

## Inverse halogen bonds intermolecular interactions

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**Abstract.** A new number of inverse halogen bonds (IXBs) intermolecular interaction system of Y-F $\cdots$ DB<sub>2</sub> (D=C, N, O or S; B=O and S; Y=Cl) have been investigated at B3LYP/6-311++g(d, p) computational level. According to the BSSE corrected interaction energy, it can be concluded that the stability of the five IXBs complexes of the ClF $\cdots$ DB<sub>2</sub> system increases in the order of ClF $\cdots$ CS<sub>2</sub> < ClF $\cdots$ CO<sub>2</sub> < ClF $\cdots$ NO<sub>2</sub> < ClF $\cdots$ O<sub>3</sub> < ClF $\cdots$ SO<sub>2</sub>. Comparing the ClF monomer with ClF moiety of the complexes, the chemical shifts of F atoms all increased by a certain degree and presented a trend to downfield. This indicates that the electrons flow from ClF to DB<sub>2</sub> (D=C, N, O or S; B=O or S) and the IXBs form between ClF and DB<sub>2</sub>.

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## 1 Introduction

Intermolecular interaction plays an important role in the fields of physics, biology, chemistry and materials science. It has captured the interest of chemists for a long time and reports about its theory and experiment have been well presented [1–7]. It has been found that a lot of physical and chemical phenomena are closely related to the intermolecular weak interactions including hydrogen bond [8–10],  $\pi$ -cation [11], halogen bond (XB) [12–16], lithium bond [17–19], etc. Among these intermolecular interactions studied, halogen bond is an earlier and more extensively studied ones, and it is an interesting interaction analogous to hydrogen bond [20]. Halogen bonding is the noncovalent interaction between halogen atoms (Lewis acids) and neutral or anionic Lewis bases [21]. Most published works of XB are of

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the type D···X-Y (Y=C, N or halogen) in which X, the situs of electron acceptor, is Lewis acid (X=Cl, Br, I or F), and D (D=O, S, N or  $\pi$  electron system), the situs of electron donor, is Lewis base.



Figure 1: The electron transfer directions.

In the XB aforementioned, the D (D=O, S, N or  $\pi$  electron system) atom plays the role of electron donor for the XB systems, and X (X=Cl, Br, I or F) atom plays the role of electron acceptor (Fig. 1(a)). Our question is if there is an inverse electron transfer direction in some special D···X-Y systems? To answer this question, we propose to study a new class of unconventional XB where the halogen atom will provide electrons and another non-halogen atom will accept them (inverse halogen bond (IXB), Fig. 1(b)). The term IXB is used for defining any noncovalent interaction involving halogens as electron donors.

Recently, the inverse hydrogen bonds (IHBs) between  $\text{XeH}_2$  and hydride and fluoride derivatives of Li, Be, Na and Mg have been studied theoretically [22]. So, we are interested in knowing if there are any IXBs interactions, and how the interactions take place. And we consider a particular set of molecules formed by “donors” and “acceptors” of electrons as shown in Table 1, where F atoms in Cl-F is electronically rich enough to provide electrons in the formation of a IXB, and D atoms in  $\text{DB}_2$  (D=C, N, O or S, B=O or S) with electronically poor property are the halogen bond electron acceptors. Thus, given the absence of both experimental and theoretical studies on the inverse halogen bonds interactions of  $\text{DB}_2$  with  $\text{ClF}$ , the present study reports the results of a DFT-B3LYP theoretical study on the nature of the mentioned interaction. In order to compare, the normal XBs, the  $\text{CH}_3\text{F} \cdots \text{DB}_2$  (D=C, N, O or S; B=O or S) systems are also calculated.

## 2 Method and results

All possible geometries obtained by a full optimization on the surface of inverse halogen-bonded and normal halogen-bonded systems obtained at the B3LYP/6-311++g (*d,p*) computational level are depicted in Fig. 2. The equilibrium geometries of  $\text{ClF} \cdots \text{CS}_2$  and  $\text{H}_3\text{C} \cdots \text{O}_3$  were confirmed to be transition states by analytical frequency computations, and the other equilibrium geometries as minima. Some of the key geometrical parameters optimized for these complexes, stretching frequencies and interaction energies ( $\delta E_{CP}$ ) with basis set superposition error (BSSE) corrections are gathered in Table 1.

It is found that for the  $\text{Cl-F} \cdots \text{DB}_2$  and  $\text{H}_3\text{C-F} \cdots \text{DB}_2$  systems the Cl-F or C-F bonds length (R) are elongated due to the formation of the inverse or normal halogen bonds. For the normal XBs of  $\text{H}_3\text{C-F} \cdots \text{DB}_2$  system, this bond elongation leads to a red shift of the C-F stretching