© Indian Academy of Sciences

REGULAR ARTICLE

Insight into 1:1 complexes of H$_2$O with NF$_3$ and CF$_2$Cl$_2$: a quantum chemical approach

NAZILA ABDI[a], ABDOLVAHAB SEIF[a,b,*], KHALED AZIZI[a], MOEIN GOODARZI[c] and ALIMORAD RASHIDI[b]

[a]Department of Chemistry, University of Kurdistan, Sanandaj, Iran
[b]Nanotechnology Research Center, Research Institute of Petroleum Industry, Tehran, Iran
[c]Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, Iran
E-mail: abdolvahabseif@gmail.com

Abstract. The competition of hydrogen, halogen and pnicogen bonding to the stability of the atmospheric complexes is interesting, especially where the molecules by the most abundant greenhouse effect in the atmosphere are subject of interest. In the present work, we have computationally studied the addition of H$_2$O to the NF$_3$ and CF$_2$Cl$_2$ molecules to reveal the electronic and structural features of the NF$_3$-H$_2$O and CF$_2$Cl$_2$-H$_2$O complexes through DFT, MP2 and CCSD (T) methods. The interaction energies, geometry and electronic properties including charge transfer, energy gap, NEDA and AIM analyses of all the complexes were calculated to discuss the nature and strength of intermolecular interactions. The results indicate that the role of halogen bonding is more obvious than that of hydrogen and pnicogen bonding, and compared with the NF$_3$, CF$_2$Cl$_2$ is more effectively stabilized by the H$_2$O molecules.

Keywords. H$_2$O; NF$_3$; CF$_2$Cl$_2$; NEDA; AIM; CCSD(T).

1. Introduction

Weak non-covalent interactions have great importance in the development of materials, electronic devices, protein engineering, design of peptides, organometallic, supramolecular chemistry and so on.[1–6] In recent years, due to the development of quantum chemical methods, a great deal of interest has been paid to the study of these types of inter- and intramolecular interactions.[7] Hydrogen bonding which widely exists in chemical and biological systems is a well-known noncovalent interaction that is responsible for the structure and properties of a wide range of molecular complexes.[8–10] While for many years, hydrogen bonding is known as the most important noncovalent interaction, in the two past decades, other types of weak interactions have been identified and studied in detail.[11–14] For example, the halogen-bonding interaction has received considerable interest because of its important role in crystal engineering and protein-ligand interactions.[15–17] A net attractive interaction between an electrophilic region associated with a covalently bonded halogen atom in a molecular entity

and a nucleophilic region in another, or the same, molecular entity is defined as halogen bonding.[18] Since the similarities between hydrogen and halogen bonding have been confirmed experimentally,[19] investigations of systems including both these interactions can be treated as a matter of interest. Such a situation could occur through the interaction of H$_2$O with each of the fluorinated nitrogen trifluoride (NF$_3$) and dichlorofluromethane (CF$_2$Cl$_2$) species. Moreover, there is pnicogen bonding in which a pnicogen atom (N, P, or As) within a Lewis acid interacts with a Lewis base.[20]

Implementation of these concepts in atmospheric chemistry can provide a more comprehensive understanding of the role of these types of intermolecular interactions in atmospheric changes. This is especially important when it is realized that fluorine-containing chemicals constitute about 30% of agricultural and 25% of pharmaceutical compounds.[21,22]

NF$_3$ molecule as one of the most important fluorinated compounds is colorless, odorless, toxic, non-flammable, chemically stable at room temperature and generally used as a fluorinated agent.[23] At high temperatures, NF$_3$ through dissociation into NF$_2$ and free

fluorine radical has a strong oxidation potential capable of being used for rocket fuels.[24] It has also been used as gas filler for increasing the brightness and life of lamps and as agent for welding alloys.[25,26] By the extraordinary progress of the electronics industry since the early 1980s, much effort has been devoted to the use of NF_3 as an etching cleaning agent, a laser and a cleaning gas.[27–29] Moreover, as an environmentally preferable substitute compound for sulfur hexafluoride or fluorocarbons, NF_3 is found to reduce ozone damage.[30] However, its effects as a greenhouse gas are much longer than other recognized contaminants as CO_2.[31,32] Since, at present a large amount of NF_3 is used either as an etchant or as a cleaning gas in the world, the dramatic increase of its concentration in the atmosphere should be taken seriously and further studied. Studying the interactions between NF_3 and different chemical species within the atmosphere can be considered as an important attempt in this regard.[33–35]

Amongst the atmospheric chemical species, a special place should be assigned to chlorofluorocarbons (CFCs). This is due to the fact that the usage of CFCs in industry as foam propellants and refrigerants release a significant amount of these chemicals into the atmosphere.[36,37] It has been confirmed that CFCs which persist for a very long time in the troposphere efficiently absorb the radiation and have a high global warming potential.[38] A specific example of CFCs is CF_2Cl_2 (CFC-12) which is a nonflammable, nontoxic and relatively inert compound and its first ozone destructive effect was reported in 1974.[39] Considering the applied importance and atmospheric effects of CF_2Cl_2, studying its stability and reactivity in different media has been the subject of much research.[40,41] In this regard, it has been confirmed that for gaseous CF_2Cl_2 at energies < 15 eV, the electron-mediated dissociation including C–Cl bond cleavage is the dominated reaction.[42,43] Moreover, co-adsorption of CF_2Cl_2 with H_2O on a Ru (0001) substrate leads to a ∼ 100 × enhancement of Cl^- ion yields in electron-stimulated desorption, compared to the yield from CF_2Cl_2 adsorbed alone.[44] On the other hand, a recent study indicates that the CF_2Cl_2 molecules adsorbed on the ice nanoparticles do not form clusters, and no Cl fragments are observed from their photodissociation.[45] It can be seen that in all of these studies, the stability of CF_2Cl_2 has been somewhat considered. The stability of complexes of CF_2Cl_2 with light gases such as CO_2 and N_2O molecules has also been theoretically investigated, recently.[34,46] The results have shown that the interaction of N_2O with CF_2Cl_2 is more effective than that of CO_2. In a recent study, coordination of

electron-donating ether oxygen atoms to the electron-deficient SF_3 groups has been cited as the main reason for the high thermal stability of aryl fluorinated compounds.[47] Accordingly, it is important to investigate whether a similar situation could exist in the interaction between H_2O and fluorinated NF_3 and CF_2Cl_2 molecules.

It has been shown that atmospheric water vapor is responsible for more than 60% of the natural greenhouse effect.[48] H_2O also plays an important role in many reaction cycles of atmospheric chemistry as exemplified in the production of the OH radical. Therefore, the investigation of the interaction between H_2O and other chemical species could be regarded as a target subject in atmospheric studies. As a special case, studying of the intermolecular interactions of H_2O with the fluorinated species such as NF_3 and CF_2Cl_2 could be of great potential importance in atmospheric processes.

To the best of our knowledge, no effort has been made to provide a theoretical description of the role of non-covalent intermolecular interactions and also its detailed electronic analyses especially in the scheme of AIM and NEDA for the complexes of H_2O with either NF_3 or CF_2Cl_2 molecules. These two molecules were chosen as they are present a lot in the atmosphere and also a good pattern to compare the conventional intermolecular interactions of hydrogen, halogen and pnicogen bonding at the same complexes. In the present paper, we report the results of *ab initio* quantum chemical calculations on the NF_3-H_2O and the CF_2Cl_2-H_2O systems. The DFT method was also used to study the accuracy of the results of M06-2X functional. Interestingly, the binding energies of this function are very close to CCSD(T) method. However, the main objective of the present work is to reveal the electronic and structural properties of NF_3-H_2O and CF_2Cl_2-H_2O systems. Besides, the water adsorption treatment of the halogenated species could also open a new window toward the use of halogenated functional groups on adsorbents.

2. Computational details

All structural optimizations were performed at the MP2[49] level of theory using aug-cc-pVDZ basis set with its reliability for a range of noncovalent interactions being demonstrated.[50,51] Harmonic vibrational frequency calculations were also performed at the same level to confirm whether the predicted structures are real minima and to estimate the zero-point vibrational energies (ZPE). Single point (SP) energies have

been computed using aug-cc-pV(D and T)Z basis set for all the atoms at the MP2, CCSD(T) and M06-2X levels.[52,53] The selection of M06-2X is mainly due to its superiority over the other functionals within DFT in the description of weak interactions.[54] The stabilization energies (SE) for the complexes are calculated by the following equation:

$$SE = E_{X-H2O} - E_X - E_{H2O} \qquad (1)$$

where E_{X-H2O}, E_X and E_{H2O} are the energies of complex and the isolated monomers, respectively. The interaction energy for all the studied complexes was corrected for the basis set superposition error (BSSE).[55] The molecular electrostatic potential (MEP) on the 0.001 a.u isodensity envelope, representing the van der Waals surface was calculated using WFA code.[56] In order to analyze the electron density in bond critical points (ρ_{BCP}) the AIM theory with the AIM2000[57,58] program was used at the MP2/aug–cc–pVDZ level. The natural energy decomposition analysis (NEDA)[59] was used to estimate the contributions of the electrostatic, polarization, charge transfer, exchange, and deformation components in interaction energies. Finally, natural bond orbital (NBO) analysis[60] was performed at the MP2/aug–cc–pVTZ level to investigate the status of charge transfer between electron donor and electron acceptor species. A preliminary assessment showed that the accuracy of electrostatic charges estimated by MP2/aug–cc–pVTZ method is the same accuracy of CCSD(T)/aug–cc–pVTZ, but with much less CPU time. All the calculations were performed using the GAMESS suit of program.[61]

2.1 Theoretical background

A molecule's electrostatic potential, V(r), has proven to be an effective guide for its reactive behavior. V(r) is the potential that is created by the molecule's nuclei and electrons at any desired point r and is given by:

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')\,dr'}{|r - r'|} \qquad (2)$$

where Z_A and $\rho(r')$ are the charge on nucleus A, located at R_A, and electronic density function, respectively. The sign of V(r) depends on whether the effects of the nuclei or the electrons are dominant at any point.

The AIM methodology, within Bader's theory, provides valuable information toward understanding the interaction between interactive monomers. According to this theory, the nature of chemical bonds and molecular reactivity can be denoted by topological analysis of total electric density, $\rho(r)$, and its corresponding Laplacian, $\nabla^2\rho(r)$, at critical points (CP). The negative values of $\nabla^2\rho(r)$ show the addition of potential energy at bond critical points (BCP) which is the speciality of shared interactions (for example covalent bonds). In contrast, positive values of $\nabla^2\rho(r)$ are associated with depletion of electrostatic charge along the bond path, which is a specification of closed-shell interactions (such as hydrogen bonds). Generally, applying this method to complexes composed by molecules provides the opportunity to discuss the status of BCPs. The $\rho(r)$ and $\nabla^2\rho(r)$ are used to describe the strength and the characteristic of the bonds. The larger $\rho(r)$ corresponds to the stronger bond, the $\nabla^2\rho(r) < 0$ indicates the existence of covalent bond, and $\nabla^2\rho(r) > 0$ corresponds to the ionic bond, hydrogen bond or establishment of dispersion forces. The $-G_C/V_C$ ratio, being G_C and V_C, respectively, the kinetic and potential energy density at BCP was used as a measure of the degree of covalency in non-covalent interactions. Values greater than 1 generally indicates a non-covalent interaction without covalent character while ratios smaller than unity are indicative of the covalent nature of the interaction. Sum of these two quantities equals total energetic density ($H = Gc + Vc$).

3. Results and Discussion

After considering many initially guessed structures, different complexes were located on the extremum points in potential energy surfaces (PES) of NF_3-H_2O and CF_2Cl_2-H_2O systems. Here, only those complexes placed at the real minima (ZPE-corrected negative interaction energies) on the PES are discussed. Four sections are considered to interpret the results of the present study: monomers, geometry and interaction energy of complexes and analysis of intermolecular interactions and finally electronic properties of complexes.

3.1 Monomers

Figure 1 shows the MEP profile of studied monomers and the quantitative description of this image is shown in Table 1. In Figure 1, red and blue colors show, respectively, the most positive and the most negative regions on the MEP surface of the monomers. From
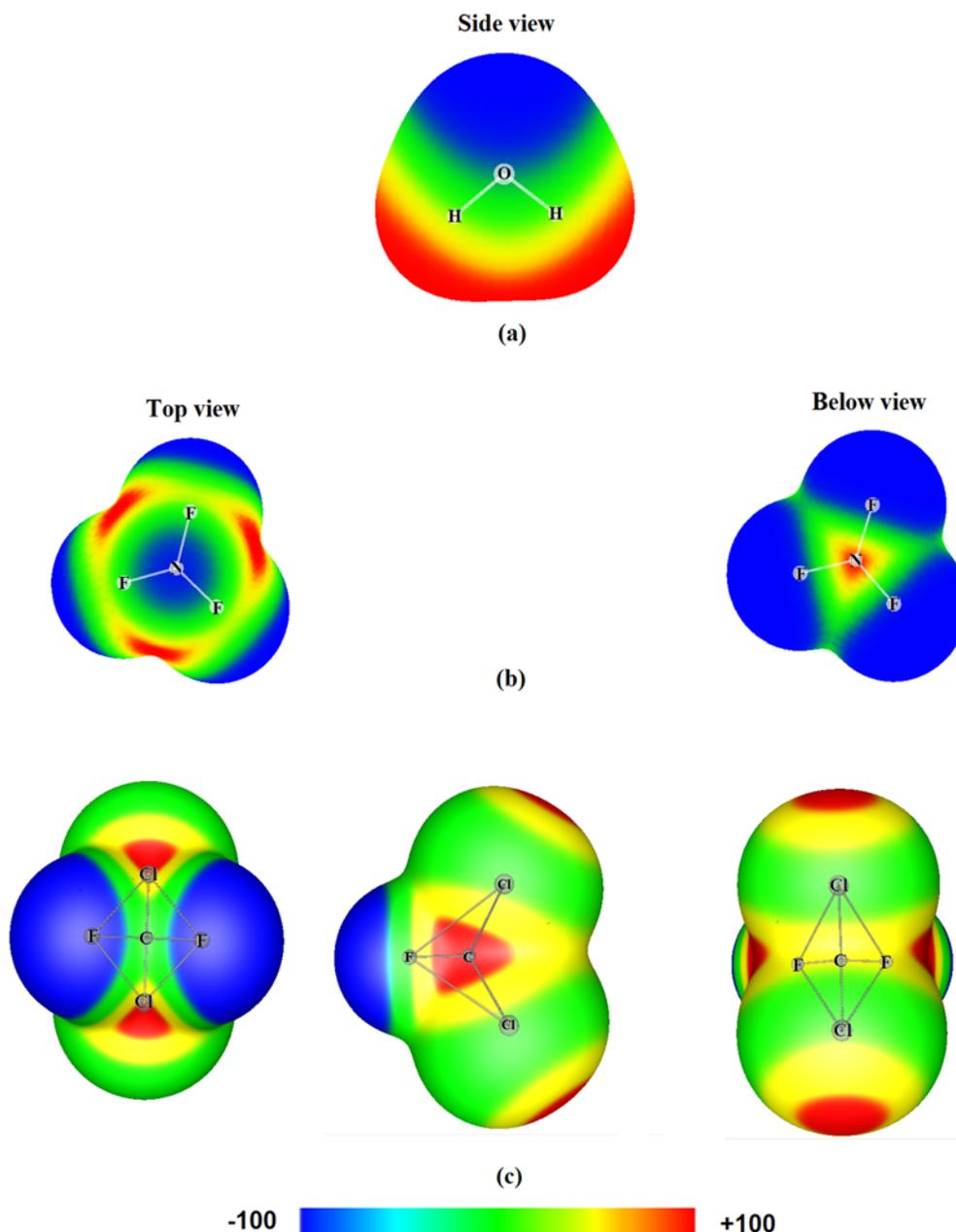
Side view

(a)

Top view   **Below view**

(b)

(c)

-100 ▮▮▮▮▮▮▮▮▮▮ +100

Figure 1. Schematic representation of the MEP on the 0.001 au electron density isosurface of the monomers; (a) H_2O, (b) NF_3 and (c) CF_2Cl_2.

Table 1. Maximum (V_S,max) and minimum (V_S,min) values of the electrostatic potentials ($kJ.mol^{-1}$) on the 0.001 au electron density isosurface of the isolated monomers.

Monomer	$V_{s,max}$	$V_{s,min}$
H_2O	109.9	− 106.2
NF_3	84.5	− 3.3
CF_2Cl_2	60.4	− 17.4

this illustration, it is obvious that NF_3 is negative from the head of F atoms. Its positive regions (σ-holes) are mainly localized in the middle of two F atoms.

According to Politzer and Murray, using the concept of the σ-hole, the halogen atom is described as a positive region on the MEP surface.[62] Therefore, it seems that a vector summation of the σ-hole productive forces is created within the NF_3.

Furthermore, there is another weak and somewhat inaccessible positive region in the center of the triangle formed by F atoms and below the central atom (Figure 1 (below view)).[33]

Similar to NF_3, F atoms in CF_2Cl_2 are negative while Cl atoms are positive. There are two kinds of local positive regions on the MEP of CF_2Cl_2. One of them is concentrated around the C atom (Figure 1, side

view) and the other region is symmetrically placed on Cl atoms (Figure 1, below view). In general, regions having positive V(**r**) tend to interact favorably with negative sites and vice versa.

3.2 *Geometry and the role of interaction forces in stabilization of complexes*

3.2a *NF$_3$-H$_2$O system*: Association of H$_2$O and NF$_3$ molecules leads to the formation of some real minima that the more stable complexes are shown in Figure 2. The geometry of the complexes (regarding AIM analysis) at the MP2/aug-cc-pVDZ computational level are depicted in this graph. As can be seen, the N1 complex has an "open structure", whereas the other two complexes are "closed" with two nonlinear interactions. Table 2 shows the values of SE of the complexes at the six computational levels. It is obvious that N1 is the most stable complex regarding Table 2.

3.2b *CF$_2$Cl$_2$-H$_2$O system*: Some real minima were found on the PES of the CF$_2$Cl$_2$-H$_2$O system of which the most stable ones were selected for discussion and shown in Figure 3. The values of SE of this complex at six computational levels are reported in Table 2. As in the case of the NF$_3$-H$_2$O system, the largest amount of SE at all computational levels corresponds to the single "open structure" dimer, C1. It should be noted that there is good agreement between our results of SE of C1 complex and the previously reported values of interaction energy of the most stable configuration of CF$_2$Cl$_2$–H$_2$O system, calculated at the MP2 and CCSD levels.[45] As a result, the interatomic distance (2.97 Å) of Cl from CF$_2$Cl$_2$ and O from H$_2$O molecule and also interaction energy (7.91 kJ.mol^{-1}) of C1 complex at the CCSD(T) method conjugated with aug-cc-pVTZ are very close to the result of very accurate CCSD(T)/ CBS scheme for the same complex for which the interatomic distance and interaction energy are 3.05 Å and 8.44 kJ.mol^{-1}, respectively. On the other hand, the DFT-based results fit well with these findings.
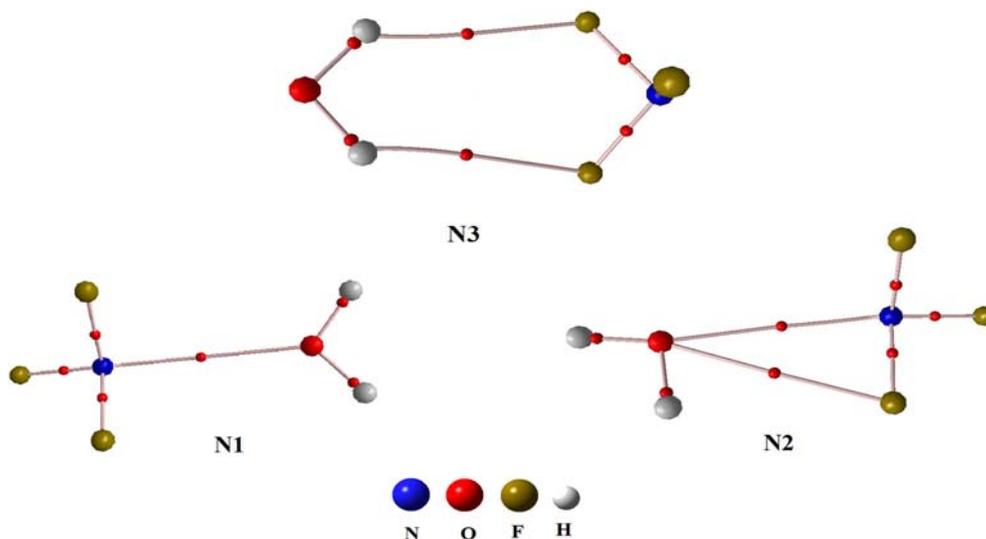

Figure 2. Molecular graphs of NF$_3$-H$_2$O system obtained at the MP2/aug–cc–pVDZ level (small circles on bonds show bond critical points (BCPs)).

Table 2. Stabilization energies (kJ.mol^{-1}) of the NF$_3$-H$_2$O and CF$_2$Cl$_2$- H$_2$O systems estimated by MP2, CCSD (T) and M06-2X methods.

	MP2/aug-cc-pVXZ		CCSD(T)/aug-cc-pVXZ		M06-2X /aug-cc-pVXZ	
Complex	X = D	X = T	X = D	X = T	X = D	X = T
N1	− 3.832 (− 1.677)[a]	− 4.265	− 4.237	− 4.824	− 5.262	− 5.246
N2	− 3.739 (− 0.801)	− 3.363	− 3.455	− 4.030	− 4.554	− 4.493
N3	− 2.076 (− 0.378)	− 2.854	− 3.127	− 3.621	− 3.106	− 3.759
C1	− 5.203 (− 2.957)	− 6.776	− 4.909	− 7.916	− 7.882	− 7.730

[a]The values in parenthesis were corrected for ZPE.

All energy values are corrected with BSSE.

The fact that in both studied systems (NF_3-H_2O and CF_2Cl_2-H_2O) the largest amount of SE corresponds to non-hydrogen bonding including configurations led us to the result that trapping of fluorinated NF_3 and CF_2Cl_2 species by classic hydrogen bonding donor H_2O molecule is not necessarily established just through hydrogen bonding.

Regarding the values of SE in Table 2, at all computational levels, C1 is more stable than N1. This indicates that the O…Cl interaction within the C1 complex is stronger than O…F in N1. We will discuss this further in Section 4.3, however, based on these results we expect that compared to NF_3, CF_2Cl_2 molecules are more effectively trapped by H_2O.

Our results showed that by taking into account ZPE values for both studied systems, the SE of many complexes are considerably reduced so that for almost all configurations the SEs turn to positive values. However, it should be remembered that for each
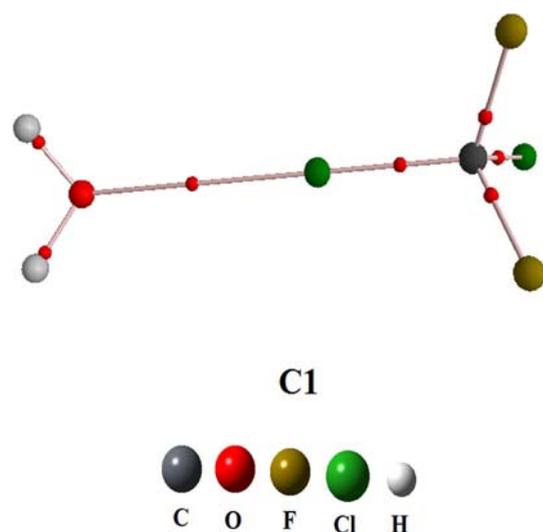

Figure 3. Molecular graph of CF_2Cl_2-H_2O system obtained at the MP2/aug–cc–pVDZ level (small circles on bonds show bond critical points (BCPs)).

system there is at least one structure confirming the stability of configuration. Here, we focused on stable complexes. Moreover, the results demonstrate that for most dimers of both studied systems the absolute amount of SE at the M06-2X computational level is slightly larger than those of MP2 and CCSD(T) levels. This is in line with reports that the M06-2X functional found describes non-covalent interactions properly[54] and it confirms our true selection of the quality of application of DFT in this study. It is interesting to note here that the water adsorption treatment of the halogenated species could also open a new window toward the use of new functional groups on nanomaterial adsorbents.

3.3 *Analysis of intermolecular interactions*

In this section, the nature of intermolecular interactions, in particular concerning the results of the AIM analysis and their role in the stability of dimers is discussed in detail. Table 3 and also Figures 2 and 3 represent the results obtained from the AIM analysis at the MP2/aug–cc–pVDZ level. The first, second and third columns in Table 3 show the type of complex, the kind of interactions and the intermolecular distance, respectively. The values of ρ_{BCP} range from 0.0036 to 0.0112 au in NF_3-H_2O and CF_2Cl_2-H_2O systems which lies in the commonly accepted range of ρ_{BCP} for hydrogen bonding.[63] The values of $\nabla^2\rho_{BCP}$ are positive for all the intermolecular interactions and the last column in Table 3 shows $1.1 < - $ Gc/Vc. Based on these values, the nature of interactions in all complexes is accorded to the non-covalent bonding or establishment of dispersion forces.

In the most stable configuration of NF_3-H_2O system, N1, the N…O interaction between NF_3 and H_2O (as a Lewis base) might be treated as an example of pnicogen bonding.[20] On the other hand, according to

Table 3. Interatomic distances and bond critical point data (a.u) calculated for all complexes.

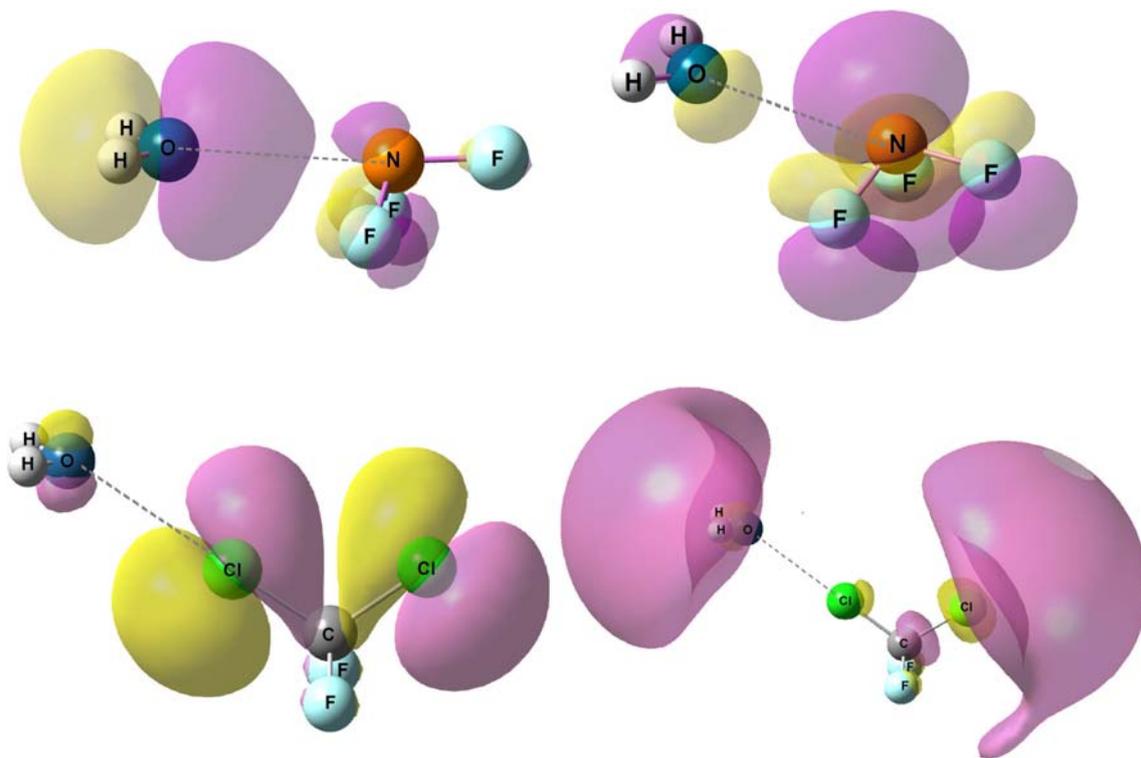| Complex	Interaction (H_2O)….(NF_3 or CF_2Cl_2)	Distance (Å)	ρ_{BCP} (a.u)	$\nabla^2\rho_{BCP}$ (a.u)	$-$ Gc/Vc
H_2O-NF_3					
N1	O…N	3.006	0.0065	0.0270	1.2382
N2	O…F	2.938	0.0067	0.0337	1.1712
	O…N	2.986	0.0067	0.0296	1.2345
N3	H…F	2.707	0.0036	0.0189	1.3699
	H…F	2.707	0.0036	0.0189	1.3699
H_2O-CF_2Cl_2					
C1	O…Cl	2.971	0.0112	0.0455	1.1389
	C…Cl	1.758	0.2074	0.3002	$-$ 0.3336
CF_2Cl_2					
CF_2Cl_2	C…Cl	1.766	0.2009	0.3104	$-$ 0.3257

Figure 4. The electronic density distribution (EDD) of the HOMO (left) and the LUMO (right) of N1 configuration of NF$_3$-H$_2$O system (up) and C1 configuration of CF$_2$Cl$_2$-H$_2$O system (down).

Wolters and Bickelhaupt a substantially classic electrostatic character for this interaction is expected.[64] However, the interaction pattern of the complex N1 is corresponded to the situation in which NF$_3$ molecule interact with H$_2$O, from its side region, between two F atoms. Considering Figure 1, this is an electrostatic interaction based on a halogen bonding between a positive region observed on the MEP, included between two F atoms, and negative O atom. Thus, it seems that the formation of halogen bonding is more highlighted than pnicogen one for this complexation.

To illustrate the issue, the electronic density distribution (EDD) of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of N1 is calculated and shown in Figure 4. As can be seen, instead of a uniform distribution throughout the molecule, the EDD is almost concentrated on the monomers indicating the electrostatic dominant nature of this interaction. Figure 4 shows that a similar situation stands for the C1 configuration of CF$_2$Cl$_2$- H$_2$O system. Therefore, the main role in the formation of NF$_3$-H$_2$O complexes should not be taken into account for hydrogen bonding interactions.

As mentioned above, the strongest bond in CF$_2$Cl$_2$-H$_2$O system is O⋯C which occurs within C1 and its strength is properly confirmed by the large amounts of both of ρ_{BCP} and $\nabla^2\rho_{BCP}$ in Table 3. In addition, these data indicate that the value of the ρ_{BCP} at the O⋯Cl critical point in C1 complex is larger (twice) than that of O⋯F in N1 complex, which shows a more crucial role of halogen bond formation in the C1 complex related to the N1 one. This can be assigned to the bigger size of accessible σ- holes of Cl related to the F atom.[65] Moreover, it can be seen that in none of the two studied systems, F atoms participate in halogen bonding. This is in line with the general observation that F atoms usually do not form halogen bonds.[66]

The results of AIM in Table 3 illustrate that the properties of the C-Cl bond did not change upon the interaction between CF$_2$Cl$_2$ and H$_2$O. This finding is consistent with the lack of Cl fragments in the photodissociation of CF$_2$Cl$_2$ adsorbed on ice.[45]

The results of the partitioning of the interaction energies trough NEDA analysis are reported in Table 4. As can be seen, for the more stable complexes in each system (N1 and N2 from NF$_3$-H$_2$O and C1 from CF$_2$Cl$_2$-H$_2$O), the electrostatic term is the more attractive component and the charge transfer term is placed at the second stage of importance. This is consistent with the fact that it has recently been shown that the electrostatic and charge transfer terms play an important role in the stabilization of the complexes containing halogen and pnicogen bonds.[14,15,67]

Table 4. Values of the NEDA components (kJ.mol^{-1}) in the H_2O-NF_3 and H_2O-CF_2Cl_2 systems.

Complex	Electrostatic	Charge transfer	Polarization	Exchange + deformation
NF$_3$-H$_2$O				
N1	− 6.95	− 2.55	− 0.75	3.47
N2	− 6.86	− 3.26	− 0.71	4.56
N3	− 1.09	− 4.90	− 0.25	1.72
CF$_2$Cl$_2$-H$_2$O				
C1	− 10.71	− 2.80	− 1.72	7.99

Table 5. The amounts and elements of charge transfer, dipole moment and HOMO-LUMO gap for interaction between H_2O and fluorinated NF_3 and CF_2Cl_2 species.

Complex	Don → Acc	Orbitals	E(2) (kJ.mol^{-1})	CT |e|	Dipole moment (D)	HOMO-LUMO gap (eV)
NF$_3$-H$_2$O						
N1	NF$_3$ → H$_2$O	LP(N) → σ*(O)	1.59	− 0.0023	2.56	14.78
N2	NF$_3$ → H$_2$O	LP(N) → σ*(O)	1.42	− 0.0027	2.11	14.79
N3	NF$_3$ → H$_2$O	LP(F) → σ*(O-H)	0.29	− 0.0024	2.61	14.89
CF$_2$Cl$_2$-H$_2$O						
C1	H$_2$O → CF$_2$Cl$_2$	LP(O) → σ*(C-Cl)	4.94	0.0026	2.92	13.28

Our results also show that the role of the polarization term is trivial in the stabilization of complexes. The relatively large exchange-deformation term of N3 and C1 configurations might be attributed to a nonlocalized positive electrostatic potential field between interacting atoms in N1 and the large size of the σ-hole of C atom in C1, respectively.

3.4 *The electronic properties of the complexes*

In order to determine the role of the charge transfer, CT, a donor-acceptor analysis, using NBO scheme at the MP2/aug-cc-pVDZ computational level, was applied on the complexes and their amounts were listed in Table 5. As the data in Table 5 illustrates, the amounts of charge transfer (CT) and energy of second-order perturbation (E$^{(2)}$) of all configurations of both systems are small. This can be mainly due to the existence of highly electronegative atoms within the interacting monomers which in turn led to strong electrostatic interactions and the failure to transfer the charge density from one to another.[68–70]

This situation is also consistent with the minor role of charge transfer term in the interaction energy which is given by the NEDA in Table 4. However, one can see that amongst the studied configurations, C1 has the maximum E$^{(2)}$ which along with a large electrostatic term has led to the largest amount of SE. This also confirms that for this system, the second-order perturbation and charge transfer terms are not the most important ones.

The values of the dipole moment of studied complexes are also listed in Table 5. Since the dipole moments are causing long-range interactions between monomers, it is important to understand to what extent the formation of dimmers can affect the interaction between complexes and surrounding water molecules. At the MP2/aug-cc-pVDZ computational level, the dipole moment of H_2O, NF_3 and CF_2Cl_2 molecules are calculated as 2.01, 0.45 and 0.75 D, respectively. Therefore, regarding the large amounts of the dipole moment of almost all of the complexes of H_2O-NF_3 system and C1 complex of H_2O-CF_2Cl_2 system, one can expect the attraction of more water molecules to these systems is possible. This means that the complexations which increase the dipole-dipole forces may affect the interaction, reaction and even dissociation of other molecules like CO_2, N_2O[46] and also many other halogenated species present in the atmosphere. In general, considering its most important atmospheric complexes should be valuable to determine the probability of the given interaction/reaction/dissociation. For example, using halogen bonding, the H_2O-CF_2Cl_2 complex has a bit more interaction energy method than that of CO_2-CF_2Cl_2 at the

CCSD(T).[46] On this basis, the interaction, and consequently reaction/dissociation, of CF_2Cl_2 in the prior case may happen easier than the later.

Moreover, it is important to note to what extent the formation of dimmers can affect the reactivity or chemical stability of NF_3 and CF_2Cl_2 monomers. To do this, the difference between the energies of HOMO and LUMO of complexes are calculated at the MP2/aug-cc-Pvdz level and the results are given in Table 5. As can be seen, all complexes investigated in this work are relatively highly stable. It should be noted that at the same level of calculation, the HOMO-LUMO gap of H_2O, NF_3 and CF_2Cl_2 molecules are calculated as 14.81, 18.42 and 14.76 eV, respectively. Therefore, in both studied systems, the energy gap due to the formation of dimers is reduced and the effect is more pronounced for the NF_3-H_2O system. Koopman's approximation[71] predicts increase the reactivity of the complexes. If any of the NF_3 or CF_2Cl_2 molecules interact with more than one molecule of H_2O, the question of the reduction of the energy gap would be such that processes such as bond breaking, halogen radical formation and ozone layer depletion would occur. We notice at the end that, although no experimental data is presented here, the validity of the predictions could be established, as there are good agreements between quantum chemical-based results and experiments for the interaction between species.[72–76]

4. Conclusions

We studied the properties of 1:1 complexes of H_2O with NF_3 and CF_2Cl_2 molecules at different computational levels. The results show that the nature of interactions in all complexes is accorded to the noncovalent bonding. For both H_2O-NF_3 and H_2O-CF_2Cl_2 systems at all computation levels, the most stable configuration is an open-structure which is stabled through non-hydrogen bond interactions. Based on the results of NEDA, within the more stable complex of each binary system, the electrostatic term is the more attractive component of SE. The results of AIM in accordance with the previous reports indicate that the properties of the C-Cl bond did not change upon the interaction between CF_2Cl_2 and H_2O. The results of NBO analysis show that the amounts of CT and E(2) of all configurations of both systems are small. The large amounts of the dipole moment of almost all complexes of both H_2O-NF_3 and H_2O-CF_2Cl_2 systems show that attracting more water molecules to these systems are possible. Finally,

regarding the Koopman's approximation in both studied systems the reactivity of the moieties increased upon complexation.

References

1. Berger R, Resnati G, Metrangolo P, Weber E and Hulliger J 2011 Organic fluorine compounds: a great opportunity for enhanced materials properties *Chem. Soc. Rev.* **40** 3496
2. Babudri F, Farinola G M, Naso F and Ragni R 2007 Fluorinated organic materials for electronic and opto-electronic applications: the role of the fluorine atom *Chem. Commun.* 1003
3. Jäckel C and Koksch B 2005 Fluorine in peptide design and protein engineering *Eur. J. Org. Chem.* **2005** 4483
4. Zheng H, Comeforo K and Gao J 2008 Expanding the fluorous arsenal: tetrafluorinated phenylalanines for protein design *J. Am. Chem. Soc.* **131** 18
5. Hughes R P 2010 Fluorine as a ligand substituent in organometallic chemistry: a second chance and a second research career *J. Fluor. Chem.* **131** 1059
6. Thakur T S, Kirchner M T, Bläser D, Boese R and Desiraju G R 2010 C–H⋯F–C hydrogen bonding in 1, 2, 3, 5-tetrafluorobenzene and other fluoroaromatic compounds and the crystal structure of alloxan revisited *CrystEngComm* **12** 2079
7. Scheiner S 2015 *Noncovalent Forces* (Springer: Berlin)
8. Grabowski S J 2006 *Hydrogen Bonding: New Insights* (Springer: Berlin)
9. Jeffrey G A and Saenger W 2012 *Hydrogen Bonding in Biological Structures* (Springer Science & Business Media: Berlin)
10. Thomas J C, Goronzy D P, Dragomiretskiy K, Zosso D, Gilles J, Osher S J, Bertozzi A L and Weiss P S 2016 Mapping buried hydrogen-bonding networks *ACS Nano.* **10** 5446
11. Klinkhammer K W and Pyykko 1995 Ab initio interpretation of the closed-shell intermolecular E. cntdot.. cntdot.. cntdot. E attraction in dipnicogen ($H2E$-$EH2$)$_2$ and dichalcogen (HE-EH)$_2$ hydride model dimers *Inorg. Chem.* **34** 4134
12. Sanz P, Yáñez M and Mó O 2002 Competition between X⋯H⋯Y intramolecular hydrogen bonds and X⋯Y (X = O, S, and Y = Se, Te) chalcogen–chalcogen interactions *J. Phys. Chem. A* **106** 4661
13. Vila A, Vila E and Mosquera R A 2006 Topological characterisation of intermolecular lithium bonding *Chem. Phys.* **326** 401
14. Politzer P, Murray J S and Concha M C 2008 σ-hole bonding between like atoms; a fallacy of atomic charges *J. Mol. Model.* **14** 659
15. Meyer F and Dubois P 2013 Halogen bonding at work: recent applications in synthetic chemistry and materials science *CrystEngComm* **15** 3058

16. Wilcken R, Zimmermann M O, Lange A, Joerger A C and Boeckler F M 2013 Principles and applications of halogen bonding in medicinal chemistry and chemical biology *J. Med. Chem.* **56** 1363

17. Metrangolo P and Resnat G 2015 *Halogen Bonding II* (Springer: Berlin)

18. Politzer P, Murray J S and Clark T 2014 σ-Hole bonding: a physical interpretation In *Halogen Bond. I* (Springer: Berlin) p. 19

19. Arman H D 2008 *Halogen bonding: fundamentals and applications* (Springer Science & Business Media: Berlin)

20. Scheiner S 2013 Detailed comparison of the pnicogen bond with chalcogen, halogen, and hydrogen bonds *Int. J. Quantum Chem.* **113** 1609

21. Müller K, Faeh C and Diederich F 2007 Fluorine in pharmaceuticals: looking beyond intuition *Science* **317** 1881

22. Wang J, Sánchez-Roselló M, Aceña J L, del Pozo C, Sorochinsky A E, Fustero S, Soloshonok V A and Liu H 2013 Fluorine in pharmaceutical industry: fluorine-containing drugs introduced to the market in the last decade (2001–2011) *Chem. Rev.* **114** 2432

23. Scheele R, McNamara B, Casella A M and Kozelisky A 2012 On the use of thermal NF_3 as the fluorination and oxidation agent in treatment of used nuclear fuels *J. Nucl. Mater.* **424** 224

24. Merlet P and Fluorine F 2013 *Compounds with Oxygen and Nitrogen* (Springer Science & Business Media: Berlin)

25. Tyagi A and Chatterjee D S 2013 Liquid crystal display: environment & technology *Int. J. Environ. Eng. Sci. Technol. Res.* **1** 2

26. Tsakiris V, Kappel W and Alecu G 2011 Solid state diffusion welding of Cu-Fe/Al/Ag and Al-Ni dissimilar metals *J. Optoelectron. Adv. Mater.* **13** 1176

27. Hagimoto Y, Ugajin H, Miyakoshi D, Iwamoto H, Muraki Y and Orii T 2008 Evaluation of the plasmaless gaseous etching process *Solid State Phenom.* **134** 7

28. Kompa K L and Walther H 2013 *High-Power Lasers and Applications: Proceedings of the Fourth Colloquium on Electronic Transition Lasers in Munich*, June 20–22, 1977 (Springer: Berlin)

29. Oh H J, Lee J H, Lee M S, Shin W G, Kang S Y, Kim G D and Ko D H 2014 NF_3/NH_3 dry cleaning mechanism inspired by chemical and physical surface modification of Si, SiO_2, and Si_3N_4 *ECS Trans.* **61** 1

30. Reichardt H, Frenzel A and Schober K 2001 Environmentally friendly wafer production: NF_3 remote microwave plasma for chamber cleaning *Microelectron. Eng.* **56** 73

31. Tsai W T 2008 Environmental and health risk analysis of nitrogen trifluoride (NF_3), a toxic and potent greenhouse gas *J. Hazard. Mater.* **159** 257

32. Robson J I, Gohar L K, Hurley M D, Shine K P and Wallington T J 2006 Revised IR spectrum, radiative efficiency and global warming potential of nitrogen trifluoride *Geophys. Res. Lett.* **33**

33. Blanco F, Alkorta I, Rozas I, Solimannejad M and Elguero J 2011 A theoretical study of the interactions of NF_3 with neutral ambidentate electron donor and acceptor molecules *Phys. Chem. Chem. Phys.* **13** 674

34. Seif A, Bagherzadeh R, Goodarzi M and Azizi K 2013 Ab initio study of 1: 1 complexes of nitrogen trifluoride with nitrous oxide and carbon dioxide in vacuo *J. Chem. Sci.* **125** 1277

35. McNamara B, Scheele R, Kozelisky A and Edwards M 2009 Thermal reactions of uranium metal, UO_2, U_3O_8, UF_4, and UO_2F_2 with NF_3 to produce UF_6 *J. Nucl. Mater.* **394** 166

36. Jacob D 1999 *Introduction to Atmospheric Chemistry* (Princeton University Press: Princeton)

37. Finlayson-Pitts B J and Pitts J N 2000 *Chemistry of the Lower and Upper Atmosphere* (Academic Press: California)

38. Lu Q B 2013 Cosmic-ray-driven reaction and greenhouse effect of halogenated molecules: culprits for atmospheric ozone depletion and global climate change *Int. J. Mod. Phys. B* **27** 1350073

39. Molina M J and Rowland F S 1974 Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone *Nature* **249** 810

40. Torkpoor I, Heidari M, Janjanpour Nezhad, Salehi N, Gharibzadeh F and Edjlali L 2018 Insight into Y@X2B8 (Y = Li, CO_2 and Li-CO_2, X = Be, B and C) nanostructures: a computational study *Chem. Rev. Lett.* **1** 2

41. Shiryaeva E S, Tyurin D A and Feldman V I 2016 Mechanisms of radiation-induced degradation of $CFCl_3$ and CF_2Cl_2 in noble-gas matrixes: an evidence for "Hot" ionic channels in the solid phase *J. Phys. Chem. A* **120** 7847

42. Ingólfsson O, Weik F and Illenberger E The reactivity of slow electrons with molecules at different degrees of aggregation: gas phase, clusters and condensed phase *Int. J. Mass Spectrom. Ion Process.* **155** 1

43. Kiendler A, Matejcik S, Skalny J D, Stamatovic A and Märk T D 1996 Dissociative electron attachment to using a high-resolution crossed-beams technique *J. Phys. B* **29** 6217

44. Solovev S, Kusmierek D O, Madey and T E 2004 Negative ion formation in electron-stimulated desorption of CF_2Cl_2 coadsorbed with polar NH_3 on Ru (0001) *J. Chem. Phys.* **120** 968

45. Poterya V, Kočišek J, Lengyel J, Svrčková P, Pysanenko A, Hollas D, Slavíček P and Fárník M 2014 Clustering and photochemistry of freon CF_2Cl_2 on argon and ice nanoparticles *J. Phys. Chem. A* **118** 4740

46. Seif A, Ebrahimi S, Vessally E and Goodarzi M 2013 Comparative study on the stabilities and properties of heterodimers containing the intermolecular interactions of CF_2Cl_2 with the isoelectronic and isostructure species of N_2O and CO_2 *Struct. Chem.* **24** 1737

47. de Paul Nziko V and Scheiner S 2015 Intramolecular S···O chalcogen bond as stabilizing factor in geometry of substituted phenyl-SF_3 molecules, (n.d.) *J. Org. Chem.* **80** 2356

48. Ollila A 2013 Analyses of IPCC's warming calculation results *J. Chem. Biol. Phys. Sci.* **3** 2912

49. Møller C and Plesset M S 1934 Note on an approximation treatment for many-electron systems *Phys. Rev.* **46** 618

50. Dunning Jr T H, Peterson K A and Wilson A K 2001 Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited *J. Chem. Phys.* **114** 9244

51. Nziko V de P N and Scheiner S 2014 Chalcogen bonding between tetravalent SF4 and amines *J. Phys. Chem. A* **118** 10849

52. Becke A D 1993 Becke's three parameter hybrid method using the LYP correlation functional *J. Chem. Phys.* **98** 5648

53. Zhao Y, Schultz N E and Truhlar D G 2006 Design of density functionals by combining the method of constraint satisfaction with parametrization for thermo-chemistry, thermochemical kinetics, and noncovalent interactions *J. Chem. Theory Comput.* **2** 364

54. Cohen A J, Mori-Sánchez P and Yang W 2011 Challenges for density functional theory *Chem. Rev.* **112** 289

55. Boys S F and de Bernardi F 1970 The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors *Mol. Phys.* **19** 553

56. Bader R F W 1990 *Atoms in Molecules. A Quantum Theory* (Clarendon: Oxford)

57. Bader R F W, Carroll M T, Cheeseman J R, Chang C 1987 Properties of atoms in molecules: atomic volumes, *J. Am. Chem. Soc.* **109** 7968

58. Biegler-Konig F, Schonbohm J and Bayles D 2001 AIM2000—a program to analyze and visualize atoms in molecules *J. Comput. Chem.* **22** 545

59. Glendening E D 1996 Natural energy decomposition analysis: explicit evaluation of electrostatic and polarization effects with application to aqueous clusters of alkali metal cations and neutrals *J. Am. Chem. Soc.* **118** 2473

60. Reed A E, Curtiss L A and Weinhold F 1988 Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint *Chem. Rev.* **88** 899

61. Schmidt M W, Baldridge K K, Boatz J A, Elbert S T, Gordon M S, Jensen J H, Koseki S, Matsunaga N, Nguyen K A, Su S J 1993, EXECUTION OF GAMESS BEGUN 21: 01: 54 LT 10-JUL-2006 *J. Comput. Chem.* **14** 1347

62. Politzer P, Murray J S and Clark T 2013 Halogen bonding and other σ-hole interactions: a perspective *Phys. Chem. Chem. Phys.* **15** 11178

63. Koch U and Popelier P L A 1995 Characterization of CHO hydrogen bonds on the basis of the charge density *J. Phys. Chem.* **99** 9747

64. Wolters L P and Bickelhaupt F M 2012 Halogen bonding versus hydrogen bonding: a molecular orbital perspective *ChemistryOpen* **1** 96

65. Murray J S, Paulsen K and Politzer P 1994 Molecular surface electrostatic potentials in the analysis of non-hydrogen-bonding noncovalent interactions *J. Chem. Sci.* **106** 267

66. Metrangolo P, Neukirch H, Pilati T and Resnati G 2005 Halogen bonding based recognition processes: a world parallel to hydrogen bonding *Acc. Chem. Res.* **38** 386

67. Wei Y, Li Q, Li W, Cheng J and McDowell S A C 2016 Influence of the protonation of pyridine nitrogen on pnicogen bonding: competition and cooperativity *Phys. Chem. Chem. Phys.* **18** 11348

68. Reed A E, Curtiss L A and Weinhold F 1988 Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint *Chem. Rev.* **88** 899

69. Banerjee P and Chakraborty T 2018 Weak hydrogen bonds: insights from vibrational spectroscopic studies *Int. Rev. Phys. Chem.* **37** 83

70. Seif A and Massahi S 2014 Theoretical study on the properties and stabilities of complexes formed between SO 4 (C2v) and isostructure species of CO_2, CS_2, and SCO *J. Mol. Model.* **20** 2488

71. Parr R G and Yang W 1989 *Density-Functional Theory of Atoms and Molecules* (Oxford Univ. Press: New York)

72. Hudgens J W, Johnson III R D, Tsai B P and Kafafi S A 1990 Experimental and ab initio studies of electronic structures of the trichloromethyl radical and cation *J. Am. Chem. Soc.* **112** 5763

73. Pourreza A, Askari S, Rashidi A, Seif A and Kooti M 2019 Highly efficient SO_3Ag-functionalized MIL-101 (Cr) for adsorptive desulfurization of the gas stream: experimental and DFT study *Chem. Eng. J.* **363** 73

74. Tehrani N H M H, Alivand M S, Maklavany D M, Rashidi A, Samipoorgiri M, Seif A and Yousefian Z 2019 Novel asphaltene-derived nanoporous carbon with NS-rich micro-mesoporous structure for superior gas adsorption: experimental and DFT study *Chem. Eng. J.* **358** 1126

75. Hensen K, Stumpf T, Bolte M, Näther C and Fleischer H 1998 Experimental investigations and ab initio studies on hexacoordinated complexes of dichlorosilane *J. Am. Chem. Soc.* **120** 10402

76. Gharakhani F, Vessally E, Esrafili M D and Seif A 2015 The interaction energies between glycoluril clip and thiophenol derivatives using density functional theory calculations *J. Sulfur Chem.* **36** 351