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To cite this article: Abedien Zabardasti, Aliyar Mahdizadeh & Saeid Farhadi (2016): The intermolecular complexes of SSF$_2$ with HF, H$_2$O, NH$_3$, HCN and CH$_3$OH molecules, Journal of Sulfur Chemistry, DOI: 10.1080/17415993.2016.1246550

To link to this article: http://dx.doi.org/10.1080/17415993.2016.1246550

Published online: 17 Nov 2016.
The intermolecular complexes of SSF₂ with HF, H₂O, NH₃, HCN and CH₃OH molecules

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ABSTRACT
Intermolecular complexes of thiothionyl-fluoride (SSF₂) with HY molecules (HY = HF, H₂O, NH₃, HCN and CH₃OH) have been studied theoretically at the MP2/aug-cc-pVTZ computational level. The SSF₂ can have both hydrogen and chalcogen-bond (CB) interactions with HY molecules. The central S atom of SSF₂ as a better electron acceptor gives stronger adducts with HY molecules. CB interactions for the central S atom correlate with red shift of the S=S band. The QTAIM and NBO analyses were carried out on SSF₂ complexes.

ARTICLE HISTORY
Received 26 May 2016
Accepted 6 October 2016

KEYWORDS
Theoretical study; hydrogen bonding; chalcogen bonding; QTAIM; thiothionyl-fluoride; NBO

1. Introduction

Throughout the last decades, a growing amount of experimental and theoretical effort has been devoted to non-covalent interactions due to their widespread importance in many fields of chemistry and biochemistry [1–3]. Although investigations have usually focused on the most common hydrogen-bond non-covalent interaction, recently, attention for other types of intermolecular interactions, such as halogen bond [4–6] and chalcogen bond (CB), has grown [7].

Another type of the intermolecular interaction the so-called the σ-hole was first proposed by Politzer et al. [8–12] The ‘σ-hole’ concept refers to the electron-deficient outer lobe of a p orbital, which can act as an electron-pair acceptor from a Lewis base. Thus, halogen bonding is derived from σ-hole bonding [8–11]. The σ-hole interaction is also
called CB for Group-VI and pnicogen bond for Group-V atoms [8,11]. Correspondingly, \(\sigma\)-hole interaction among Group IV atoms and Lewis bases may be termed as ‘tetrel bond,’ since they include the elements of Group IV [12].

Halogen bonding as a subset of \(\sigma\)-hole interactions occurs between the \(\sigma\)-hole of a halogen atom and a Lewis base [13]. Chalcogen group (VI) elements have two \(\sigma\)-holes and their non-covalent interactions are called chalcogen bonding [14,15]. Pnictogen bonding [16] is commonly used in the literature for these type of \(\sigma\)-hole interactions for group V of the periodic table. Finally, for group IV atoms, which form four \(\sigma\) bonds, one can expect to have four \(\sigma\)-holes and the term tetrel bond is used [17].

In recent years, disulfides have been investigated with increasing interest due to their importance in biochemistry and atmospheric processes [18,19]. The biological activity of several molecules, such as proteins, enzymes and antibiotics, is characterized by the presence of the disulfide connection. A number of experimental [20,21] and theoretical studies [22–26] of the structural and energetic features of several disulfide molecules have been carried out that gives useful information about the electronic mechanism involved in the S–S bond breaking. Disulfides XSSX and respective isomers SSX2 (X = H, CH3, F, Cl, etc.) were intensely studied [21,27–34]. Although most S2X2 systems exist in the disulfide form (XSSX, C2 symmetry), isomeric thiothionyl-structures (SSX2, Cs symmetry) were also found. The two isomers of disulfur difluoride (i.e. FSSF and SSF2) have been isolated, recognized and established [33,34]. A reasonable inference for the isomerization direction between the SSF2 and FSSF compounds should be from SSF2 to FSSF. Of course, the total energy, computed at different levels of theory for FSSF, is lower than that of SSF2. This also shows that the stability of SSF2 is lower than that of FSSF [24,35]. Both experimental and theoretical studies show that the S–F bonds in SSF2 are shorter than in FSSF because there is a difference of electronegativity between S and F in SSF2 compared to FSSF [36–38]. Thiothionyl-fluoride (S = SF2) shows two types of sulfur atoms (Scheme 1). The central (apical) and terminal (basal) S atoms of SSF2 could act as electron acceptors and form CB interactions (\(F^{\delta}-S^{\delta+} \ldots Y^{\delta-}-H^{\delta+}\) and \(S^{\delta}-S^{\delta+} \ldots Y^{\delta-}-H^{\delta+}\), respectively) with Lewis bases. In contrast, F atoms of SSF2 as electron donors are appropriate sites for hydrogen-bond interactions (\(S^{\delta+}-F^{\delta-} \ldots H^{\delta+}-Y^{\delta-}\)) with HY molecules. The aim of the current study is to investigate the intermolecular interactions of SSF2 with HY molecules (HY = HF, H2O, NH3, HCN and CH3OH). Herein, we studied the structural parameters and electronic properties of intermolecular complexes. Also stretching frequencies including new vibration modes were identified in which their oscillators were shifted to low or high regions in the infrared spectrum relative to original monomers. Topological analyses on the basis of the Bader’s Quantum Theory of Atoms in Molecules (QTAIM) [39–42] were conducted. The present study has attempted to, at least qualitatively, identify the strength and the covalent character of the interaction. The QTAIM results are useful to show which

![Scheme 1. Schematic structure of SSF2.](image)