an exception, slightly deviating from the linear arrangement of the $\text{C—H} \cdots \text{F}$ interaction. Nonlinear hydrogen-bonded systems were successfully constrained to the C_{2v} symmetry. For the $[\text{C}_2\text{mim}]\text{Cl}$ ionic liquid, all possible configurations of the imidazolium ring with the Cl anion were optimized without any symmetry constraints at the MP2/6-311+G(d,p) level of theory. Charges in the

systems under study were performed using the CHELPG scheme by Breneman and Wiberg²⁵ by fitting the electrostatic potential generated from the MP2/6-311+G(3df,2p) electronic densities. The net charge transfer was calculated as the difference in charges between the calculated charge on the anion in the complex and the negative charge of unity (as in the noninteracting anion).

The SAPT calculations for the model systems and six ion pairs of the [C₂mim]Cl ionic liquid were performed using the SAPT2008.2 program²⁶ in combination with the aug-cc-pVDZ basis set. SAPT represents a multiple-perturbative approach in which interaction energy components stem from the zeroth-order wave function taken as the product of HF determinants of both ions. The intramonomer electron correlation corrections are calculated by means of a many-body perturbation theory. In this approach, the interaction energy can be decomposed into the following four fundamental components: electrostatic, also referred to as attractive Coulomb interaction (E_{Elst}); exchange (E_{Exch}) or Pauli repulsion; induction (E_{Ind}); and dispersion (E_{Disp}). The electrostatic component can be classically described as attractive interaction between original charge densities of interacting ions. Although the first-order electrostatic component can be easily calculated at the HF level of theory, electron correlation effects may affect the monomer charge densities, and therefore, higher-order corrections due to multipole–multipole interactions may not be neglected.

The induction component arises from interaction of permanent multipole moments of one monomer and the induced multipole moments on the other and is a result of the charge distribution distortion in one ion due to an external field generated by another ion. The dispersion part stems from instantaneous multiple moments in both monomers due to fluctuation in electron density, and therefore, interionic correlation effects of electron motions have to be considered. The repulsion (exchange) component is very difficult to describe classically because mathematically, it is equivalent to electron tunneling between the monomers' orbitals. Repulsion corrections of a higher order give rise to additional types of interaction, such as induction-exchange and dispersion-exchange components, and show extent of quenching of induction and dispersion energies as a result of the antisymmetrization of the induction and dispersion wave functions, respectively. At present, first-, second-, and third-order corrections can be calculated within the SAPT formalism. With respect to the traditional supermolecular approach, the total interaction energy in the third-order SAPT approximately corresponds to a fourth-order, many-body perturbation theory, thus allowing for accurate description of the interaction energy. Due to its formalism, the SAPT approach does not suffer from the basis set superposition error as the supermolecular approach, and thus, no additional consideration of mixing of molecular orbitals of monomers is necessary.

To compare the SAPT total energies, the interaction energies of hydrogen-bonded complexes were calculated at the MP2 level of theory in combination with the 6-311+G(3df,2p) basis set using the following expression:

$$E_{\text{int}} = E(A \cdots B) - E_{\text{AB}}^{\text{AB}}(A) - E_{\text{AB}}^{\text{AB}}(B) \quad (1)$$

where $E_{\text{AB}}^{\text{AB}}(A)$ and $E_{\text{AB}}^{\text{AB}}(B)$ are the energy of the fragment A and the fragment B in the complex AB, respectively, calculated using the basis functions of the whole complex (AB).

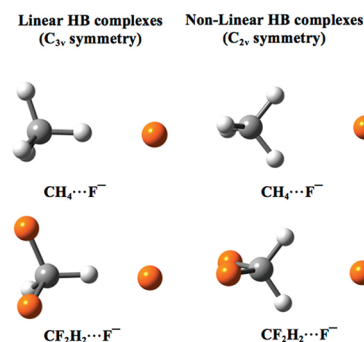


Figure 1. Examples of linear and nonlinear hydrogen-bonded complexes studied.

Four fundamental components of the interaction energies were calculated using the following expressions:²⁷

$$\begin{aligned} E_{\text{Elst}} &= E_{\text{Elst}}^{(10)} + E_{\text{Elst, resp}}^{(12)} + E_{\text{Elst, resp}}^{(13)} \\ E_{\text{Ind+X}} &= E_{\text{Ind, resp}}^{(20)} + {}^tE_{\text{Ind}}^{(22)} + E_{\text{Exch - Ind, resp}}^{(20)} + {}^tE_{\text{Exch - Ind}}^{(22)} \\ E_{\text{Disp+X}} &= E_{\text{disp}}^{(20)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)} + E_{\text{Exch - Disp}}^{(20)} \\ E_{\text{Exch}} &= E_{\text{Exch}}^{(10)} + \epsilon_{\text{Exch}}^{(1)}(\text{CCSD}) \end{aligned} \quad (2)$$

where “resp” corresponds to calculations, in which orbitals of the first interacting ion were distorted to the external field generated by the second interacting ion; the terms $E_{\text{Exch - Ind, resp}}^{(20)}$, ${}^tE_{\text{Exch - Ind}}^{(22)}$, and $E_{\text{Exch - Disp}}^{(20)}$ represent the exchange energies from quenching the induction and dispersion interaction due to antisymmetrisation of the wavefunctions. The fifth component, $\delta E_{\text{int, resp}}^{\text{HF}}$ to the interaction energy collects all third- and higher-order induction and exchange-induction terms and was calculated using the following expression:

$$\delta E_{\text{int, resp}}^{\text{HF}} = E_{\text{int}}^{\text{HF}} - E_{\text{Elst}}^{(10)} - E_{\text{Exch}}^{(10)} - E_{\text{Ind - Exch}}^{(20)} - E_{\text{Exch - Ind, resp}}^{(20)} \quad (3)$$

For the sake of simplicity, further in the text, the terms $E_{\text{Ind+X}}$ and $E_{\text{Disp+X}}$ are referred to as induction and dispersion, respectively. Together with the individual components of interaction energies described above, the interaction energy was split into two main components: total attractive energy and repulsion (i.e., exchange) energy. The following terms were combined to calculate the total attractive energy:

$$E_{\text{Attr}}(\text{tot}) = E_{\text{Elst}} + E_{\text{Ind+X}} + E_{\text{Disp+X}} + \delta E_{\text{int, resp}}^{\text{HF}} \quad (4)$$

RESULTS AND DISCUSSION

Model Systems: Geometries and Interaction Energies. The optimized structures of the model hydrogen-bonded systems are shown in Figure 1, and the optimized C–H and H···X distances and interaction energies are given in Table 1. The variable degree of fluorination was introduced into the hydrogen-bonded complexes to increase a positive charge on the carbon atom in the CH₄, CH₂F₂, and CHF₃ molecular series, thus forcing an increase in the electrostatic interaction. There are clear differences between the neutral and charged complexes. First, the interaction energies of the charged complexes are much stronger

Table 1. Equilibrium Distances of the C–H and H···X Bonds (in Å) in the Model Hydrogen-Bonded Systems and Interaction Energies Calculated at the MP2 and SAPT Levels of Theory (in kJ mol^{−1})

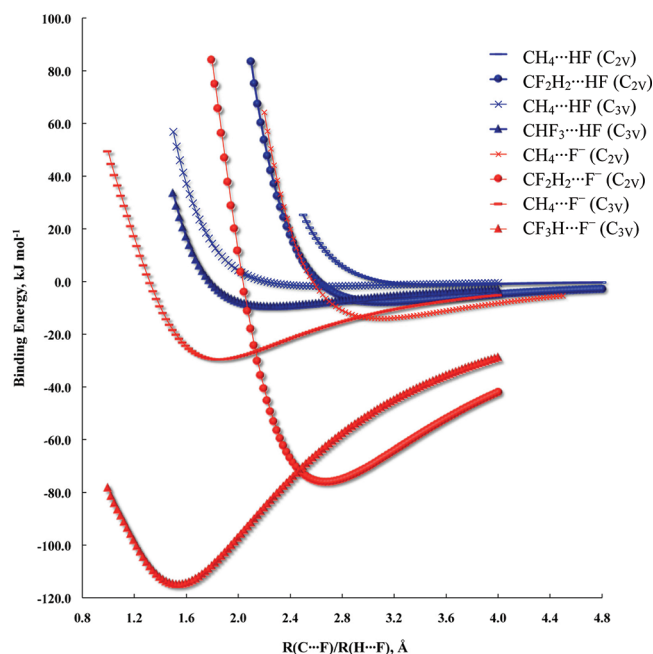
complexes	R_e (C–H)	ΔR^a	R_e (H···X)	E_{int} (MP2)	E_{int} (SAPT)
H ₃ C–H···F–H (C _{2v})	1.085	0.000	2.456	−0.6	−0.8
H ₃ C–H···F–H (C _{3v})	1.085	0.000	2.662	−1.2	−1.4
F ₂ HC–H···F–H (C _{2v})	1.086	−0.001	2.027	−6.5	−6.8
F ₃ C–H···F–H (C _{3v})	1.084	−0.002	1.174	−7.7	−8.1
H ₃ C–H···F (C _{2v})	1.085	0.000	2.007	−12.7	−14.1
H ₃ C–H···F (C _{3v})	1.108	0.023	1.855	−25.8	−26.3
F ₂ HC–H···F (C _{2v})	1.080	−0.007	1.596	−74.8	−75.6
F ₂ HC–H···F ^b	1.111	0.024	1.655	−85.1	−87.1
F ₃ C–H···F (C _{3v})	1.133	0.047	1.538	−120.0	−123.8
H ₃ C–H···Cl (C _{2v})	1.085	0.000	2.686	−6.9	−7.8
H ₃ C–H···Cl (C _{3v})	1.090	0.005	2.665	−10.6	−11.5
F ₂ HC–H···Cl (C _{2v})	1.083	−0.004	2.205	−50.0	−51.2
F ₃ C–H···Cl (C _{3v})	1.096	0.009	2.230	−65.3	−66.2
MAD				1.0	0.0

^a As calculated with respect to the R(C–H) distance of 1.085, 1.087, and 1.086 Å in MP2-optimized geometries of the individual CH₄, CF₂H₂, and CHF₃ molecules, respectively. ^b Symmetry close to C_{3v}, with the nearly linear arrangement of the C–H bond and the F anion.

compared with those of the neutral complexes, in the latter case falling in the range of the traditional linear hydrogen bond between −0.8 and −8.1 kJ mol^{−1}. In the charged complexes, the interaction energies increase many-fold with increasing fluorination on the methane, becoming as high as −123.8 kJ mol^{−1} for CHF₃···F[−], thus indicating the increasing role of the Coulomb attractive interaction in hydrogen bonding. The energetic range of hydrogen bonding in the negatively charged complexes approaches that of some covalent bonds. Importantly, the interaction energies in charged complexes with linear (C_{3v}) and non-linear (C_{2v}) hydrogen bonds do not differ significantly, with the non-linear complexes being only slightly weaker. For example, the difference in the strength of the hydrogen bond is only 11.5 kJ mol^{−1} between the C_{3v} and C_{2v} complexes for CF₂H₂···F[−] and 14 kJ mol^{−1} between the nonlinear CF₂H₂···Cl[−] complex and the linear CF₃H···Cl[−] complex.

Second, in the neutral complexes, the C–H bond length does not significantly alter with increasing fluorination of the methane, whereas the negatively charged complexes exhibit some clear trends. For example, in the neutral methane complexes, hardly any change is observed in the C–H bond distance; however, elongation of the C–H bond up to 0.047 Å occurs in the charged complexes with linear hydrogen bonds. The charged complexes with nonlinear hydrogen bonds exhibit either no change or a small shortening of the C–H bond up to 0.007 Å. It can be clearly seen that the C–H bond elongation does not appear to correlate with the strength of the interaction.

On the other hand, the H···X distance generally decreases with increasing interaction energy, regardless of the type of hydrogen bonding, that is, linear or nonlinear. The H···X distance decreases more significantly in neutral complexes, by ~1.3 Å, on going from CH₄ to CF₃H, whereas in charged complexes, the difference between CH₄ and CF₃H is only ~0.5 Å. It has to be noticed that a large decrease of the H···X bond in the neutral complexes is accompanied by a relatively small change in interaction energies, with a maximum of 6.3 kJ mol^{−1}, whereas shortening of the H···X bond in charged complexes corresponds to much larger changes in

**Figure 2.** Potential energy surfaces of increasing the C···F distance in complexes with nonlinear hydrogen bonding and the H···F distance in complexes with linear hydrogen bonding as calculated at the MP2/6-311+G(3df,2p) level of theory using relaxed scans.

energies, such as 110 kJ mol^{−1} in fluorides and 59 kJ mol^{−1} in the chlorides.

The H···X bond is shortest in the negatively charged complexes with nonlinear hydrogen bonding, with the interaction energy being only slightly weaker. Obviously, bringing the anion closer to the C–H bond increases the Coulomb attraction, thus compensating for the nonlinearity of hydrogen bonding and producing energy similar in strength to traditional hydrogen-bonded complexes. Compared with fluoride, the chloride anion has a more delocalized charge and sits farther away from the C–H bond in the complexes as a result of not only increased

Table 2. Components of Interaction Energies in the Model Hydrogen-Bonded Complexes; Total Attractive Energy, $E_{\text{Attr}}(\text{tot})$; Percentage of Electrostatic Interaction Contribution into the Total Attractive Energy, % Elst; and Net Charge Transfer, NCT^a

complexes	E_{int} (SAPT)	E_{Elst}	$E_{\text{Ind+X}}$	$E_{\text{Disp+X}}$	$\delta E_{\text{int}}^{\text{HF}}$	E_{Exch}	$E_{\text{Attr}}(\text{tot})$	% Elst	NCT
H ₃ C–H...F–H (C _{2v})	−0.8	−0.3	−0.2	−1.8	−0.1	1.5	−2.4	13	−0.021
H ₃ C–H...F–H (C _{3v})	−1.4	−1.2	−0.2	−1.9	−0.2	2.1	−3.5	34	−0.031
F ₂ HC–H...F–H (C _{2v})	−6.8	−7.5	−0.6	−3.5	−0.3	5.1	−11.9	63	−0.039
F ₃ C–H...F–H (C _{3v})	−8.1	−9.9	−1.2	−3.8	−0.7	7.4	−15.6	63	−0.022
H ₃ C–H...F (C _{2v})	−14.1	−10.5	−19.6	−8.7	−1.1	25.8	−39.9	26	0.031
H ₃ C–H...F (C _{3v})	−26.3	−40.4	−35.0	−16.2	−10.4	75.7	−102.0	40	0.023
F ₂ HC–H...F (C _{2v})	−75.6	−96.7	−28.9	−16.3	−6.7	73.0	−148.6	65	0.044
F ₂ HC–H...F ^b	−87.1	−124.9	−46.2	−22.2	−20.7	127.0	−214.0	58	0.080
F ₃ C–H...F (C _{3v})	−123.8	−179.4	−60.8	−27.9	−34.4	178.7	−302.5	59	0.128
H ₃ C–H...Cl (C _{2v})	−7.8	−5.3	−8.1	−6.2	−0.8	12.5	−20.4	26	0.023
H ₃ C–H...Cl (C _{3v})	−11.5	−12.0	−11.0	−8.5	−2.7	22.7	−34.2	35	0.020
F ₂ HC–H...Cl (C _{2v})	−51.2	−63.6	−10.9	−12.1	−5.0	40.4	−91.6	69	0.042
F ₃ C–H...Cl (C _{3v})	−66.2	−88.2	−18.5	−16.1	−13.5	70.0	−136.3	65	0.088

^a All energies are given in kJ mol^{−1}. ^b Symmetry close to C_{3v}, with the nearly linear arrangement of the C–H bond and the F anion.

radius of the chloride anion but also the interplay of Coulomb attractive and repulsive interactions; this phenomenon will be explained in more detail below.

Model Systems: Potential Energy Surfaces and Components of Interaction Energies. The potential energy surfaces of the hydrogen-bonded model systems are presented in Figure 2. For the sake of simplicity, only fluoride-based model systems are shown in the graph. The potential energy surfaces were generated with respect to increasing distance between the fluorine atom in the linear HB complexes or the fluoride anion in the nonlinear complexes and the hydrogen atom of the C–H bond. The contrast between the minima of the neutral and charged complexes is rather striking. In addition to weak interaction energies, the neutral complexes have very shallow minima on the PESs, whereas most of the charged complexes (with the exception of the CH₄...F[−]) are located in very pronounced minima, indicating strong intermolecular interactions similar to some covalent bonds. It has to be noticed that for the charged systems, the minima become more pronounced with increasing fluorination of the methane molecule, that is, increased charge on the carbon atom. This finding indicates that there must be a different interplay of the fundamental forces in neutral and charged hydrogen-bonded complexes.

To investigate this observation further, interaction energies were decomposed into fundamental components such as Coulomb attraction, repulsion, induction and dispersion (Table 2).

The neutral methane-based complexes with a negative charge on the carbon of −0.38e have a small electrostatic energy, contributing only 13% to the overall attractive interaction energy. Dispersion interaction appears to significantly contribute the overall stabilization of the complex, thereby producing weak interaction energies. As the carbon atom becomes positive in the case of CH₂F₂ and CHF₃, the electrostatic contribution reaches about 60% of the total attractive energy for both the linear and nonlinear complexes.

Compared with the neutral complexes, in the negatively charged complexes with the fluoride anion, the induction and dispersion contributions become substantial and fall between −20 and −60 kJ mol^{−1} and −8 and −28 kJ mol^{−1}, respectively. Obviously, the negatively charged anion induces a larger dipole moment on the interacting species than the neutral HF molecule,

and thus, inductive forces of the ion-induced dipole type begin to play an important role in the final interaction energy. In the methane-based complexes, the increased repulsion interaction results in weaker overall interaction. In the case of the HB complexes, with increasing fluorination on methane (CH₂F₂ and CHF₃), the repulsion energy increases even further as the fluoride sits closer to the C–H bond compared to HF. For both linear and nonlinear complexes with CH₂F₂ and CHF₃ the electrostatic and induction components contributes >79% to the total attractive energy, thus indicating that the nature of hydrogen bonding in charged complexes with a positive charge on the carbon atom is driven mainly by attractive Coulomb forces and inductive forces, with the latter being more important in linear complexes.

For the negatively charged complexes with the chloride anion, the induction does not increase as much compared to the fluoride-based complexes and falls between −8 and −18 kJ mol^{−1}. For the complexes with CH₂F₂ and CHF₃, the role of the electrostatic interaction dominates the complex stability, with the induction component contributing only 13%. Compared with the corresponding fluoride complexes, the dispersion term reduces to about −15 kJ mol^{−1} as a result of the chloride sitting farther away from the C–H bond by ~0.5 Å compared with F[−]. Although the interplay between the fundamental components is slightly different, the final result is similar to the fluoride-based complexes with CH₂F₂ and CHF₃, as the electrostatic and induction forces begin to also contribute >79% to the overall stability.

In summary, the main energetic difference between neutral and charged hydrogen-bonded model complexes is the role of induction and Coulomb attraction in stabilizing hydrogen bonding. Understandably, anions are capable of inducing stronger dipole moments in the interacting species than in neutral molecules; those with a less delocalized charge impose a larger moment. Coulomb attraction becomes particularly important in negatively charged complexes when the charge on the electronegative atom forming the hydrogen bond is positive. There is, of course, a subtle interplay among induction, Coulomb attraction, and repulsion because the charged HB complex adopts the geometry that can ensure the strongest interaction. Induction increases faster with decreasing distance between electronegative

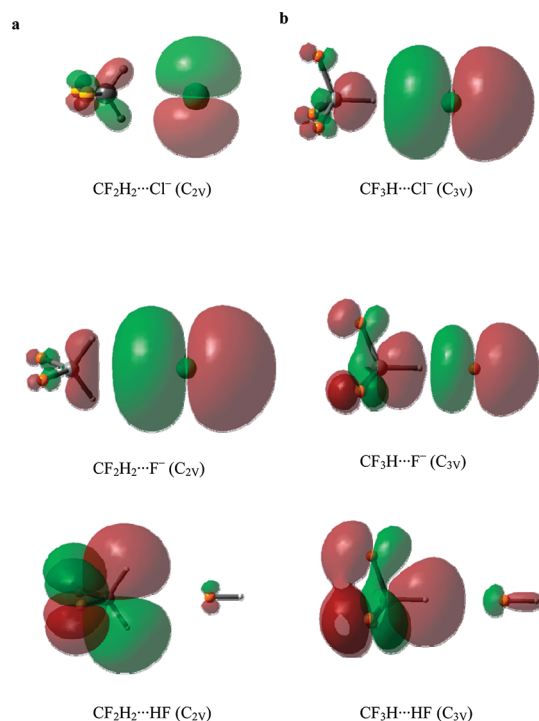


Figure 3. HOMOs of model systems with (a) nonlinear and (b) linear hydrogen bonds.

atoms compared with Coulomb attraction. Since the repulsion is dependent on the number of electrons, bulkier anions need to reside at longer distances. In contrast to the neutral complexes, dispersion plays only a marginal role in charged complexes.

Model Systems: Charge Transfer. In the negatively charged HB complexes, there is a positive net charge transfer (NCT); that is, a portion of the negative charge on the anion is transferred over to the substituted methane, thus making the carbon atom less positive (see Table 2). The nonlinear HB complexes have less positive NCT values compared with the linear HB complexes. For the nonlinear complexes, the charge transfer is accompanied by the shortening of the C–H bond, thus blue-shifting the hydrogen bond vibration in the infrared spectra. Our results are in agreement with those of Schlegel et al., who established that the charge transfer was also smaller in blue-shifted neutral complexes and attributed blue shifting in HB to increased repulsive forces.²⁰ The neutral complexes exhibit negative NCT values; this trend is expected for HB complexes with the polar molecules such as HF.^{2,20}

The presence of the net charge transfer also indicates the presence of an orbital overlap for the charge to be transferred between interacting species. The HOMO orbitals in the fluorides and chlorides as well as the neutral systems are shown in Figure 3. Analysis of these orbitals indicates that there is, indeed, a partial orbital overlap for all of the HB complexes studied, independent of whether hydrogen bonding can be classed as red- or blue-shifted. It was previously established that >58% of the overall stabilization is a result of the electrostatic interaction in all of the negatively charged complexes, with a positive charge on the carbon atom in CH₂F₂ and CHF₃. Hence, it is not surprising that the total interaction energy correlates very well with the net charge transfer ($R^2 > 0.90$), as shown in Figure 4. Analysis of the graph indicates that the linear and nonlinear complexes form

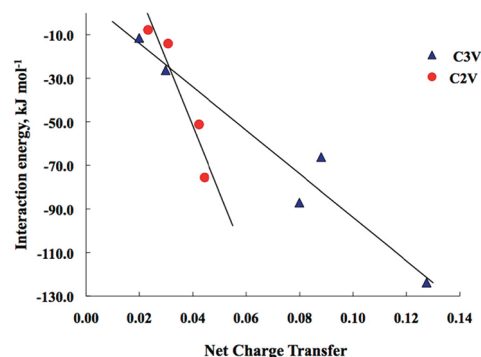


Figure 4. Correlation between net charge transfer and interaction energies in charged hydrogen-bonded complexes.

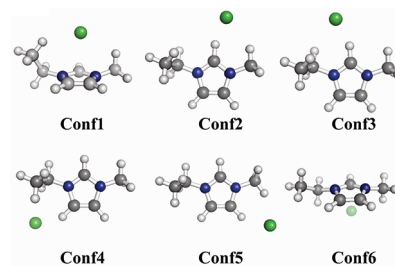


Figure 5. Optimized geometries of all possible ion pairs in 1-ethyl-3-methyl-imidazolium chloride, [C₂mim]Cl.

separate linear trends with different slopes, with the trend for the nonlinear complexes being steeper by a factor of 3. The interaction energy increases much faster with increasing net charge transfer in the nonlinear complexes, indicating the growing role of Coulomb attraction that would ensure a stronger interaction. The Coulomb attraction might be the result of further increased positive charge on the carbon atom in CH₂F₂ and CHF₃ due to hydrogen bonding, as was identified in blue-shifted neutral complexes.²⁰ These findings further confirm the previously established trends that the inductive forces are stronger in linear charged HB complexes compared with nonlinear ones.

Ionic Liquid Ions: Geometry Effect. Six different conformations of the chloride anion interacting with the imidazolium cation have been considered (see Figure 5). Two of them (referred to here as Conf1 and Conf6) represent a typical ion–ion interaction, in which the anion interacts either above or below the plane of the imidazolium ring. Four other conformations (referred to here as Conf2, Conf3, Conf4, and Conf5) are best described as hydrogen-bonded complexes. In these, the chloride anion is positioned in the plane of the C2–H, C4–H, or C5–H bonds, thus following the definition of the traditional hydrogen bond. The main geometric parameters associated with the described interactions are presented in Table 4. The major difference in geometry stems from the C2–H bond lengthening for the in-plane interactions, such as Conf2 and Conf3, whereas there is a slight shortening of the C2–H bond in the cases of the anion interacting from above and below the imidazolium plane. Elongation of the C2–H bond is also observed for the C4–H and C5–H bonds, but to a lesser extent. The C–H...Cl angle is not perfectly linear in the hydrogen-bonded systems because of the presence of two alkyl groups in the ring that introduce additional interactions with the

Table 3. MP2-Optimized Geometry Parameters of the Ion Pairs of $[\text{C}_2\text{mim}]\text{Cl}^a$

configuration	R_e (C–H) ^b	ΔR (C–H) ^c	R (C···Cl)	R (H···Cl)	\angle (C–H···Cl)
Conf1	1.076	−0.004	2.693		74
Conf2	1.126	0.046	3.025	1.899	159
Conf3	1.123	0.043	3.026	1.903	156
Conf4	1.104	0.024	3.095	1.991	148
Conf5	1.105	0.025	3.117	2.012	150
Conf6	1.076	−0.004	2.656		72

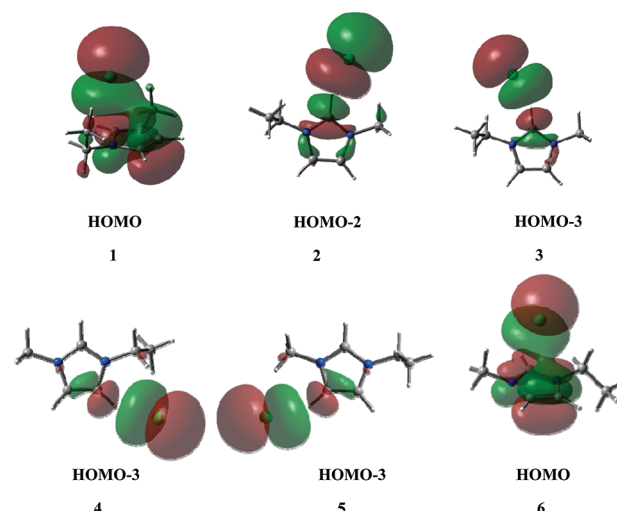
^a All distances are given in Å. ^b Calculated with respect to R_e (C–H) of 1.080 Å in the C_2mim cation. ^c For Conf1, Conf2, Conf3, and Conf6, the C–H bond corresponds to the C2–H bond; for Conf4 and Conf5, to the C4–H and C5–H bonds, respectively.

anion, thus reducing the hydrogen bond angle to the range of 148–159°. Another noticeable difference between typical ion–ion and hydrogen-bonded interactions is the C···Cl distance. In Conf1 and Conf6, the chloride sits much closer to the H atom, by ~ 0.33 Å, compared with Conf2 and Conf3, with the H···Cl distance reaching 3.12 Å for Conf5. When comparing the C···Cl distances with those of the $\text{CH}_2\text{F}_2\cdots\text{Cl}^-$ and $\text{CHF}_3\cdots\text{Cl}^-$ systems, it becomes clear that the anion is drawn much closer to the cation. In the case of the above/below plane conformations, the C···Cl distances are very similar to those of the $\text{CH}_2\text{F}_2\cdots\text{F}^-$ and $\text{CHF}_3\cdots\text{F}^-$ complexes.

Ionic Liquid Ions: Charge Transfer and Components of Interaction Energy. Interaction energies, their components and net charge transfer of the ion-pair conformations are listed in Table 4. Surprisingly, very similar net charge transfer is observed in both types of interactions. For example, the NCT value of Conf1 is only 0.006 below those of Conf2 and Conf3. Slightly higher values for the in-plane conformations might indicate only a marginally larger electrostatic interaction. As in the case of the negatively charged HB complexes, the net charge transfer correlates linearly with the interaction energy. As can be seen from Figure 6 the orbital overlap between the chloride anion and the C_2mim cation is observed in all of the conformations studied. Therefore, the net charge transfer does not seem to be a good criterion for identifying hydrogen bonding in imidazolium-based ionic liquids.

Analysis of Table 4 reveals that the ion–ion interaction from above and below the imidazolium plane is thermodynamically most preferable and is about 10 kJ mol^{-1} more stable than the in-plane conformations with hydrogen bonding, Conf2 and Conf3. Decomposition of the interaction energy reveals that the energetic difference between Conf1 and Conf2/Conf3 comes mainly from the attractive electrostatic interaction and dispersion interaction. The contribution from higher electrostatic terms such as multipole–multipole forces is larger in Conf2 and Conf3, whereas Coulomb attraction clearly dominates in Conf1. In Conf2 and Conf3 the Coulomb contribution is slightly weaker by ~ 7 – 10 kJ mol^{-1} , resulting in 75% of the overall contribution to the total attractive energy, compared with 78% in Conf1.

Surprisingly, the induction energy is similar in both ion–ion and hydrogen bonding interactions, averaging to -64 kJ mol^{-1} , which is very similar to that in the $\text{CHF}_3\cdots\text{F}^-$ HB complex. The net charge transfer is slightly more positive in Conf2 and Conf3, which is in accord with the stronger higher electrostatic terms. Since the charge transfer is almost identical for conformations

**Figure 6.** Molecular orbitals of six ion-pair configurations of $[\text{C}_2\text{mim}]\text{Cl}$ representing the charge transfer between the cation and anion.

from above/below and in the plane, it might explain why the scaling of the charge on the imidazolium ionic liquids works quite well in classical MD simulations in terms of transport properties and total free energies.²⁸ The second difference comes from the dispersion component that contributes -54.3 kJ mol^{-1} to the interaction energy in Conf1, which is 14 to 17 kJ mol^{-1} stronger compared with the in-plane conformations. Obviously, stronger dispersion can be achieved in Conf1 as a result of the fact that the chloride anion can be located closer to the imidazolium ring, whereas in the hydrogen-bonded ion-pair conformations, the elongated C2–H bond would prevent the Cl anion from approaching the cation closer.

The hydrogen bonds in Conf2 and Conf3 cannot necessarily be thought of as traditional hydrogen bonds because the electrostatic and dispersion contributions are considerably larger than in the neutral HB systems. The electrostatic component is ~ 50 times that of the neutral systems, whereas the dispersion is ~ 20 times larger. Compared with the negatively charged HB complexes with the chloride anion (see Table 2), the electrostatic component dominates by at least a factor of 5, whereas the dispersion component is 6 times larger. It is clear that both Coulomb attraction and induction should increase between oppositely charged species. A significant charge transfer between the electronegative atoms involved in hydrogen bonding should result in a significant elongation of the C–H bond. Thus, hydrogen bonding in imidazolium ionic liquids can be thought of as 5 times the traditional hydrogen bond in charged systems with regard to interaction energy as well as bond elongation. It should be noted that the HF level of theory predominantly accounts for electrostatic, induction, and exchange interactions. In the imidazolium ion pairs, interaction energies calculated at the HF/6-311+G(3df,2p) level of theory overestimate the sum of the electrostatic, induction, and exchange terms from SAPT by 14 kJ mol^{-1} for Conf1, Conf2, and Conf3 and 7 – 8 kJ mol^{-1} for Conf4 and Conf5 (for more detail, see Table 4). These energies still fall short of the total interaction energy, and no obvious distinction among Conf1, Conf2, and Conf3 can be drawn.

Comments on the Nature of Hydrogen Bonding in Imidazolium-Based ILs. In this study, we have shown that the total interaction energy and charge transfer could not be considered as good criteria for distinguishing hydrogen bonding from the

Table 4. Interaction Energies of the [C₂mim]Cl Ion Pairs Calculated at HF, MP2 and SAPT Levels of Theory; Components of Interaction Energies; Total Attractive Energy, $E_{\text{Attr}}(\text{tot})$ Interaction; Percentage of the Electrostatic Interaction Contribution into Total Attractive Interaction Energy, % Elst; and Net Charge Transfer, NCT^a

	E_{int} (HF)	E_{int} (MP2)	E_{int} (SAPT)	E_{Elst}	$E_{\text{Ind+X}}$	$E_{\text{Disp+X}}$	$\delta E_{\text{int}}^{\text{HF}}$	E_{Exch}	$E_{\text{Attr}}(\text{tot})$	% Elst	NCT
Conf1	−367.2	−401.0	−407.0	−470.6	−63.3	−54.3	−18.7	199.8	−606.9	78	0.241
Conf2	−373.0	−392.7	−397.1	−434.8	−63.7	−37.8	−40.6	179.7	−576.9	75	0.247
Conf3	−371.3	−393.0	−397.5	−437.4	−64.2	−40.2	−38.9	183.2	−580.7	75	0.248
Conf4	−329.6	−364.3	−358.0	−400.3	−55.7	−36.0	−29.7	163.6	−521.7	77	0.215
Conf5	−328.8	−360.4	−362.8	−405.2	−56.7	−40.6	−27.1	166.7	−529.6	77	0.211

^a All energies are given in kJ mol^{−1}.

ion–ion interaction. The typical ion–ion interaction when the anion is located above/below the imidazolium ring is more energetically preferable than the C2–H hydrogen-bonded ion pairs by about 10 kJ mol^{−1}. Both types of interactions are electrostatically driven, with the electrostatic component being weaker by only 7–10 kJ mol^{−1} in the HB ion pairs. Dispersion is more important (by ~14–17 kJ mol^{−1}) for typical ion–ion interactions in imidazolium ILs and can be possible only because of the fact that the anion can move closer to the cation with no steric hindrance. Thus, hydrogen bonding in imidazolium ionic liquids introduces only a slight difference into the interplay of the fundamental energetic components compared with a typical ion–ion interaction, as Coulomb attraction dominates due to the ions of opposite charges involved. Obviously, chloride prefers to sit closer to the ring if approached from above or below the plane, because stronger electrostatic and dispersion interactions can be achieved, thus resulting in a more stable conformation. It is expected that with increasing distance between the interacting charged species, the difference between the two types of interactions will become negligible. The HB is certainly easier to break in the case of the in-plane conformations as a result of the decreased dispersion component, but once broken, the typical ion–ion interactions remain.

On the basis of the presented data, hydrogen bonding in ionic liquids cannot be considered as regular hydrogen bonds, as otherwise observed in complexes between neutral species; the energetics and bond elongation are strongly exaggerated in systems incorporating charged species as a result of the increase in electrostatic and induction forces. From an experimental point of view, elongation of the C–H bond seems to be the only reliable indicator for judging the presence of hydrogen bonding. A vibrational red shift is expected in hydrogen-bonded ion pairs, whereas the ion–ion interaction is more likely to produce a slight blue shift. It should be noticed that since dispersion is more important for the above/below the imidazolium ring interionic interactions, the choice of the level of theory becomes very crucial. DFT functionals that do not take dispersive forces fully into account have to be assessed before any conclusions are drawn. On the basis of the analysis presented, it can be foreseen that if the dispersion part of the interaction is not treated accurately enough, the shortcomings might result in the reverse trend for interaction energies, and, hence, some DFT functionals might rank the in-plane conformations as more energetically stable as a result of an increased electrostatic component that is already treated satisfactorily.

CONCLUSIONS

Hydrogen bonding in neutral model complexes is stabilized by both electrostatic and dispersion interactions, whereas in charged

complexes with fluoride and chloride anions, both Coulomb attraction and induction play a more significant role, contributing around >58% of the overall attractive energy. This highlights the importance of the induced dipole moment by the anions in stabilization of hydrogen bonding in charged complexes. In the ion pairs of imidazolium-based ionic liquids, the main difference between the typical ion–ion interactions (such as Conf1 and Conf6) and hydrogen-bonded complexes (Conf2 and Conf3) is in a slightly decreased electrostatic contribution (by 7 to 10 kJ mol^{−1}) in the latter. Overall, the Coulomb attraction and inductive forces dominate the energetics of imidazolium-based ion pairs and contribute between 86% and 88% of the overall attractive energy. The thermodynamic preference for the anion to interact from above/below the imidazolium ring plane comes mainly from a stronger dispersion component (by ~14–17 kJ mol^{−1}) as compared with the in-plane interactions. This larger component can be achieved only as a result of the fact that the anion is located closer to the imidazolium ring. The charge transfer differs only slightly for the complexes with typical ion–ion interactions from those with hydrogen bonding and, therefore, cannot serve as a reliable criterion for identifying the presence of hydrogen bonding in ionic systems. From an experimental point of view, the elongation of the C2–H bond resulting in a red shift of the C–H stretching vibrations seems to be a reliable measure, whereas a slight blue shift is indicative of typical ion–ion interactions. The findings of this work reveal a subtle energetic interplay in the ion pairs of imidazolium-based ionic liquids with hydrogen bonding compared with those with typical ion–ion interactions due to dispersion forces, thus highlighting the importance of accurate treatment of electron correlation effects for reliable calculations of thermodynamic properties of imidazolium-based ionic liquids.

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