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Computational Study of the Nature of Tetrel Bond

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COMPUTATIONAL STUDY OF THE NATURE OF TETREL BOND

by

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COMPUTATIONAL STUDY OF THE NATURE OF TETREL BOND

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Western Michigan University, 2018

For more than a hundred years, the type of a chemical bond has been distinguished according to the relative electronegativities of chemical units at the ends of a bond. Whereas, the bond of unequally electronegative on both ends is called a polar covalent or even ionic bond or a non-polar covalent bond in case of both equal. Regardless the type of bonded elements, the whole idea for the bond was believed to be electron driven only. In the 20th century the development of the idea, that not just the electronic relation but specific elements are also able to characterize the type of chemical bonds they establish, changed to the knowledge of chemical bonding. Atoms change the means of their interactions when bonded to other atoms and can activate some newly generated energy states to establish bonds only by electron density interactions.

Subsequently, individual groups of elements are investigated for their characterized behaviors of bonding. In addition to the widely well studied non-covalent interactions like hydrogen, halogen, pnicogen bonds etc., in this study tetrel bond is theoretically investigated for its nature of interaction using the energy decomposition analysis based on the block localized wavefunction (BLW) method and explained using tools like electron density maps and orbital correlation diagrams. The general idea we got is that the driving force behind tetrel interactions is the electrostatic attraction, backed up by polarization and charge transfer between the frontier orbitals of the involved molecules.

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INTRODUCTION

Non-covalent Interactions

In chemistry we always see chemical moieties coming together and making bonds, involving electrons through transferring or sharing them. Beside, the chemical bonds like covalent and ionic, other chemical molecules have been recognized which bond with each other but no sharing or transfer of the electrons are involved. The cause of such bonding is the existence of non-covalent interactions where electrons are not involved directly. Now, these interactions with the indirect involvement of electrons called non-covalent interaction can be both intermolecular, bringing different molecules together, or intra-molecular, enclosing different nodes on the same molecule. In general, these interactions are known to be very low in energy as the strength of an individual bond, but they are of great use when applied in a huge number, holding together large crystals and supermolecules.

As the name indicates, a noncovalent interaction does not include a complete electron transfer or sharing to become an ionic or covalent bond, as it is established by interactions of an electron deficient with an electron rich point. These interacting ends of activity can be located on different molecules[1] (intermolecular) or can be different nodes on the same molecule[2]

(intramolecular). This type of interactions between molecules are explored within a wide range of chemical entities as radicals,[3] metal hydrides,[4] pi systems[5] and molecules that include atoms from halogen,[6,7] pnicogen,[8–10] chalcogen[11] group of elements and some other elements on the periodic table like (Si, Ge, Pb, Sn).[12–14] According to the literature, these bonds are comparable to the hydrogen bond[6,11,15] in many characteristics as directionality,[6] bond length, bond strength for multiple reasons. Studies have uncovered the effects of such intermolecular interactions, in properties and chemical structures of essential molecules of life as RNA, DNA, proteins, and water.[16] And some recent research expectations are strong about their wide range of applications in crystal engineering,[17] supramolecular chemistry, and catalysis.[18] They are also studied for their ability to strengthen the intramolecular bonds within a molecule.[19]

Hydrogen Bond

A hydrogen bond is an attractive interaction that is mostly seen in the form of A-H…D, where A and D denotes and electron acceptor and an electron donor, respectively. The attraction is normally assigned to H and D points of interaction, where hydrogen plays a positive role. The strength and length of the hydrogen bond is seen to cause some blue or red shifting in the frequency of A-H bond. A

hydrogen bond can be established between any atom groups with the attraction ability to develop the interaction. So, the fact that a hydrogen bond is a characteristic of the hydrogen atom, is denied. The energy decomposition study on hydrogen bond describes it as mostly an electrostatic interaction, and the geometry and energy of a hydrogen bond depends on substitution and other changes made to molecular structure of interacting systems. For example, a recent study confirms the strengthening of an intramolecular hydrogen bond due to the resonance in molecule[2]. An ab initio method study, using the density functional theory DFT(B3LYP) with a large basis set including polarization and diffused functions, evaluated by the electron-correlated method MP2, calculated the hydrogen bonding energy as a difference between the total complex molecule energy and the energy for each involved fragment individually.[20] The study proposes the electron donating ability of donor group accounting for strengthening the hydrogen bond, which was made evident by studying different electron acceptors and electronegative substitution on both donor (D) and acceptor (A) molecules.

Halogen Bond

Since its contradicting behavior for being considered as a more electron dense end of a covalent bond to be attractive by electropositive points, halogen bonds are studied from 1960's in the form of R-X…B as X being a halogen atom interacting with a nucleophilic chemical unit B, as they are seen to be attracted by electronegative nodes. The mystery was explained on the bases of an electrostatic interaction through a mechanism called σ hole[21], a region of positive electrostatic potential located on the halogen due to the covalent bond. Since then, the electrostatic potential has been the base to study and explore all non-covalent interactions. A non-covalent interaction is explained based on the different aspect of an electrostatic cause. Electrostatic potential study of halogen bond confirms the presence of interacting energies like electron correlation, Pauli exchange, London energies, charge transfer of the lone pair electrons of the donor molecule to antibonding orbitals of halide molecule and polarization effect.[6,11]

σ Hole

The σ hole[22] is the region located on the opposite to the covalent bond to an electronegative atom, which has a positive electrostatic potentials due to a half-filled p orbital along the covalent bond of the electronegative atom,

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surrounded by a negative electron cloud belt around the atom. The negative belt is established by the filled p orbitals of the atom. The increase of electronegativity of the atoms, bonded to tetrel atom, withdraws more electron density from the tetrel site. This causes a stronger electron-deficient site resulting in a stronger σ hole interaction. σ hole has provided the ability to investigate similar interactions as chalcogen and pnicogen bond that includes elements from 6A and 5A groups of elements respectively, from the periodic table.

The factors that are responsible for the stability of such interactions are negotiated over the time, and it has been known that mostly equal contributions of electrostatic, inductive and dispersion forces are accounted for the stability. But once again the ability of a donor atom is also known responsible for being a high charge transfer energy contributor. The lastly mentioned interactions are known for their higher directionality compared to hydrogen bond.[11]

Tetrel Bond

Pnicogen and tertrel are the most recent terms used for non-covalent interactions. The term (pnicogen) initiates from an article by the Hey-Hawkins[9] group in 2011 and for the first time in 2013, Frontera and coworkers suggested the term tetrel bond.[18] Tetrel bonds are usually referred to those noncovalent

interactions established by a set of atoms referred to as tetrel atoms because of their ability to accept electrons through various chemical mechanisms, simplified as Lewis acids.[18] Moving down one more group of elements on the periodic table, elements like (C, Si, Ge) from the 4A group are studied for this specific set of interactions called tetrel bonds. These interactions are studied in an ($H_3Y…TrH_3X$) like systems where (Y) and (X) are usually an electron donor and an electronegative atom respectively with the (Tr) as one of the mentioned tetrel atoms. A recent study, backed up by Valence Bond Self Consistent Field (VBSFC) and Breathing Orbital Valence Bond (BOVB) at the DFT level of theory,[14] explains these interactions to be strengthened by factors like the electron donating ability of the donor fragment and the electronegativity difference between (X) and (Tr) atoms and as a major energy contributor, charge transfer forces are accounted for tetrel bond stabilization. The study investigated the strengthening factors of the tetrel bond in comparing $H_3N…SiH_3X$ to $H_3As…CH_3X$ complexes (X=halogen atom). The former complex, including a well polarized and directional lone electron pair on nitrogen is interacting with a molecule that has a large difference of electronegativity between Si and its covalently bonded halogen, had a stronger tetrel interaction. While the same interaction for the latter complex is weaker, because here a weak donor, known for its diffused lone pair orbital (As), is interacting with a molecule where a small

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electronegativity gap between C and halogens were observed. In some systems where (Si and Ge) are the tetrel atoms interacting with ammonia, the study shows a contradiction between the strength of the tetrel interactions and (HSAB) theory. Accordingly, a hard molecule is interacting better with a soft molecule but a tetrel interaction between two soft molecules or two hard molecules should be stronger. Consequently, a hard substitution to the soft molecule in a strong tetrel complex should weaken the tetrel interaction because of the change to the hardness of the soft molecule.

METHODOLOGY

Here in this study, we have used the energy decomposition approach to investigate the tetrel bond in some of the well-documented systems[5,6,14,23–26] in a conformation like (D⋯CH$_3$X) consisting of carbon atom as tetrel group representative, interacting with (ClF, PH$_3$, NH$_3$, SH$_2$, and H$_2$O) as donor molecules (D) and Lewis acids while the X substitutions are (F, Br, Cl and OH) radicals (Figure 1). Similar systems have been previously studied but the motive for this analysis is the use of Block Localized Wavefunction (BLW) method of energy decomposition to investigate, explain and compare the nature, support and stability factors of the intermolecular tetrel interactions.

Block Localized Wavefunction

BLW energy decomposition method, used for this study, has been able to distinguish each and every physically meaningful quantity of energy change and their contributions to overall interaction energy involved in intramolecular[2] and intermolecular[10] interactions, by localizing the electrons within blocks, restricting the electron transfer between interacting molecules. And this method enables us to have the energy change for each physically meaningful move, made by the fragments in a complex, initiating from a stable monomer state to a stable
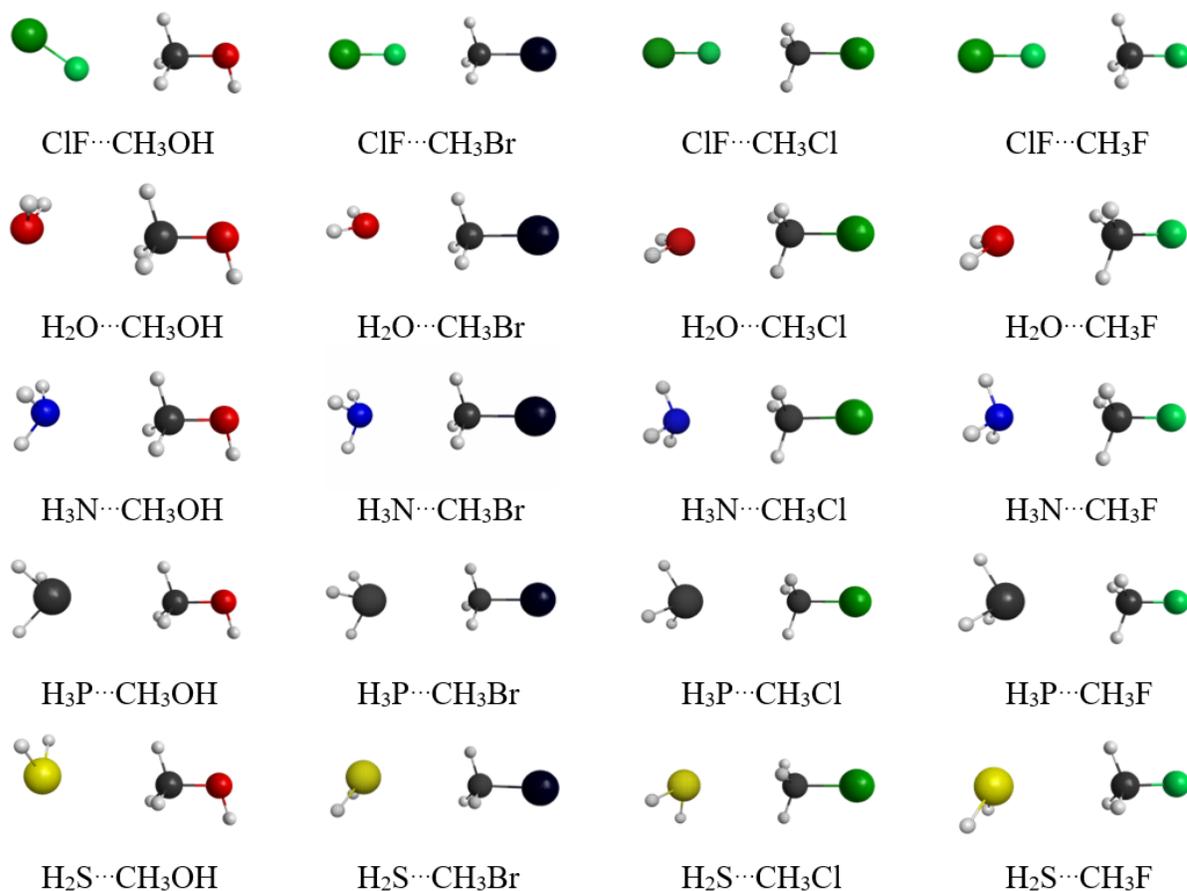
Figure 1. Optimal geometries of studied complexes

interacting complex.[27,28] The very first energy change is called deformation energy (ΔE_{def}) the energy for this step comes from a change in the stable geometry of a monomer to the one as in complex while moving toward forming the complex. The second energy term comes from approaching molecules to each other with frozen molecular orbitals where the change is only electrostatic but still we have the electron exchange forbidden, and the third step is when the exchange of electrons is allowed, for an energy term denoted as (ΔE_{ex}). Because of the computational difficulty of the exchange energy in DFT level of theory,

both electrostatic and Pauli exchange energies are added in one called Heitler-London energy (ΔE_{HL}). The next energy term is polarization (ΔE_{Pol}), occurring as an energy lowering step, due to the redistribution of the electron densities among the monomers after the electron exchange completion. In the end, we get another energy change for electron delocalization in the complex which denotes the charge transfer energy (ΔE_{CT}). The last two energy terms are always negative for being stabilizing steps for the complex. As a correction for the basis set super position error (BSSE), an electron correlation energy based on Boyd and Bernardi method for counterpoise correction[29] is added to the charge transfer as it can affect the charge transfer energies in higher level of computations.

Computational Details

The geometries of all complexes and monomers were optimized at both MP2/6-311+G** and DFT(wB97x-D)/6-311+G** level of theories for comparison purposes, in Gaussian16[30] software and re-optimized for the BLW energy decomposition analysis at the DFT(M06-2x)/6-311+G** level of theory[31] with all the frequency calculations for minima structure confirmation at the same level of theory, conducted on our in-house modified version of quantum mechanical software Gamess. Orbital correlation diagrams were plotted in Microsoft Excel application and electron density differential maps were plotted in Gaussview6 software[32] based on BLW orbital and density calculations.

Interaction energy was taken as the difference between a complex and total energy of isolated monomers' energies, with basis set superposition error (BSSE) considered based on the Boys and Bernardi method.[29]

RESULTS AND DISCUSSION

Table 1 contains deformation, electrostatic, polarization, charge transfer, and the binding energies for M06-2x, MP2, and wB97x-D with the optimal bond length for the tetrel interaction in all complexes of this study. The binding energies from our calculations with the M06-2X functional are highly comparable to the ones from MP2 and wB97x-D calculations. The overall results from our computations show electrostatic potential energies being the main contributor to the tetrel interactions supported by polarization and charge transfer as stability factors. The tetrel bond length ranges from $ClF\cdots CH_3Br$ 2.819 Å up to 3.655 Å $H_3P\cdots CH_3Br$ and the binding energy ranges from the weakest 3.03 kJ/mol for $ClF\cdots CH_3OH$ to the strongest for $H_3N\cdots CH_3F$ complex 11.00 kJ/mol Table 1. These results fall in a reasonable range for a non-covalent interaction and lays in a good comparison with other non–covalent interactions investigated with similar[2,10] and different[6,33,34] theoretical methods. As a key factor for the strength of a tetrel interaction, the increase of the difference between the electronegativity of C/X results in a more positive σ hole, and the electron donating ability of the donor molecule[14], which causes a stronger interaction. Therefore, in the former complex, due to the smaller electronegativity difference between carbon and (X=OH) interacting with a less polar molecule (D=ClF), the tetrel interaction is the weakest. However, in the

latter complex, a more polarized lone pair donor (D=NH$_3$) is interacting with the most positive σ hole among these complexes, due to a large electronegativity difference between carbon and fluorine, and the tetrel interaction is stronger than others in this study. The interaction energy corroborates the fact that it increases with the increase of electronegativity of X in a sequence of (OH < Br < Cl < F) substitutions within every set of Lewis acids, followed by the increase of Heilter–London energy as shown in Figure 2. This confirms that the increase of electronegativity of (X) results in an increase in the electronegativity gap between the carbon atom and bonded (X) substitution which in turn creates more electrophilicity of the σ hole, created along the (C–X) bond on the carbon end of the molecule. Likewise, within the same donor molecule, a very fine correlation can be seen between the (D··C) tetrel bond length in the optimal geometry and the interaction energy calculated by BLW computational method. Figure 3 shows a similar correlation where NH$_3$ is the donor monomer as an example.

As this is not broad enough to explain a non–covalent interaction like this, we can also look in to some other characteristics of the changes that accompany the movements and physical changes occurring to molecules toward forming a tetrel interacting complex. Correspondingly, comparisons of different (D) monomers with the same (X) substitution confirms that a Lewis acid interacts more strongly with a more polarized electron donor like ammonia. The tetrel

interaction is also enhanced with the polarizability increase in (ClF < H$_2$S < PH$_3$ < H$_2$O < NH$_3$) sequence of donor molecules against the same electrophilicity. The same electrophilicity is brought by the same X substituent.

Table 1
Energy components in kJ/mol and tetrel bond length in Å from BLW computations compared with energies from MP2 and wB97x−D computations

Complex	$E_{(Def)}$	$E_{(HL)}$	$E_{(Pol)}$	$E_{(CT)}$	$E_{(M06-2X)}$	$E_{(MP2)}$	$E_{(WB97XD)}$	$R_{(D...C)}$
CH$_3$OH···ClF	0.17	-2.43	-0.13	-0.47	-3.03	-1.42	-1.98	2.875
CH$_3$Br···ClF	0.15	-3.04	-0.51	-0.75	-4.30	-2.44	-2.96	2.821
CH$_3$Cl··· ClF	0.02	-3.20	-0.50	-0.63	-4.33	-2.34	-2.99	2.827
CH$_3$F··· ClF	0.04	-3.55	-0.49	-0.42	-4.46	-2.51	-3.03	2.819
CH$_3$OH···H$_2$O	0.06	-4.85	-1.06	-0.36	-6.27	-3.34	-4.51	2.947
CH$_3$Br···H$_2$O	0.09	-7.20	-1.46	-0.57	-9.23	-5.50	-7.30	2.918
CH$_3$Cl···H$_2$O	0.06	-7.55	-1.43	-0.54	-9.52	-5.59	-7.65	2.907
CH$_3$F···H$_2$O	0.13	-8.67	-1.22	-0.47	-10.37	-6.60	-8.04	2.869
CH$_3$OH···H$_2$S	0.14	-2.53	-0.37	-0.50	-3.40	-1.42	-2.63	3.555
CH$_3$Br···H$_2$S	0.77	-3.60	-0.59	-0.41	-4.60	-2.22	-4.43	3.557
CH$_3$Cl···H$_2$S	0.02	-3.65	-0.55	-0.64	-4.84	-2.31	-4.50	3.544
CH$_3$F···H$_2$S	0.05	-4.00	-0.60	-0.81	-5.41	-2.57	-4.83	3.499
CH$_3$OH···NH$_3$	0.01	-4.20	-1.30	-0.87	-6.37	-3.38	-5.55	3.146
CH$_3$Br···NH$_3$	0.02	-6.35	-1.85	-1.39	-9.59	-5.54	-8.54	3.092
CH$_3$Cl···NH$_3$	0.16	-6.79	-1.78	-1.33	-9.89	-5.67	-9.03	3.083
CH$_3$F···NH$_3$	0.24	-8.11	-1.54	-1.36	-11.00	-6.95	-9.79	3.036
CH$_3$OH···PH$_3$	0.13	-2.29	-0.70	-1.10	-4.09	-1.70	-3.53	3.653
CH$_3$Br···PH$_3$	1.01	-3.58	-0.73	-0.50	-4.81	-2.63	-4.85	3.655
CH$_3$Cl···PH$_3$	0.01	-3.63	-0.73	-0.74	-5.09	-2.67	-4.92	3.639
CH$_3$F···PH$_3$	0.06	-4.16	-0.75	-0.85	-5.76	-3.05	-5.36	3.592

The effect of polarizability of the Lewis bases (electron donors) in our study can also be confirmed by its energy contributions to binding energies as

shown in Table 1. For the example of ammonia as a donor molecule, it is always stabilized by higher polarization and charge transfer energies than other donors.

Additionally, from geometry comparison of independent monomers to the geometry in the tetrel complex, we found a small change in the stretching vibrational frequency up to ~16 cm^{-1} of the C–X bond, as the tetrel bond is established. This finding is consistent with the electron transfer from the donor lone pair orbitals to an antibonding orbital of the acceptor molecule (n→π*). This kind of electron transfer always results in the lengthening of the C–X bond.
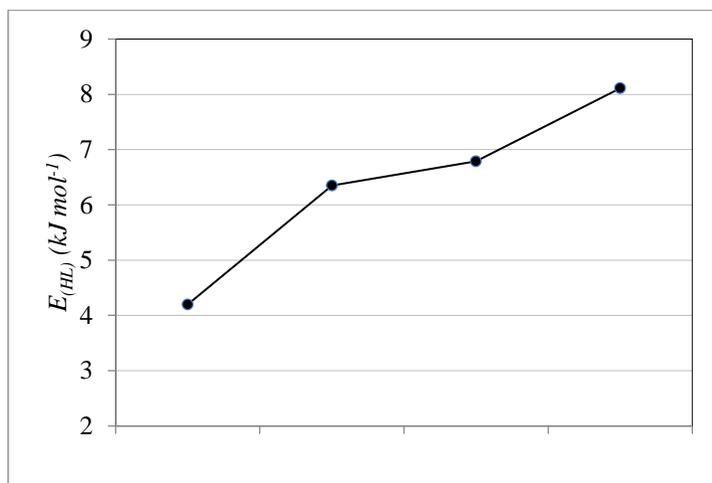
Figure 2. Correlation between the electrostatic energy term and the increasing electronegativity of (X), where NH$_3$ is picked as the donor group.
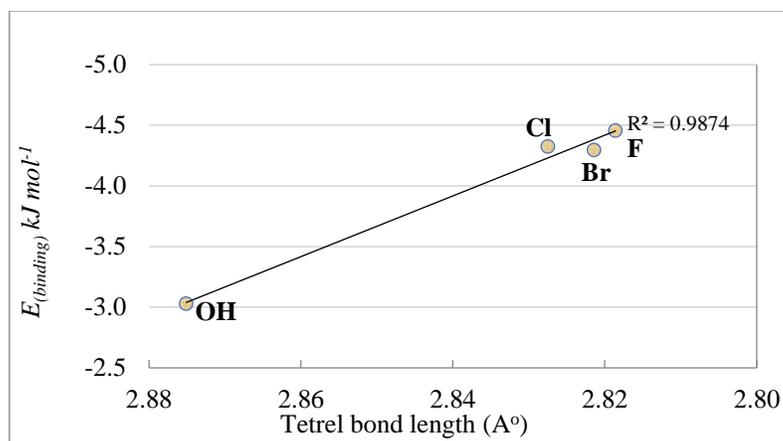
Figure 3. Correlation between bond length and total binding energy for ClF as a donor monomer

Orbital Correlation Diagrams

An essential and broadly applied theoretical approach is to plot out the orbital correlation diagram, which makes it easy to predict the path of the energy changes accompanied by a chemical reaction. One of the paths to track these energy changes is by tracking the orbital energy levels for the frontier ones from the very stable reactant molecules to the ones in a stabilized product molecule. There is no chemical reaction involved in the formation of these complexes studied here, but only non-covalent interactions. And the energies for such interaction are very low to be compared with the energy of a chemical bond. However, the energy levels of the orbitals in a molecule can be altered by electron density movements initiated by any potential arround[10]. Therefore, orbital energy level variations of the frontier orbital (HOMO – LUMO), on the monomers in this study, can also be observed along the path from an individually

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optimal state to the state of interacting with another monomer as a complex. As mentioned earlier, BLW method can provide physically meaningful interpretation of the energy portions that backs up tetrel interactions in these complexes. It also gives the access to any change in the energy levels of the frontier orbitals which are due to external potentials. In this case, the external potential to reshuffle the energies in the involving orbitals is the potential of the approaching molecule. Therefore, orbital correlation diagrams based on BLW energy computations are studied.
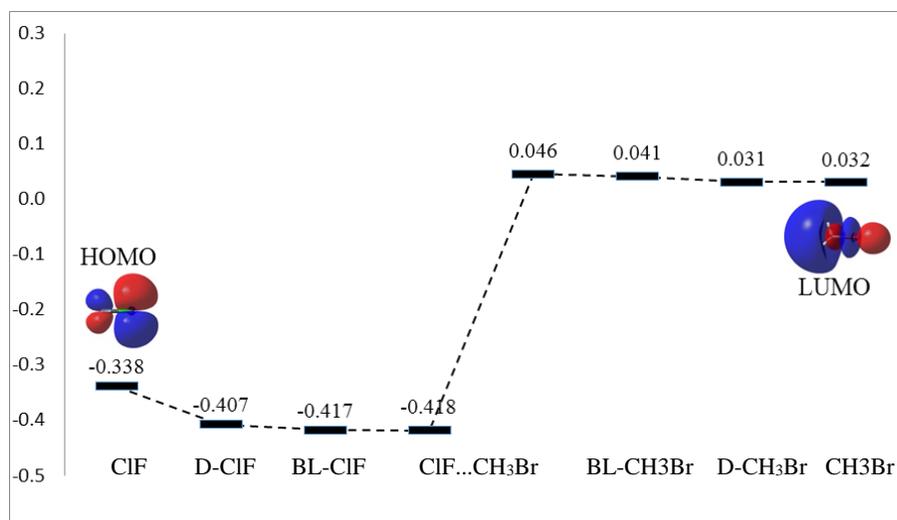
Figure 4. Orbital correlation diagram for $CH_3Br...FCl$. D (deformed), BL (block localized)

The information retrieved from these diagram computations contain the energies for the frontier orbitals in the optimal state of each monomer, their changes and hence the gap between them, which can be compared with the energy parameters that supports the associated tetrel interactions. For more

clarifications, we verified the orbital correlations diagram for $CH_3Br^{...}ClF$ complex, observing the HOMO orbital energy level shifting on chlorine monofluoride interacting with the LUMO energy level on methyl bromide. Figure 4 shows the orbital correlation diagram in which the initial energy gap between the HOMO of chlorine monofluoride and the LUMO of methyl bromide in their isolated optimal state is about 0.370 au (10.07 eV). Once the two molecules approach each other, due to their electrostatic potentials and their effects on one another, the atomic relocation occurs in the geometry of a complex but within each monomer itself. Because of this deformation process, we call the energies level of the frontier orbitals for this stage as deformed orbital energy. The slightly stabilized HOMO of chlorine monofluoride opposing a little further destabilized LUMO on methyl bromide increases the energy gap of the orbitals by (1.85 eV). It is observable that monomers coming closer to each other with their electron densities polarized within monomers, have given even more enlarged HOMO – LUMO gap as total difference of (2.42 eV) leaving the energy gap between the frontier orbitals at about (12.48 eV). With the electron flow allowed between the monomers forming the tetrel bounded complex, the orbitals are further stabilized, as a hyper–conjugative interaction energy for the transfer of electrons from the ClF bonding orbitals to the CH_3Br LUMO, by a difference of 14.78 kJ/mol of energy. The electron transfer stability can be evaluated from

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the HOMO level change from the BL-ClF to the complex, which is about 0.001

a.u., comparable to the CT energy term in Table 1 (-0.75 kJ/mol) in magnitude.

Based on the frontier orbital interaction study between the monomers, we can

say that the electron transfer has usually played a key role to stabilize such

complexes as we can compare them in Table 2. The energy level changes of the

Table 2
HOMO and LUMO energies in (Hartree) and gap energies in (eV) from both BLW and DFT
computations at the complex geometries

	BLW			DFT		
	HOMO	LUMO	Gap	HOMO	LUMO	Gap
Chlorine monofluoride (ClF)						
CH₃OH	-0.411	0.079	13.31	-0.418	0.046	12.64
CH₃Br	-0.417	0.041	12.48	-0.417	0.076	13.43
CH₃Cl	-0.416	0.071	13.25	-0.417	0.096	13.98
CH₃F	-0.415	0.096	13.91	-0.413	0.077	13.33
Water Molecule H₂O						
CH₃OH	-0.391	0.073	12.65	-0.394	0.076	12.79
CH₃Br	-0.402	0.053	12.39	-0.406	0.071	12.98
CH₃Cl	-0.402	0.084	13.24	-0.406	0.100	13.78
CH₃F	-0.401	0.107	13.84	-0.409	0.115	14.27
Ammonia NH₃						
CH₃OH	-0.338	0.087	11.56	-0.339	0.088	11.65
CH₃Br	-0.347	0.054	10.89	-0.348	0.075	11.51
CH₃Cl	-0.347	0.085	11.74	-0.349	0.103	12.27
CH₃F	-0.346	0.108	12.36	-0.349	0.119	12.73
Phosphine PH₃						
CH₃OH	-0.331	0.080	11.18	-0.331	0.081	11.19
CH₃Br	-0.338	0.042	10.32	-0.337	0.075	11.21
CH₃Cl	-0.337	0.073	11.14	-0.337	0.091	11.63
CH₃F	-0.337	0.099	11.86	-0.337	0.107	12.08
Hydrogen Sulfide (H₂S)						
CH₃OH	-0.324	0.079	10.97	-0.332	0.058	10.62
CH₃Br	-0.332	0.041	10.15	-0.331	0.081	11.22
CH₃Cl	-0.331	0.071	10.94	-0.331	0.105	11.85
CH₃F	-0.331	0.097	11.65	-0.324	0.080	11.01

orbitals can partially be visualized by plotting their density differential maps viewing the movement directions for electron densities of the molecules.

Electron Density Differential

The difference in electron density allocations can be observed while being approached by another molecule (polarization) and while electrons are transferred between two molecules (charge transfer). Electron density differential (EDD) maps can be drawn based on BLW computational method. The difference between electron densities for the state where two molecules are together and when the densities have affected each other (optimal BLW) explains the polarization effect while plotting the difference between the densities of optimal DFT orbitals of the complex and its BLW densities represents the charge transfer effects on the densities. Based on these EDD maps, we can explain the loss and gain of densities and thus the attraction and repulsion sites for electrons, so we can better predict the movement direction of the electrons. Figure 5 shows the electron density changes for $CH_3Br^{...}ClF$, and clearly explains that as the ClF molecule approaches CH_3Br (a), with their electrons forbidden to transfer, the electron density of ClF polarizes toward F from Cl end of the molecule, creating a more electron dense site at fluorine end (blue). For CH_3Br, its electron density moves away from hydrogen atoms,

confirmed by a loss of electron density (red) toward the more electronegative substituent (Br) which creates an electron vacant site on σ hole near the carbon atom located across the methyl bromide molecule (red).

(a)   (b)
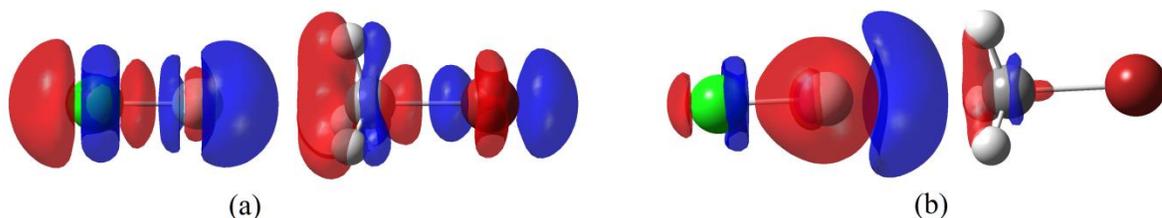
Figure 5. Electron Density Differential maps for $CH_3Br^{...}ClF$ at (0.0001 au) iso-density value, (a) polarization (b) charge transfer, Red color showing density loss and Blue showing density gain on molecules

Correspondingly, when electron transfer between the monomers is allowed, Figure 5(b) represents the electron density movements toward the positive site of CH_3Br (σ hole) from ClF molecule. We can see a huge density loss on fluorine (red) and a gain of electron density toward CH_3Br (blue), where the interacting cloud should be located.

Analysis of Complexes

Energy and geometry parameters for chlorine monofluoride binding with each of the four Lewis acids in this study are listed in Table 1, and represent interesting facts. A consistent correlation between electrostatic energies following the electronegativity sequence of (X) substitute can be observed. This has also affected the polarization energy in a similar manner, followed by

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binding energies with its length. But a slight contradiction can be noted in the charge transfer energies with X=F and Br. The charge transfer for methyl fluoride (0.421 kJ/mol) is a little lower than for methyl bromide (0.573 kJ/mol). The reason can be found in Table 2 as the localized (BLW) HOMU–LUMO orbital energy level gap (12.48 eV) for $CH_3Br\cdots ClF$ is smaller than the gap for $CH_3F\cdots ClF$ (13.91 eV), due to a lower LUMO orbital energy level on CH_3Br. The smaller energy gap of $CH_3Br\cdots ClF$ is expected to result in stronger electron transfer. Similar correlations, for electrostatic, electron transfer and binding energies comparable to the corresponding length, are perceived when the donor molecule of the complex is (D=H_2O) even following the location exchange of X=F and Br on the list for the former reasoning as in case of ClF molecule as donor. But the latter shows stronger polarization energies due to the more polarized electron density from H_2O as donor molecule compared to ClF. Figure 6 demonstrates a stronger polarization for electron density movements on CH_3Br for H_2O as approaches compared to ClF Figure 5a. The larger amount of density polarized toward Br with a density loss on hydrogens of the methyl bromide accompanied with more depolarized density, getting away from the σ hole, adding to its positivity. The hydrogens on the water molecules also display a great contribution, polarizing the density toward the lone pairs of the oxygen molecule.
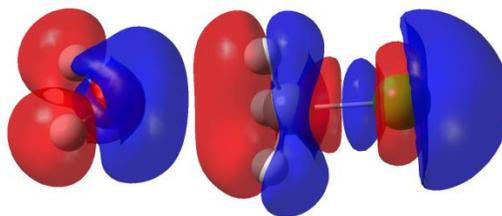
Figure 6. Electron Density Differential map for $CH_3Br...H_2O$ polarization at (0.0001 au) isodensity value, Red color showing density loss and Blue showing density gain on molecules

Complexes with ammonia and water molecules as a donor are among the complexes that have a stronger support of polarization energy among others Table 1. To our knowledge, the reason for this polarization is the higher electron density of lone pairs being donated later, which is even more polarized in NH_3. Although the overall binding energy increase is consistent with the decrease of the tetrel bond length for ammonia which is also in agreement with the electrostatic energy increase with electronegativity of (X) substituent. However, unlike the previous complexes, the energy gap variations of the frontier orbitals for BLW do not follow the charge transfer energy changes as the latter should increase with the decreasing of the former. The higher polarization energies in this study for $CH_3X^{...}NH_3$ complexes can be confirmed by their EDD maps in comparison with one of the poorly polarized complexes such as $CH_3Br^{...}H_2S$. Figure 7a shows when NH_3 molecule approaches CH_3Br, a huge electron density movement occurs compared to the approach of H_2S in Figure 7b. Due to steric repulsion from the electron density on ammonia, greater electron gain is seen on

bromide in the case of NH_3, leading to the deletion of electron densities from the methyl site. This increases the positivity of the σ hole for an even stronger attraction point for electrons.[21]. While in case of hydrogen sulfide, the electron density gain on bromide is weaker causing a weaker σ hole and less attractive for the electrons coming from other monomers. Based on its structure[35–37], H_2S is less polarized, thus it is not able to interact along its C_{2v} axis but has turned to one side for the tetrel interactions while NH_3 and PH_3 are interacting to a much closer angle along there symmetry, C_{3v}. Subsequently, enhanced electron transfer is expected from NH_3 to CH_3Br compared with the $H_2S{\cdots}CH_3Br$ complex. Data in Table 1 confirms our prediction.

Interestingly, the complexes where phosphine is the donor molecule or the Lewis base, are also in accord with the previous complexes. Phosphine complexes also follow similar correlations between energy components of their tetrel interaction and the orbital energy correlations between the frontier orbitals in the monomers for the complex.

(a)   (b)
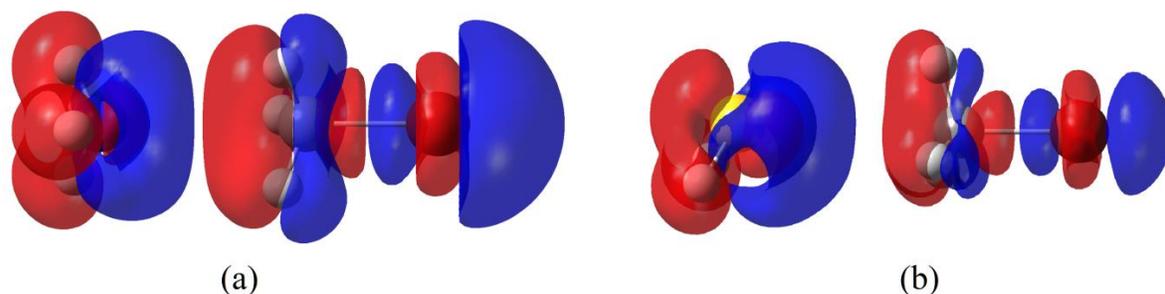
Figure 7. EDD maps showing the polarization (with iso-density value 0.0001 au) for (a) $CH_3Br...NH_3$ (b) $CH_3Br...H_2S$. Red and blue colors show density loss and gain, respectively
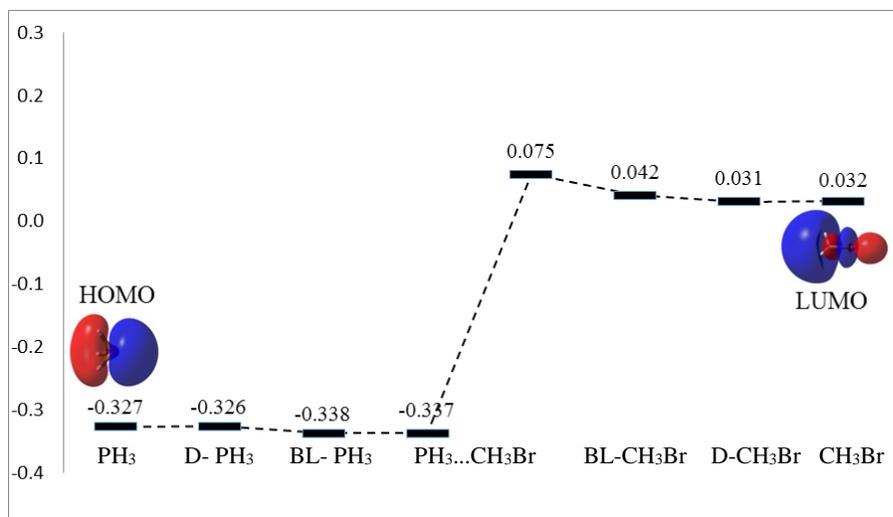
Figure 8. Orbital correlation diagram for $CH_3Br...PH_3$. D (deformed), BL (Block Localized)

The complexes where the donor is a phosphine molecule in this study are among the systems with higher charge transfer energies as well but the percentage of contribution for Heilter-London energy is lower than most of the other complexes of our study. The Heilter-London energy consists of both Pauli exchange and electrostatic energies. Figure 8 supports the reason for the charge transfer, as earlier mentioned that both a smaller HOMO–LUMO energy level gap between the monomers and higher HOMO energy of the donor monomer can help make the electron transfer easier and give a more stabilized complex as well. Figure 4 shows that the optimal HOMO energy level of ClF is close to the HOMO energy level of PH_3 in Figure 8, which should follow similar approximates for block localized energy gap resulting better charge transfer between methyl bromide and chlorine monofluoride. But as can be realized for

chlorine monofluoride the stabilization energy stage for the HOMO energy level is the deformation step, stabilized by (1.9 ev), much higher than PH_3 (0.02 eV). While the deformation energy changes for PH_3 being unnoticeable which leaves the gap closer for block localized energy levels as well. Hence, when electron transfer completes, there is a higher destabilization for the LUMO of CH_3Br.

CONCLUSION

The well discussed non–covalent interaction, tetrel bond, is investigated in this work with interaction energy decomposition analysis, with attempt to find out the driving forces for such kind of interactions.

The adopted energy decomposition method for the study is the BLW method at the M06-2X/6-311+G (d,p) level of theory to acquire an enhanced knowledge of the overall physically energetic activities of molecules establishing the bond. Complexes bound by tetrel interactions were investigated for their bonding energy and geometry parameters compared to every energy change involved in the interaction itself. The data analyses are done through EDD maps and orbital correlation diagrams exploration.

The results from our study declare that the driving force behind the tetrel interaction is the electrostatic forces activated between monomers of the complex to complete an electron transfer between the interacting orbital (normally the HOMO) of an electron donor to the LUMO orbital of a Lewis acid.

Furthermore, the strength and stabilization of the tetrel interaction depend on the nature of the monomers. In case of polar Lewis base like NH3, the system stabilizes in a deformation stage. When the Lewis base is a less polar donor molecule like (PH3), the deformation energy is not huge but the energy gap

between the frontier orbitals are increased, right before the electron transfer, which enhances electron transfer and stabilizes the complex with the completion of electrons transfer.

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