***Ab initio* study of 1:1 complexes of nitrogen trifluoride with nitrous oxide and carbon dioxide in vacuo**

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Abstract. Quantum chemical calculations are carried out in order to investigate the heterodimers of NF₃ with isoelectronic and isostructure species of N₂O and CO₂ in gas phase within the MP2 (Møller–Plesset perturbation) and CCSD(T) levels. Three and four minima are located on the potential energy surfaces of NF₃–CO₂ and NF₃–N₂O systems at the MP2/aug-cc-PVDZ level, respectively. Single-point energy calculations at the MP2/aug-cc-PVTZ and CCSD(T)/aug-cc-PVDZ levels confirm results obtained at the MP2/aug-cc-PVDZ level show that atmospheric roles of NF₃–N₂O and NF₃–CO₂ systems are similar. The atom in molecules theory was applied to analyse the nature of intermolecular interactions. Also, natural bond orbital (NBO) analysis has been used in order to obtain charge transfer quota among heterodimers.

Keywords. Atmosphere; nitrogen trifluoride; carbon dioxide; nitrous oxide; atom in molecules (AIM).

1. Introduction

Non-covalent intermolecular interactions bridge the gap between free molecular systems and the corresponding condensed phases. The complexes formed by these non-covalent intermolecular interactions are significant *per se*. From a theoretical point of view, researchers have pointed out great interest in the investigation of their complexes.^{1–5}

Investigation of non-covalent intermolecular interactions of NF₃ with isoelectronic and isostructure species of N₂O and CO₂ should be very interesting because NF₃, N₂O and CO₂ species have important influences in the Earth's atmosphere.

Nitrogen trifluoride, NF₃, is a man-made gas that once released into the atmosphere circulates from the surface to the stratosphere hundreds of times before it is destroyed by solar ultraviolet radiation. NF₃ is nearly chemically inert in the atmosphere, but very effective in absorbing infrared radiation that the Earth emits. By trapping this infrared radiation, NF₃ becomes a potent greenhouse gas. Also, it is one of the most extensively used per fluoro compounds (PFCs) in the semiconductor industry to etch and cut the silicon substrate for computer chips, and cleaning in plasma-enhanced chemical

vapour deposition (PECVD) processes.^{6–8} NF₃ is also used in hydrogen fluoride and deuterium fluoride lasers, which are types of chemical lasers. It is interesting that as an environmentally preferable compound substitute for sulphur hexafluoride or per fluorocarbons, NF₃ is found to reduce the rate of damage in the atmosphere.⁹ With respect to more traditional fluorinated gases such as CF₄ and C₂F₆, NF₃ offers advantages of avoiding carbon contamination residues, boosting productivity by greater than 30%, and decreasing effluent emissions by 90%.^{10,11} However, similar to other industrially important PFCs,^{12,13} NF₃ is a potential greenhouse gas, with an atmospheric lifetime of about 740 years. In terms of kilograms emitted, NF₃ is about 17,200 times more effective as a greenhouse gas than carbon dioxide.¹⁴ High-volume applications such as DRAM computer memory production, the manufacturing of flat panel displays and large-scale production of thin-film solar cells in regions with insufficient ecological awareness continues to increase the emission of NF₃.^{15,16}

Recently, interactions between NF₃ and different chemical species such as solid state, ionic and molecular form of materials have been studied both computationally and experimentally. In a thorough study, Antoniotti *et al.*¹⁷ analysed the nature of NF₃ adsorption on solid surfaces. Their results revealed the first theoretical evidence for the behaviour of NF₃ as a functional Lewis base when interacting with neutral Lewis

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acids. Furthermore, the complexes formed between NF_3 with ionic (M^+ , $\text{M} = \text{H}, \text{Li}, \text{Na}$ and K)¹⁸ and also neutral ambidentate electron donor species (HF , FCl , HCN , and HNC)¹⁹ have been analysed, computationally.

Nitrous oxide (N_2O) is a harmful climate gas with tremendous global warming potential (GWP). When it compared to carbon dioxide (CO_2), as isoelectronic and isostructure species, N_2O has 310 times the ability per molecule of gas to trap heat in the atmosphere.²⁰ In addition to greenhouse influences, N_2O can act as destructive factor of ozone layer. It is produced by both natural and human-related sources. It is also produced naturally from a wide variety of biological sources in soil and water, particularly microbial action in wet tropical forests.

To the best of our knowledge, there is no available information in the literature regarding either theoretical or experimental studies of the complexes containing non-covalent intermolecular interactions of NF_3 with CO_2 and N_2O . Thus, the present study reports a detailed examination of the stability of $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems. This theoretical study provides valuable information on environmental problems such as greenhouse influences.

2. Computational details

All calculations have been performed with the Gaussian 03 quantum chemical package.²¹ Geometries of the isolated NF_3 , CO_2 and N_2O moieties and their heterodimers are fully optimized at the second-order Møller–Plesset perturbation method (MP2)²² in conjunction with the aug-cc-pVDZ basis set²³ within the frozen core (FC) approximation on the singlet potential energy surface (PES). As shown in table 1, the optimized geometries of NF_3 ,²⁴ CO_2 ²⁵ and N_2O ²⁶ at the MP2/aug-cc-pVDZ level are in good agreement with those of the experiment. To gain reliable relative energies of each heterodimer, single-point energy calculations at the MP2/aug-cc-pVTZ and $\text{CCSD(T)/aug-cc-pVDZ}$ levels were carried out on the optimized geometries of MP2/aug-cc-pVDZ . Harmonic vibrational frequency calculations have been performed at

the MP2/aug-cc-pVDZ level to confirm the nature of all heterodimers as local minima (with the number of imaginary frequencies $\text{NIMAG} = 0$) and enable the evaluation of the zero-point vibrational energies (ZPEs). Stabilization energy of the heterodimers in the present study was calculated as the difference between the energy of the heterodimers and the sum of the energies of the isolated monomers in their minimum configuration. The counterpoise (CP) method²⁷ has been used to take into account the basis set superposition error (BSSE) in the calculation of the energies and present the energies without any BSSEs. The atoms in molecules (AIM) methodology²⁸ has been used with the AIM2000²⁹ programs to analyse the electron density in bond critical point of the systems considered at the MP2/aug-cc-pVDZ level. Finally, the natural bond orbital (NBO) technique was employed to investigate the charge transfer processes occurring at atomic charges using the NBO-3 program.^{30–32}

3. Results and discussion

Nomenclature that has been used for the classification of different structures of the heterodimers is based on linear molecules that are used (C for CO_2 and N for N_2O) and the numbering of these heterodimers conforms to the ordering of the intermolecular interaction energy (corrected for ZPE and BSSE). The calculated binding energies for different heterodimers (without and with ZPE and BSSE corrections) in the MP2 and CCSD(T) levels are listed in table 2.

About the electronic characteristics of the solitary monomers, it is worth mentioning the presence of four minima in the molecular electrostatic potential (MEP) of the NF_3 molecule and two minima for each CO_2 and N_2O species in figure 1. Regarding NF_3 , three of them are associated with lone pairs of F-atoms and one of them with a lone pair of nitrogen atoms. Also, in the CO_2 ($\text{D}_{\infty\text{h}}$) and N_2O ($\text{C}_{\infty\text{v}}$) molecules, two minima are located in the molecular plane. It is obvious that in the N_2O molecule, more electronegativity of oxygen related to nitrogen ($\text{O}_{3.5} > \text{N}_{3.0}$) is the factor behind shift of nonbonding electrons from nitrogen to oxygen. Positive

Table 1. Geometries of NF_3 , CO_2 and N_2O species at the MP2/aug-cc-pVDZ level and experimental (bond lengths in angstrom, bond angles in degree).

Species	N–F	F–N–F	C–O	N–N	N–O
NF_3	1.385	101.6			
CO_2			1.180		
N_2O				1.174	1.190
Experimental	1.371 ²¹	102.2 ²¹	1.163 ²²	1.126 ²³	1.186 ²³

Table 2. Stabilization energies (kJ/mol) of $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems at the MP2 and CCSD(T) levels.

Heterodimers	MP2/aug-cc-pVDZ			MP2/aug-cc-pVTZ// MP2/aug-cc-pVDZ		CCSD(T)/aug-cc-pVDZ// MP2/aug-cc-pVDZ	
	E_I	$E_I + \text{BSSE}$	$E_I + \text{BSSE} + \text{ZPE}$	E_I	$E_I + \text{BSSE}$	E_I	$E_I + \text{BSSE}$
C1	−6.67	−2.88	−1.66	−5.40	−3.56	−7.38	−5.67
C2	−6.14	−2.70	−1.58	−5.13	−3.49	−6.90	−5.30
C3	−6.26	−2.67	−1.56	−5.30	−3.50	−7.11	−5.11
N1	−6.71	−3.38	−2.20	−6.27	−4.24	−7.15	−6.30
N2	−7.21	−3.42	−2.09	−6.31	−4.12	−7.60	−5.95
N3	−6.80	−2.79	−1.60	−5.17	−3.21	−6.31	−5.50
N4	−4.00	−1.35	−0.59	−3.34	−1.88	−4.12	−2.01

values of the MEP are out of the plane and around the central atoms (carbon and nitrogen).

Molecular graphs (including the critical points and bond paths) and AIM parameters of all heterodimers were reported in figure 2 and table 3, respectively. Results of NBO methodology are provided in table 4. Finally, the ranking of all heterodimers in terms of binding energies and some exponential relationships were shown in figures 3 and 4, respectively.

3.1 Structural details of $\text{NF}_3\text{--CO}_2$ heterodimers

Association of NF_3 with CO_2 monomer leads to the formation of three minima, C1, C2 and C3, on the singlet PES. Binding energies of the $\text{NF}_3\text{--CO}_2$ heterodimers

including ZPE and BSSE corrections lie in the range of 1.56–1.66 kJ/mol at the MP2/aug-cc-pVDZ level.

C1 is the most stable heterodimer of the $\text{NF}_3\text{--CO}_2$ system with a binding energy 1.66 kJ/mol after corrections with BSSE and ZPE at the MP2/aug-cc-pVDZ level. C1 heterodimer includes only one interaction between NF_3 and CO_2 monomers in which oxygen atom of CO_2 approaches F atom of NF_3 to create O...F interaction with length 3.091 Å. This is the shortest distance between the interacting atoms of O and F in the $\text{NF}_3\text{--CO}_2$ system.

In C2 heterodimer, one of oxygen atoms of CO_2 has interactions with two F-atoms of NF_3 monomer (O...F) with bond length 3.327 Å at the MP2/aug-cc-pVDZ level. Also, carbon atom of CO_2 reacts with other F-atom of NF_3 (C...F) with bond length of 2.976 Å.

Figure 1. MEP of (a) NF_3 , (b) CO_2 and (c) N_2O at ± 0.004 , 0.020 and 0.012 a.u. isosurfaces at the MP2/aug-cc-pVDZ level, respectively. The positive and negative regions of the MEP minima are indicated with violet and golden brown colours.

Figure 2. Molecular graphs of all minima obtained at the MP2/aug-cc-pVDZ level (small circles among bonds represent ring critical point (RCP), small circles on bonds represent bond critical point (BCP)).

Binding energy of C2 heterodimer (corrected with BSSE and ZPE) is 1.58 kJ/mol at the MP2/aug-cc-pVDZ level.

C3 heterodimer is located as uppermost of local minimum in the $\text{NF}_3\text{--CO}_2$ system with binding energy of 1.56 kJ/mol. C3 heterodimer includes two interactions of $\text{C}\cdots\text{F}$ with bond lengths 3.085 and 3.098 Å, and one interaction of $\text{O}\cdots\text{F}$ with bond length 3.418 Å at the MP2/aug-cc-pVDZ level. Note that the longest $\text{O}\cdots\text{F}$ and $\text{C}\cdots\text{F}$ interactions belong to this heterodimer in the $\text{NF}_3\text{--CO}_2$ system. The long intermolecular distances of this heterodimer are in agreement with the interaction energy found.

3.2 Structural details of $\text{NF}_3\text{--N}_2\text{O}$ heterodimers

Four minima have been found for the $\text{NF}_3\text{--N}_2\text{O}$ system on the singlet PES. The binding energies of these

heterodimers including BSSE and ZPE corrections lie in the range of 0.59–2.20 kJ/mol at the MP2/aug-cc-pVDZ level.

N1 is the most stable heterodimer of $\text{NF}_3\text{--N}_2\text{O}$ system with binding energy of 2.20 kJ/mol at the MP2/aug-cc-pVDZ level. N_2O and CO_2 are isoelectronic and isostructure monomers. Therefore, it should be interesting to compare the corresponding dimers in $\text{NF}_3\text{--N}_2\text{O}$ and $\text{NF}_3\text{--CO}_2$ systems. The corresponding heterodimer for N1 of $\text{NF}_3\text{--N}_2\text{O}$ system is C2 of $\text{NF}_3\text{--CO}_2$ system. Comparison of N1 and C2 heterodimers shows that both of them have two $\text{O}\cdots\text{F}$ interactions. Their main difference is the third interaction. In N1 heterodimer, middle nitrogen atom of N_2O (N_m stands for middle nitrogen atom of N_2O) reacts with F-atom of NF_3 monomer ($\text{N}_m\cdots\text{F}$ interaction), while in C2 heterodimer, C-atom of CO_2 attacks F-atom of NF_3 monomer. N1 heterodimer is merely 0.62 kJ/mol more stable than C2 heterodimer. Also, the bond lengths of

Table 3. Interatomic distances (Å) and bond critical point data (a.u) calculated at the MP2/aug-cc-pVDZ level.

Heterodimers	Interaction	Interaction distance	ρ	$\nabla^2\rho$	–G/V
C1	$\text{O}\cdots\text{F}$	3.091	0.0067	0.0334	1.2955
C2	$\text{C}\cdots\text{F}$	2.976	0.0059	0.0317	1.3964
	$\text{O}\cdots\text{F}$	3.327	0.0030	0.0159	1.4309
C3	$\text{O}\cdots\text{F}$	3.327	0.0030	0.0159	1.4300
	$\text{O}\cdots\text{F}$	3.418	0.0024	0.0137	1.5624
	$\text{C}\cdots\text{F}$	3.085	0.0046	0.0261	1.5265
	$\text{C}\cdots\text{F}$	3.098	0.0045	0.0254	1.5444
N1	$\text{N}_m\cdots\text{F}$	2.943	0.0067	0.0304	1.1979
	$\text{O}\cdots\text{F}$	3.259	0.0035	0.0184	1.3677
	$\text{O}\cdots\text{F}$	3.236	0.0037	0.0191	1.3392
N2	$\text{O}\cdots\text{F}$	3.014	0.0074	0.0348	1.1631
N3	$\text{N}_t\cdots\text{N}$	3.029	0.0065	0.0254	1.2525
N4	$\text{N}_t\cdots\text{F}$	3.306	0.0033	0.0156	1.4051
	$\text{N}_t\cdots\text{F}$	3.309	0.0033	0.0156	1.4071
	$\text{N}_t\cdots\text{F}$	3.315	0.0032	0.0154	1.4109

Symbols N_t and N_m stand for terminal and middle nitrogen atoms of N_2O , respectively.

Table 4. Charge transfer (e) and dipole momentum (Debye) calculated at the MP2/aug-cc-pVDZ level within NF₃-CO₂ and NF₃-N₂O systems.

Heterodimers		CT	Total CT	Dipole momentum
C1	CO ₂ → NF ₃	0.0003	0.0005	0.4529
	NF ₃ → CO ₂	0.0008		
C2	CO ₂ → NF ₃	0.0000	0.0008	0.5511
	NF ₃ → CO ₂	0.0008		
C3	CO ₂ → NF ₃	0.0000	0.0010	0.5814
	NF ₃ → CO ₂	0.0010		
N1	N ₂ O → NF ₃	0.0000	0.0002	0.6192
	NF ₃ → N ₂ O	0.0002		
N2	N ₂ O → NF ₃	0.0006	-0.0002	0.3892
	NF ₃ → N ₂ O	0.0004		
N3	N ₂ O → NF ₃	0.0000	0.0000	0.3716
	NF ₃ → N ₂ O	0.0000		
N4	N ₂ O → NF ₃	0.0000	0.0000	0.9464
	NF ₃ → N ₂ O	0.0000		

The symbol CT stands for charge transfer

O...F and N_m...F in N1 heterodimer are shorter than those of O...F and C...F in C2 heterodimer, respectively. It is necessary to say that N_m...F interaction is merely found in N1 heterodimer.

N2 is the second stable heterodimer of NF₃-N₂O system. Binding energy of this heterodimer (2.10 kJ/mol) is slightly lower than N1 heterodimer at the MP2/aug-cc-pVDZ level. Note that corresponding heterodimer for N2 of NF₃-N₂O system is C1 of NF₃-CO₂ system.

Figure 3. Ranking of all heterodimers obtained in both NF₃-N₂O and NF₃-CO₂ systems in terms of $E_I + BSSE + ZPE$ at the MP2/aug-cc-pVDZ level. **Figure 4.** Exponential relationships between interatomic distances (Å) and the ρ_{BCP} (a), $\nabla^2 \rho_{BCP}$ (b).

Both of them have only one interaction of O...F. Interaction distance of O-F in N2 heterodimer (3.014 Å) is shorter than that of C1 heterodimer (3.094 Å). This result is in agreement with more binding energy of N2 heterodimer with respect to C1 heterodimer.

In N3 heterodimer, lone pair of N atom of NF₃ monomer attacks terminal nitrogen atom of N₂O (denoted as N...N_t) to form interaction N...N_t with bond length 3.029 Å. Note that N...N_t interaction is observed only in N3 heterodimer of NF₃-N₂O system. Binding energy of this heterodimer is 1.60 kJ/mol at the MP2/aug-cc-pVDZ level.

N4 heterodimer is the least stable heterodimer among all heterodimers obtained in NF₃-N₂O and NF₃-CO₂ systems. This heterodimer is formed when three F-atoms of NF₃ approaches terminal N-atom of N₂O monomer to produce three N_t...F interactions with different bond lengths of 3.306, 3.309 and 3.3015 Å. Results indicate that N_t...F interaction exists only in this heterodimer. As shown in table 2, binding energy of N4 is 0.59 kJ/mol at the MP2/aug-cc-pVDZ level.

In order to evaluate the binding energy (corrected with BSSE and ZPE) of heterodimers obtained in both NF₃-N₂O and NF₃-CO₂ systems, these energies are ranked in figure 3 as N1 > N2 > C1 > N3 > C2 > C3 > N4. It can be seen that the two most dominant heterodimers in terms of binding energy belong to NF₃-N₂O system, N1 and N2. The C1 heterodimer is in the third order. Although, this result acts as deriving force to say that NF₃-N₂O system plays a more important role than NF₃-CO₂ in the atmosphere, energy difference of N1 and C1 heterodimers is only 0.54 kJ/mol at the MP2/aug-cc-pVDZ level. Therefore, it is reasonable to say that atmospheric roles of NF₃-N₂O and NF₃-CO₂ systems are similar. Note that this result is merely obtained with the investigation of binding energies. Therefore, other factors such as the atmospheric concentrations of N₂O and CO₂ species and their reaction with atmosphere molecules may influence this result.

Our results show that energy gaps and binding energies (corrected with BSSE and ZPE) of all heterodimers obtained at the MP2/aug-cc-pVDZ level are in low level of values (weak interaction). Therefore, the calculations of single-point energy have been carried out at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ levels on the optimized geometries of the MP2/aug-cc-pVDZ level. As shown in table 2, ranking of heterodimers at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ levels is similar to that of the MP2/aug-cc-pVDZ level. However, the energy gaps and binding energies (corrected with BSSE) of all heterodimers at the MP2/aug-cc-pVTZ and

CCSD(T)/aug-cc-pVDZ levels are bigger than those of the MP2/aug-cc-pVDZ level. Therefore, the results obtained from the calculations of single-point energy are in good agreement with those of MP2/aug-cc-pVDZ level.

3.3 AIM and NBO analysis

For high quantum bases, atom in molecule is one of the strong implements to analyse interactions. According to the topological analysis of electron density in the theory of AIM, ρ is used to describe the strength of a bond. In general, larger the value of ρ , stronger the bond is. The $\nabla^2\rho$ describes the characteristic of the bond. When $\nabla^2\rho < 0$, the bond is covalent; as $\nabla^2\rho > 0$, the bond is ionic, hydrogen with van der Waals interaction. Here, $\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$, λ_i is an eigenvalue of the Hessian matrix of ρ . Based on the number and sign of the eigenvalues, critical points are classified as bond critical point, BCP (3, -1), ring critical points RCP (3, +1), and cage critical points CCP (3, +3). If one of the three λ_i of critical point is positive and the other two are negative, this critical point is called bond critical point with symbol BCP (3, -1). Bond critical points are located along a maximum electron density trajectory that connects two atoms, known as bond path. In the ring critical point, one of the three λ_i of critical point is negative and the other two are positive which is denoted by RCP (3, +1). Existence of RCP indicates a molecular ring structure. Finally, when all the three λ_i are positive, we denote it by CCP (3, +3) and call it the cage critical point. Existence of CCP shows that the molecule includes cage structure. The $-G_C/V_C$ ratio, being G_C and V_C respectively, the kinetic and potential energy density at BCP, was used to measure covalency in noncovalent intermolecular interactions. Values greater than 1 generally indicate an intermolecular interaction without covalent character while ratios smaller than 1 are indicators of the covalent nature of the interaction.³³ Values of topological parameters (ρ , $\nabla^2\rho$ and $-G_C/V_C$) for each intermolecular BCP in NF₃-CO₂ and NF₃-N₂O systems are given in table 3. Molecular graphs for all heterodimers are also shown in figure 2.

As shown in table 3, ρ values are in the ranges 0.0024–0.0067 and 0.0032–0.0074 au within NF₃-CO₂ and NF₃-N₂O systems, respectively. Therefore, the range of ρ values in NF₃-CO₂ system is very close to that of NF₃-N₂O. It is interesting to know that the biggest ρ values between interacting atoms of NF₃-CO₂ and NF₃-N₂O systems belong to O...F interactions in C1 (0.0067 au) and N2 (0.0074 au). Both C1 and N2 heterodimers include only O...F interaction

between intended monomers. The investigation of values obtained for $\nabla^2\rho$ in the $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems show that all of them are small as well as positive and it should be within the following ranges: 0.0137–0.0334 a.u. for $\text{NF}_3\text{--CO}_2$ system and 0.0154–0.0348 a.u. for $\text{NF}_3\text{--N}_2\text{O}$ system. All values reported for $-G_C/V_C$ ratio of heterodimers in $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems are greater than 1, as shown in table 3. Therefore, the small electron density and positive values of $\nabla^2\rho$ with $-G_C/V_C > 1$ indicate that all intermolecular interactions in the $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems are weak interactions of noncovalent without any covalent characters. Exponential relationships can be obtained between the intermolecular distances and the values of ρ_{BCP} and $\nabla^2\rho_{\text{BCP}}$ (figure 4). Thus, when the intermolecular distance of the interacting atoms decreases, the values of ρ_{BCP} and $\nabla^2\rho_{\text{BCP}}$ increase. Values obtained for R^2 (as regression) quantity are greater than 0.97 supporting accuracy of our results in this project.

The NBO analysis is carried out to determine charge transfer quota in the $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems. Table 4 shows that values of charge transfer between monomers as well as total charge transfer in the $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems are in the range of 0.0000–0.0010 e, except N2 heterodimer. In all heterodimers of $\text{NF}_3\text{--CO}_2$ system, NF_3 monomer acts as electron main donor. In contrast, in N2 and N1 heterodimers of $\text{NF}_3\text{--N}_2\text{O}$ system, NF_3 monomer acts as electron main donor and main acceptor, respectively. Note that N3 and N4 heterodimers include no charge transfers. It is quite interesting that results obtained from dipole momentum (0.37–0.95 Debye) of heterodimers indicate that there is a relationship between dipole momentum and binding energy in $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems except N4 heterodimer. The relationship between dipole momentum and binding energy in $\text{NF}_3\text{--CO}_2$ and $\text{NF}_3\text{--N}_2\text{O}$ systems are inverse and parallel, respectively (except for N4 heterodimer).

4. Conclusion

The data and discussion in the previous sections, lead us to the following major conclusions:

- NF_3 attack on CO_2 monomer leads to formation of three minima, C1, C2 and C5. Their binding energies (corrected with BSSE and ZPE) are in the range of 1.56–1.66 kJ/mol at the MP2/aug-cc-pVDZ level.
- NF_3 attack on N_2O monomer can produce four minima, N1, N2, N3 and N4, on PES. Binding energy range of these heterodimers (cor-

rected with BSSE and ZPE) is between 0.59 and 2.20 kJ/mol at the MP2/aug-cc-pVDZ level.

- Based on the binding energies obtained at the MP2/aug-cc-pVDZ level (corrected with BSSE and ZPE), heterodimers can organize in the order $\text{N1} > \text{N2} > \text{C1} > \text{N3} > \text{C2} > \text{C3} > \text{N4}$. Although, the two most stable dimmers, N1 and N2, belong to the $\text{NF}_3\text{--N}_2\text{O}$ system, energy difference between N1 and C1 heterodimers is only 0.54 kJ/mol at the MP2/aug-cc-pVDZ level. Therefore, we cannot select $\text{NF}_3\text{--N}_2\text{O}$ system as a dominant system. It is reasonable to say that atmospheric roles of $\text{NF}_3\text{--N}_2\text{O}$ and $\text{NF}_3\text{--CO}_2$ systems are similar. Note that this result is merely obtained on the investigation of binding energies. Therefore, other factors such as atmospheric concentrations of N_2O and CO_2 species and their reaction with atmosphere molecules may influence this result.
- N1 and N2 heterodimers of $\text{NF}_3\text{--N}_2\text{O}$ system correspond to C2 and C1 heterodimers of $\text{NF}_3\text{--CO}_2$ system, respectively. Both N1 and N2 heterodimers are more stable than C2 and C1 heterodimers.
- Results obtained from the calculations of single-point energy at the MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVDZ levels are in good agreement with those of MP2/aug-cc-pVDZ level.
- In both $\text{NF}_3\text{--N}_2\text{O}$ and $\text{NF}_3\text{--CO}_2$ systems, we have found all possible interactions between F-atom of NF_3 with N_2O and CO_2 molecules. In contrast, no interactions have been found between N-atom of NF_3 with N_2O and CO_2 molecules, expect N3 heterodimer.
- Based on AIM analysis, the small electron density, positive values of $\nabla^2\rho$ and $-G_C/V_C > 1$ indicate that all intermolecular interactions in $\text{NF}_3\text{--N}_2\text{O}$ and $\text{NF}_3\text{--CO}_2$ systems are weak interactions of noncovalent without any covalent characters.
- Based on NBO analysis, the small values of charge transfer indicate a minor role in stability of dimers.

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