

C₂H₅OH ··· HX (X=OH, SH, F) interactions: Is there a carbon bond?

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Abstract. Computational study of ethanol complexes with H₂O, H₂S and HF molecules has been carried out using a MP2 level of theory. Carbon bonding and hydrogen bonding interactions have been analyzed in this study for all the complexes. The interaction between the carbon atom of CH₂ group of ethanol and electron-rich centre of other molecules such as the O atom of water has been found. In addition to C···X interaction, C-H···X interaction has also been observed for all the complexes. *Ab initio* calculations and Atoms in Molecules (AIM) theoretical calculations confirm this. The hydrogen bonding interactions with the OH group of ethanol have also been analyzed.

Keywords. Carbon bond; hydrogen bond; AIM theoretical calculation.

1. Introduction

Hydrogen bonding interaction is a well-established and the most studied non-covalent interaction.¹ Among many interactions, the halogen bond is perhaps another most studied and analyzed non-covalent interaction.² In hydrogen bonding interaction, X-H···Y-Z, the partially positively charged H atom is attracted to the negative site on the other molecule Y-Z, where X is an electronegative atom covalently bound to H.³ The halogen bond is conceptually a similar phenomenon and can be represented as R-X···Y-Z.⁴ However, in halogen bonding interaction, covalently bonded halogen atoms (X) are seen as negatively charged entities. How, then, is it possible that halogen atom can take part in interaction with negative site of Y-Z? The σ -holes concept has successfully explained this contradiction.⁵ σ -holes are defined as the regions of positive electrostatic potential on the outer surface of R-X bond. Besides halogen bonding interactions, it is now well established that covalently-bonded atoms of Groups 14, 15 and 16 can also participate in non-covalent interactions through a σ -hole.^{6,7}

The interaction of group 14 elements of periodic table is not so old. This interaction is named as a tetrel bonding. The existence of this type of interaction was investigated while studying expansion of the σ -hole concept for silicon and germanium complexes⁸ and the same group later discovered a carbon bonding interaction when they studied the similar kind of work for F₃MX molecules (M = C, Si, Ge and X = F, Cl, Br, I).⁹

However, the nature of carbon bonding was known only after the work by Mani and Arunan.^{10,11} When Ar···propargyl alcohol dimers were studied, Mani and Arunan not only found the expected OH···Ar and π ···Ar interactions but also C···Ar interaction.¹⁰ In the later work, Mani and Arunan extensively studied the complexes of methanol and fluoromethane with H₂O, H₂S, NH₃, PH₃, HF, HCl, HBr, ClF, LiF, LiCl and LiBr molecules.¹¹ The results of this work were found to be similar to hydrogen bonding interaction and this interaction can be designated as X-C···Y type interaction. This was named as carbon bonding interaction, where X is a carbon bond donor and Y is a carbon bond acceptor.

During the past years, several studies concerning the carbon bonding and the tetrel bonding were reported. These include carbon bond with π electrons,¹² tetrel bond with single electron¹³ and tetrel bond with hydrides.¹⁴ On the basis of charge density analysis, experimental evidence supporting carbon bonding in solid state was also confirmed.¹⁵

Moreover, it is now well established from the work of Mani and Arunan¹¹ that when one of the hydrogen on methane is substituted by any electron withdrawing group (F/OH), the opposite face of it can be electron deficient and thus methanol/fluoromethane gives carbon bonding. Now a question arises, what will happen if we consider ethanol? Ethanol has methyl and methylene groups and like methanol, ethanol has also electron withdrawing group (OH) in the opposite face of methylene.

The main aim of this study is to examine whether the methylene group, like the methyl group, also forms

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carbon bonding or not when any electron withdrawing group is attached in methylene group. For this, complexes of ethanol with H_2O , H_2S and HF molecules were considered in this study. Furthermore, we have also analyzed the hydrogen bonding interactions with the OH group of ethanol. High level *ab initio* calculations along with atoms in molecules (AIM) theoretical calculations^{16,17} were employed to analyze the complexes. Moreover, molecular electrostatic potential calculations were used to find the locations of electrophilic and nucleophilic attack on ethanol.¹⁸⁻²⁰

2. Computational methods

All calculations were performed using the Gaussian03 program²¹ at MP2²²⁻²⁴ level of theory with 6-311++g(d, p)²⁵ basis set. To compare the results of 6-311++g(d, p) basis set MP2 level of theory with aug-cc-pvdz^{26,27} basis set was also used to optimize the structure of water, ethanol and their complexes. We have also carried out frequency calculations for all the geometrical structures in order to affirm that they are true minima. The supramolecular approach was used to calculate the interaction energies and then counterpoise method of Boys and Bernardi was employed for BSSE correction.²⁸ The AIM calculations were performed with the AIMALL software package²⁹ using the MP2/6-311++g** wave functions.

Electrostatic potential maps were used to find the high or low electron density distributions of molecules three dimensionally. The regions of high or low electron density distributions can be used to determine how molecules interact with one another. These methods were used in many systems. One of the recent examples is work by Parajuli and Arunan.³⁰ They used electrostatic potential map of n-alkanes (propane, butane, pentane) to study $\text{X-H}\cdots\text{C}$ and $\text{C-H}\cdots\text{X}$ hydrogen bonds ($\text{X}=\text{F,OH}$). We have used the same method to plot the map of electrostatic potential surface of ethanol at 0.001 a.u. isosurface contours by using GaussView software.³¹ Furthermore, Multiwfn software was used for quantitative analysis of molecular surfaces of ethanol molecule³²

3. Results and discussion

3.1 Molecular Electrostatic Potential Surface Analysis of Ethanol

The molecular electrostatic potential surface map of ethanol is given in Figure 1. The site of high electron density region and the site of low electron density

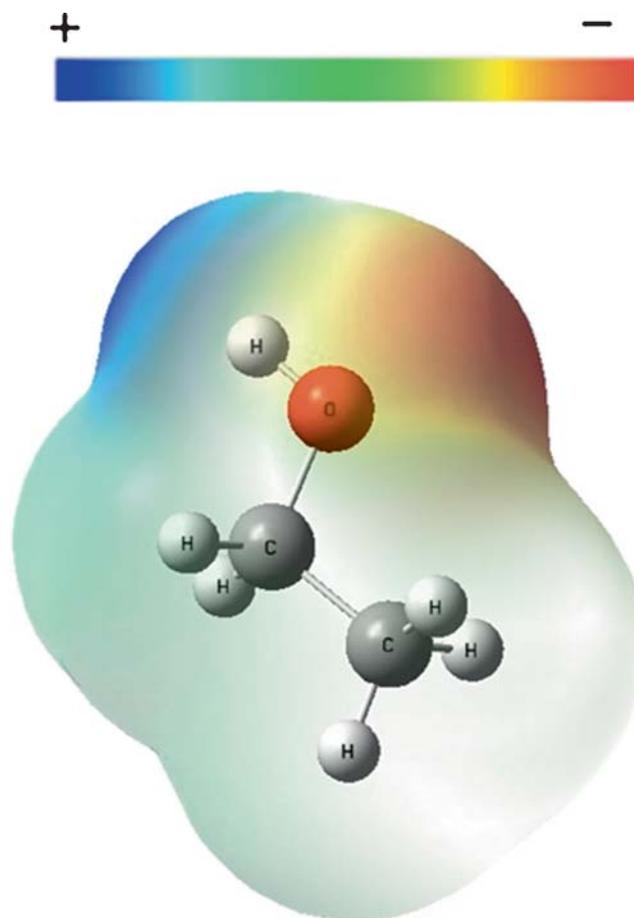


Figure 1. Map of Molecular Electrostatic Potential surface of ethanol plotted by GaussView software using MP2/6-311++g(d, p) wave functions (the color code is given in the text).

region were known from the map of electrostatic potential surface. The blue color in this map depicts the most positive value whereas the red color depicts the most negative value of molecular electrostatic potential at electron density isosurfaces. Moreover, the green color is more positive than the yellow color whereas the yellow color is more positive than the red color. This map shows that there are two distinct regions, the region with blue color along the axis of O-H and the region with red color along the axis of the C-O.

The positions and the values (first one along the axis of the O-H, second one along the axis of the C-O and the third one opposite to the OH group near to the C atom of the CH_2 group) of electrostatic potentials at 0.001 au electron density isosurface for ethanol are given in Figure 2. It is well-known that a nucleophile may approach the position of the maximum value of electrostatic potential, whereas an electrophile may approach the position of the minimum value of electrostatic potential. Furthermore, there may be other local positions of maximum/minimum values of electrostatic

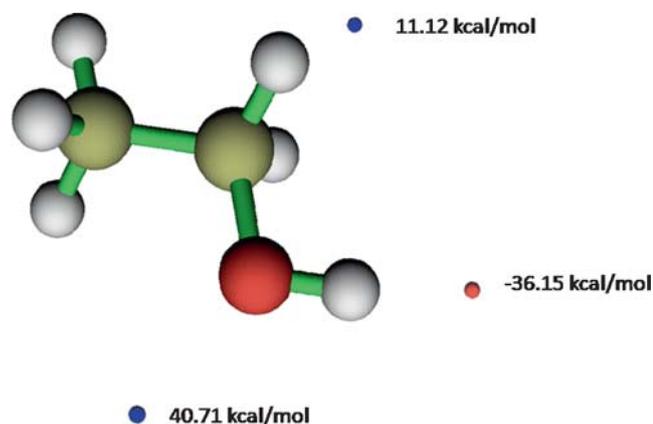


Figure 2. Positions of maximum and minimum values of electrostatic potentials at three different sites optimized at MP2/6-311++ g(d, p).

potentials in this map. We have chosen only three sites and the reasons of choosing only three sites will be discussed in the following sub sections.

3.2 Ethanol...H₂O complex

Geometries of ethanol...H₂O complexes were optimized at three different sites at MP2 level of theory with 6-311++g (d, p) and aug-cc-pvdz basis sets. The initial geometry at the first site is taken in which oxygen of water faces the opposite side of the OH group towards the carbon atom of the CH₂ group of C₂H₅OH. From electrostatic potential calculation, it was found that the positive value of electrostatic potential was observed at this site. This site was chosen to investigate whether the carbon of methylene group of ethanol would also form the carbon bond similar to methanol or not. The initial geometry of the second site was chosen along the axis of the O-H, where positive value of electrostatic potential was found. We have chosen the third site along the axis of the C-O and at this site negative value of electrostatic potential was found (Figure 2). These two sites (along the axes of O-H and C-O) were chosen to

analyze how strong hydrogen bonding would be with the OH group in comparison to the carbon bonding.

Molecular graph of ethanol...H₂O complex optimized at MP2/6-311++ g(d, p) level of theory is shown in Figure 1. Similar type of optimized structure is obtained for aug-cc-pvdz basis set (Figure S1 in Supplementary Information). Table 1 lists carbon and hydrogen bond distances and interaction energies. All the harmonic vibrational frequencies of optimized structures are positive. This confirms that the optimized structures are true minima.

All the vibrational frequencies of the optimized structures are given in supplementary information (Table S1). In the first site, it appears that the O atom of water is interacting with two atoms, one, with one of the hydrogen atoms of the CH₃ group and another, with the carbon atom of CH₂ group (Figure 3). The latter interaction can be due to carbon bonding interaction. AIM analyses confirm both the interactions. Furthermore, another parameter to characterize intermolecular interaction is distance between interacting atoms. We have calculated both carbon bond distance and hydrogen bond distance. The C...O bond distance with 6-311++ g(d, p) basis set is found to be 3.332 Å while the H...O bond distance is found to be 2.705 Å (Table 1). The same values with aug-cc-pvdz basis set were found to be 3.326 Å and 2.710 Å, respectively. With O acceptor for CH₃OH...H₂O complex,¹¹ the carbon bonding distance was found to be 3.167 Å at MP2 level theory with 6-311+G(3df,2p) basis set, suggesting our result is comparable with this. At the second site, interaction of oxygen atom of water with the hydrogen atom of OH group of ethanol has been observed and it is certainly due to well known hydrogen bonding interaction. The bond distance between H...O in this case is found to be 1.945 Å with 6-311++g (d, p) basis set while the same value with aug-cc-pvdz basis set is found to be 1.943 Å. At the third site, the hydrogen atom of water is interacting with the oxygen atom of hydroxyl group of ethanol. AIM calculations show that not only there is interaction between the hydrogen of water and the

Table 1. H...Y or C...Y distance (R) in Å and interaction energy (ΔE) in kJ/Mol for ethanol...H₂O complex. Y is acceptor atom

Complexes at	MP2/6-311++ g(d, p)		MP2/aug-cc-pvdz	
	R	ΔE	R	ΔE
Site 1	3.332 (2.705) [§]	-3.7	3.326 (2.710) [§]	-4.5
Site 2	1.945	-17.7	1.943	-18.2
Site 3	1.902 (2.851) [#]	-20.9	1.900 (2.850) [#]	-22.3

[§] The O...H distance at first site. [#] the O...H distance at third site (see Figure 3).

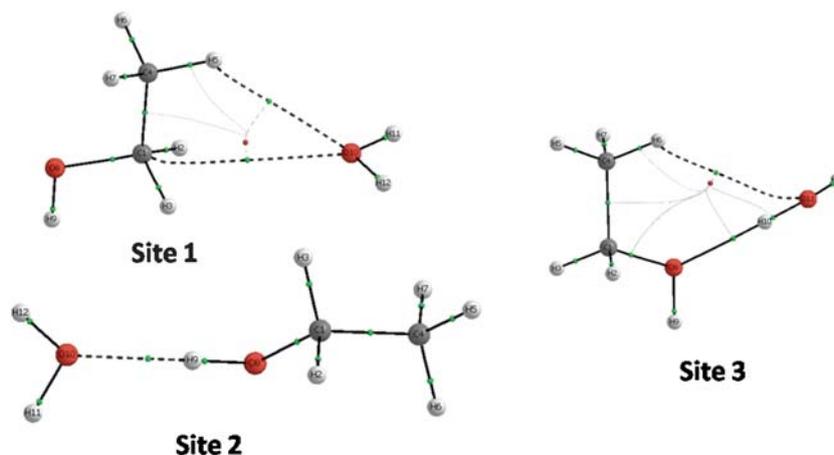


Figure 3. Molecular graph of ethanol \cdots H₂O complex at three different sites at MP2/6-311++ g(d, p) level of theory.

oxygen of ethanol but also there is interaction between the oxygen of water and one of the hydrogen atoms of the CH₃ group (Figure 3). Both the bond distances were presented in third row of Table 1.

The interaction energy is one of the most important parameters for characterizing the intermolecular interaction. The BSSE-corrected interaction energies are given in Table 1. The interaction energy for C \cdots O interaction and C-H \cdots O interaction of this complex is 3.7 kJ/mol with 6-311++ g(d, p) basis set and the same value with aug-cc-pvdz basis set is 4.5 kJ/mol. This value of interaction energy is comparable to that of CH₃OH \cdots H₂O¹¹ complex. However, for CH₃CH₂OH \cdots H₂O complex C- bond is also stabilized by C-H \cdots O hydrogen bonding (Figure 3). This means carbon bonding interaction energy for CH₃CH₂OH \cdots H₂O complex is less than that of CH₃OH \cdots H₂O complex. We also know from literature that³³ there is a linear relationship between electron density at BCP and interaction energy. The electron density at carbon bonding BCP is found to be less than that of C-H \cdots O hydrogen bonding (Table 2). Hence, one can say that carbon bond interaction energy for this complex is weaker than that of C-H \cdots O hydrogen bonding. Furthermore, the

BSSE-corrected interaction energy for hydrogen bonding of this complex is slightly less when OH group takes part as a hydrogen bond donor than when it takes part as a hydrogen bond acceptor. In the former case, this value is 17.74 kJ/mol with 6-311++g(d, p) basis set and the same value with aug-cc-pvdz basis set is 18.2 kJ/mol. The corresponding values in the latter case with 6-311++ g(d, p) basis set and with aug-cc-pvdz basis set are 20.88 kJ/mol and 22.3 kJ/mol, respectively. We found that the carbon bond and C-H \cdots O hydrogen bond interaction energy in CH₃CH₂OH \cdots H₂O complex is about six times weaker than that of O \cdots H-O hydrogen bond interaction energy.

The quantum theory of Atoms in Molecules (AIM) has been used to analyze carbon bonding as well as hydrogen bonding for this complex. Molecular graphs for ethanol \cdots H₂O complex calculated using AIM theory are shown in Figure 3. In all these complexes, bond critical points (BCP) were found at the bond paths of carbon bonding as well as of hydrogen bonding. The BCP and penetration parameters confirm the presence of C \cdots Y as well as H \cdots Y bonds in all these complexes (Y is acceptor atom). Table 2 presents electron density values $\rho(r)$ and Laplacian of electron density values

Table 2. Electron densities ($\rho(r)$) and the Laplacian ($\nabla^2\rho(r)$) values at the intermolecular BCP for ethanol \cdots H₂O complexes in atomic units and penetration parameters of acceptor and hydrogen (Δr_Y , Δr_X) in Å. Y is acceptor atom and X is donor atom.

Complex at	MP2/6-311++ g(d, p)				MP2/aug-cc-pvdz			
	$\rho(r)$	$\nabla^2\rho(r)$	Δr_Y	Δr_X	$\rho(r)$	$\nabla^2\rho(r)$	Δr_Y	Δr_X
Site 1	0.0042	0.0198	0.157	0.509	0.0041	0.0183	0.124	0.455
	0.0064 [§]	0.0213 [§]	0.248 [§]	0.264 [§]	0.0060 [§]	0.0230 [§]	0.217 [§]	0.549 [§]
Site 2	0.0236	0.0923	0.565	0.918	0.0244	0.0876	0.514	0.941
Site 3	0.0268	0.1008	0.650	0.972	0.0282	0.0985	0.628	0.995
	0.0052 [#]	0.0199 [#]	0.145 [#]	0.183 [#]	0.0052 [#]	0.0223 [#]	0.122 [#]	0.483 [#]

[§] Values of $\rho(r)$ and $\nabla^2\rho(r)$ in BCP of O \cdots H interaction at first site, [#] the same at third site (see Figure 3).

$\nabla^2\rho(r)$ at the intermolecular BCPs between interacting atoms and penetration parameters.

The characteristic of closed shell interaction is that the $\nabla^2\rho(r)$ values should be positive and these values were found to be positive in all the complexes. Moreover, the values of $\rho(r)$ and $\nabla^2\rho(r)$ at carbon bonding BCPs for CH₃OH...H₂O complex¹¹ is comparable with the results of this study. Furthermore, Table 2 shows that these values at the BCPs are within the range prescribed for C-H...O hydrogen bonds.¹⁷

3.3 Ethanol...H₂S complex

Like ethanol...H₂O complex, the geometries of ethanol...H₂S complexes were also optimized at three different sites and the first site was chosen to investigate whether the carbon of methylene group of ethanol could also form the carbon bond with S acceptor, similar to methanol or not. The molecular graphs of all optimized ethanol...H₂S complexes with 6-311++g(d, p) basis set are shown in Figure 4.

All the vibrational frequencies of the optimized structures of this complex are listed in supplementary information (Table S2). In this complex also, it looks like that the S atom of H₂S is interacting with two atoms; one, with one of the hydrogen atoms of the CH₃ group and another with the carbon atom of CH₂ group. The latter interaction could be due to carbon bonding interaction for this complex as well. Like ethanol...H₂O complex the presence of bond paths and BCPs between the S atom of H₂S and one of the H atoms of CH₃ group, and between the S atom of the

H₂S and the C atom of CH₂ group of ethanol have been observed (Figure 4). The carbon bonding distance was found to be 3.880 Å while the H...S bond distance was found to be 3.177 Å (Table 3). The C...S distance (3.713 Å) for CH₃OH...H₂S complex studied at MP2 level of theory with 6-311+G(3df,2p) basis set¹¹ is comparable to C...S distance of this study.

At the second site, the molecular graph shows that (Figure 4) there is interaction between the sulphur atom of H₂S with the hydrogen atom of OH group of ethanol and, like ethanol...H₂O complex, it is due to the well known hydrogen bonding interaction. The distance between H...S in this case was found to be 2.553 Å. At the third site, there is interaction between hydrogen atom of H₂S and the oxygen atom of hydroxyl group of ethanol and this distance was found to be 2.143 Å. Further, it was observed that not only the hydrogen of H₂S is interacting with the oxygen of ethanol but there is also interaction between H of H₂S and one of the hydrogen atoms of the CH₃ group. This distance was found to be 2.630 Å.

The interaction energy was measured for characterizing this complex. The BSSE corrected interaction energies are presented in Table 3. The interaction energy at first site was found to be very low in comparison to ethanol...H₂O complex. This value is 1.7 kJ/mol. Our result is slightly less than that of CH₃OH...H₂S complex which was optimized at MP2/6-311+G(3df, 2p) level of theory¹¹ However, like in C₂H₅OH...H₂O complex, C₂H₅OH...H₂S is also stabilized by C-H...S bonding and the carbon bonding interaction energy is less than that of CH₃OH...H₂S complex. The

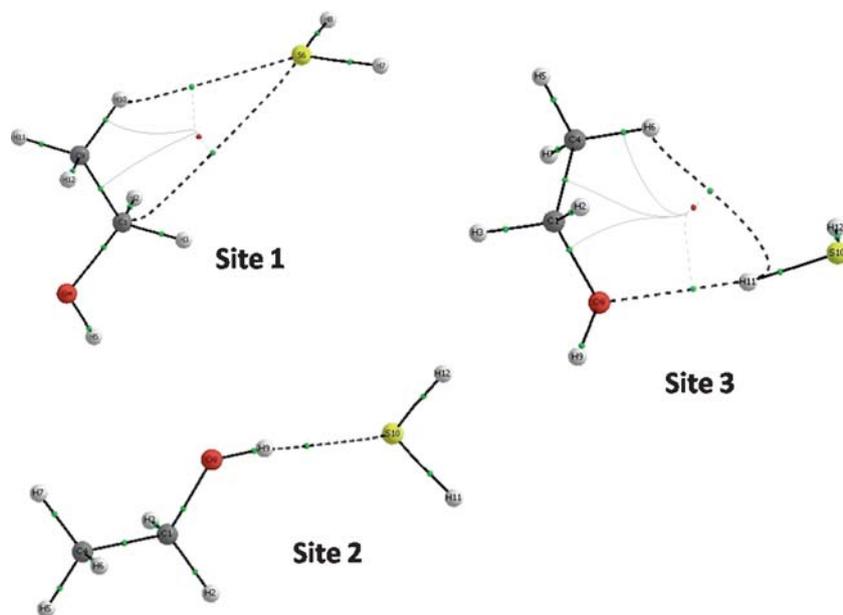


Figure 4. Molecular graph of ethanol...H₂S complexes at three different sites at MP2/6-311++ g(d, p) level of theory.

Table 3. H...Y or C...Y distance (R) in Å, interaction energy (ΔE) in kJ/mol, electron densities ($\rho(r)$) in atomic units and the Laplacian values ($\nabla^2\rho(r)$) in atomic units at the BCP for ethanol...H₂S complex and penetration parameters of acceptor and donor (Δr_Y , Δr_X) in Å. Y is acceptor atom and X is donor atom.

Complex at	MP2/6-311++ g(d, p)					
	R	ΔE	$\rho(r)$	$\nabla^2\rho(r)$	Δr_Y	Δr_X
Site 1	3.880	-1.7	0.0041	0.0138	0.0350	0.368
	3.177 [§]		0.0029 [§]	0.0113 [§]	0.0288 [§]	0.139 [§]
Site 2	2.553	-8.0	0.0133	0.0371	0.409	0.760
Site 3	2.143	-10.1	0.0181	0.0584	0.546	0.980
	2.630 [#]		0.0043 [#]	0.0153 [#]	0.354 [#]	0.138 [#]

[§] Values in S...H interaction at first site; [#] values in H...H interaction at third site (see Figure 4).

electron density at carbon bonding BCP is less than that of C-H...S hydrogen bonding (Table 3). Hence, like C₂H₅OH...H₂O complex one can say that carbon bond interaction energy for this complex is weaker than that of C-H...S hydrogen bonding. Furthermore, the BSSE-corrected hydrogen bonding interaction energy is 8.0 kJ/mol. The corresponding value when OH group acts as a hydrogen bond acceptor is 10.1 kJ/mol.

To characterize ethanol...H₂S complex, the quantum theory of Atoms in Molecules (AIM) has also been used. In this complex also, intermolecular bond critical points are found which confirms the presence of carbon bond as well as hydrogen bond. Electron density values $\rho(r)$ and Laplacian of electron density values $\nabla^2\rho(r)$ at the intermolecular BCPs are listed in Table 3. As the $\nabla^2\rho(r)$ values for all the complexes are positive, these interactions are closed shell type interactions. Moreover, the values of $\rho(r)$ and $\nabla^2\rho(r)$ at BCPs are within the range prescribed for C-H...O hydrogen bonds.¹⁷ Furthermore, the values of $\rho(r)$ and $\nabla^2\rho(r)$ at carbon bond BCP of this complex are comparable with the work by Mani and Arunan.¹¹

3.4 Ethanol...HF complex

In the third case, we have studied ethanol complex with HF molecule in order to investigate whether F acceptor can also form carbon bonding as in methanol or not. Like ethanol...H₂O and ethanol...H₂S complexes, we took three initial geometries for ethanol...HF complexes but we were able to optimize only in two sites (first site and third site).

Like other complexes, all the harmonic vibrational frequencies of optimized structures are positive for these complexes (Supplementary Information, Table S3). The molecular graphs of optimized structures are shown in Figure 5. H...Y and C...Y distances are listed in Table 4.

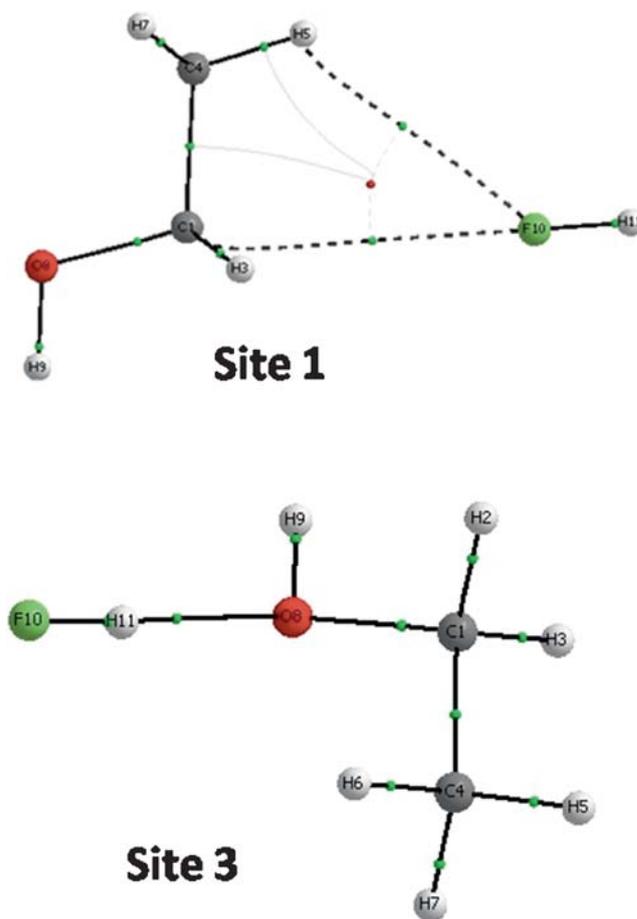


Figure 5. Molecular graphs of ethanol...HF complex at two different sites at MP2/6-311++ g(d, p) level of theory.

Like ethanol...H₂O and ethanol...H₂S complexes, there is interaction of F atom of HF and carbon atom of CH₂ group of ethanol, confirming carbon bonding similar to CH₃OH...HF complex.¹¹ This carbon bonding distance is found to be 3.321 Å. The C...F distance found by Mani and Arunan for CH₃OH...HF complex is 3.131 Å¹¹ and our result is thus comparable. Like other complexes, AIM calculations show that there is

Table 4. H...Y or C...Y distance (R) in Å, interaction energy (ΔE) in kJ/mol, electron densities ($\rho(r)$) in atomic units and the Laplacian values ($\nabla^2\rho(r)$) in atomic units at the BCP for ethanol...HF complex and penetration parameters of acceptor and donor atoms (Δr_Y , Δr_X) in Å. Y is acceptor atom and X is donor atom.

Complex at	MP2/6-311++ g(d, p)					
	R	ΔE	$\rho(r)$	$\nabla^2\rho(r)$	Δr_Y	Δr_X
Site 1	3.321	-2.4	0.0034	0.0150	0.048	0.412
	2.883 [§]		0.0031 [§]	0.0170 [§]	0.009 [§]	0.101 [§]
Site 2						
Site 3	1.673	-35.4	0.0441	0.1536	0.752	0.594

[§] The values in F...H interactions at first site, (see Figure 5).

interaction between F atom of HF and one of the hydrogen atoms of CH₃ group. This distance is found to be 2.883 Å. We observed the interaction between H atom of HF and the O atom of the OH group of ethanol and this is certainly due to hydrogen bonding interaction. This H...O distance is found to be 1.673 Å.

Both BSSE-corrected carbon bonding binding energy and BSSE-corrected hydrogen bonding binding energy are also listed in Table 4. The value of binding energy at first site is 2.4 kJ/mol. Our value at MP2 level of theory is slightly less than the stabilization energy for F acceptor for CH₃OH...HF complex (2.9 kJ/mol) at MP2/6-311+G(3df,2p) level of theory. However, like other complexes, the carbon bonding interaction is stabilized by C-H...F bonding for this complex. As the electron density at BCP of C-bond is less than that of C-H...F bond, C-bond interaction energy should be less than C-H...F bond (Table 4). Furthermore, the hydrogen bonding interaction energy in this complex is found to be 35.4 kJ/mol.

Atoms in molecules theoretical analysis was also performed for ethanol...HF complex. In all these complexes, intermolecular bond critical points were found like in other complexes. Table 4 lists electron density values $\rho(r)$ and Laplacian of electron density values $\nabla^2\rho(r)$ at the intermolecular BCPs. The $\nabla^2\rho(r)$ values are positive at intermolecular BCPs and this is a characteristic of closed shell interaction. Like in other complexes, both $\rho(r)$ and $\nabla^2\rho(r)$ values at the BCPs are within the range prescribed for C-H...O hydrogen bonds.¹⁷

4. Conclusions

Ethanol and its complexes with H₂O, H₂S and HF molecules have been studied using electrostatic potential analysis, *ab initio* (MP2/6-311++g(d, p) aug-cc-pvdz) and AIM theoretical calculations. From electrostatic potential calculations the positive value of

electrostatic potential was found on the opposite side of the OH group, near the carbon atom of the CH₂ group of C₂H₅OH. The interaction between carbon atom of methylene group of ethanol molecule and electronrich centre such as O atom of water has been found in this study. Moreover, the 'carbon bonded geometry is also stabilized by the C-H...X hydrogen bond which is found to be weak and different in comparison to methyl and other type carbon bonding interactions. We have observed bond critical points of carbon bonding interaction which support this interaction. Hydrogen bonding interactions with OH group of ethanol have also been studied and found to be stronger than carbon bonding interaction.

Supplementary Information (SI)

Tables S1–S3 list all the vibrational frequencies for all the complexes studied. Figure S1 is the Molecular Graph of ethanol...H₂O complex at three different sites at MP2/aug-cc-pvdz level of theory. Supplementary Information is available at www.ias.ac.in/chemsci.

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