Two and Three-Body Interactions
between CO, H$_2$O, and HClO$_4$

Hosseini, Seyyedeh Marziyeh; Zabardasti, Abedien*+

Department of Chemistry, Faculty of Science, Lorestan University, Khorramabad, I.R. IRAN

ABSTRACT: *Intermolecular interactions of different configurations in the HOClO$_3$···CO and HOClO$_3$···H$_2$O dyad and CO···HOClO$_3$···H$_2$O triad systems have been studied at MP2/6-311++G(2d,2p) computational level. Molecular geometries, binding energies, cooperative energies, many-body interaction energies, and Energy Decomposition Analysis (EDA) were evaluated. The results reveal that the stability of cyclic triads is more than linear ones and in the order IV > III > II > I configurations. All of the triads have diminutive energy. Red shifts of H-O stretching frequency for complexes involving HClO$_4$ as HB-donor are predicted. The electronic properties of the complexes are analysed using parameters derived from the Quantum Theory of Atoms in Molecules (QTAIM) methodology.*

KEYWORDS: *Intermolecular interactions; Cooperative; Diminutive; Many-body interaction energy; EDA; QTAIM.*

INTRODUCTION

Non-covalent interactions play a very important role in materials science, supramolecular chemistry and molecular biology [1-5]. The conventional Hydrogen Bonds (HB) as a non-covalent interaction A-H···B that involve electronegative atoms like oxygen and nitrogen have been thoroughly studied over the decades by experimental methods [1,2]. The chemical phenomenon of hydrogen bonding has also been studied extensively by quantum mechanical ab initio calculations [6-11]. Along with increasing interest to Hydrogen Bonds (HB), halogen bonds (XB) [12-14] are taken into consideration. There are numerous experimental and theoretical studies about the practical and potential applications of halogen bonds in different fields of biochemistry and supramolecular chemistry [15-23].

Based on *Molina* and *Rowland* [24] in 1974 that

chlorine resulted from the photo dissociation of chlorofluorocarbon in the stratosphere is involved in ozone-depleting catalytic cycles. So the attentions were focused on the identifying of important reactions in the stratosphere that involve chlorine species [24]. According to the suggestion by *Simonaitis* and *Heicklen*, [25] perchloric acid (HOClO$_3$) plays a more important sink role for stratospheric chlorine than HCl [25]. On the other hand, CO and H$_2$O are of primary importance in atmospheric chemistry. So, we considered it is appropriate to examine theoretically the different complexes that these systems can be formed together.

In the present study, there is discussed theoretical contribution based on the analysis of structural parameters, vibrational stretching modes and electronic properties of intermolecular model systems formed

by CO, H_2O, and $HOClO_3$. All of the structures were optimized and characterized by frequency computations at the second-order Møller–Plesset perturbation theory (MP2) as one of several quantum chemistry post-Hartree–Fock ab initio methods. This method provides good estimates of geometries and energies for noncovalent complexes with intermediate computational cost [26-28].

The molecules considered in the present article are of primary importance in atmospheric chemistry [24,25,29]. In the other hand, the design of triad structures, including CO and H_2O is interesting because of the large difference in dipole moments of the CO, (experimentally only about 0.12 D, [30] pointing from carbon to oxygen) and H_2O, (1.86 D [31,32] from hydrogen to oxygen). So far, this is the first study which reports the cooperativity and many-body interaction analysis for this designed triad in the all probably configurations.

METHODE OF CALCULATION

The optimized geometries of all structures were performed using by GAUSSIAN 09 system of codes [33]. The energy-decomposition analysis (EDA) was performed using by GAMESS package [34]. The geometries of the isolated $HOClO_3$, CO and H_2O moieties and their complexes were fully optimized at the MP2 computational levels with the 6-311++G(2d,2p) basis set [35]. Frequency calculations were performed at the same computational level in order to confirm that the structures obtained correspond to energy minima. BSSE correction was done by the counterpoise method as the most common way [36].

The AIM2000 package [37] was used to obtain bond electronic properties. The Atoms in Molecules (AIM) theory [37,38] was applied here to analyze the characteristics of the Line Critical Points (LCP) appearing in the studied systems.

RESULTS AND DISCUSSION
Structure and Stretching Frequencies

The optimization structures of different 1:1:1 triad complexes from the association of $HOClO_3$ with H_2O and CO by forming the complexes (I), (II), (III) and (IV) are illustrated in Fig. 1. To understand the properties of the systems better, the corresponding dyads are also studied. It is worth mentioning, all probably configurations have been examined and configurations with positive

frequencies have been reported. Therefore all of the structures are related to the local minimum in the potential energy surfaces.

In Table 1 the frequency shifts of the O-H stretching vibration in the dyads and triads relative to them in the isolated $HOClO_3$ molecule are gathered. As frequency values show hydrogen-bond formation has been led to a red shift in the stretching frequency of OH in $HOClO_3$ when $HOClO_3$ acts as HB donor [39] whereas blue shifts are observed when $HOClO_3$ acts as XB donor (I-$HOClO_3\cdots H_2O$ and II-$HOClO_3\cdots CO$). Interestingly, the stretching frequency of OH in triads is affected by its related dimers. In the cases that both of the dimers have the negative sign for frequency shifts Δv^{str}, the OH bond in relevant trimer finds the larger amount of red shift in comparisons with HB dimer complexes. While if the Δv^{str} values of dimers have opposite signs, the relevant trimer finds the less amount of red shift. Also, based on O-H bond length and its frequency value, a direct comparison of HB strength can be obtained upon complexation. From Table 1, when acidic hydrogen interacts with other monomers directly (I, III, IV-$HOClO_3\cdots CO$ and II-$HOClO_3\cdots H_2O$), the strength of the O-H bond in perchloric acid decreases in comparison with isolated $HOClO_3$. While indirectly interaction leads to increase of frequency, the decrease of HB length and thus increasing the bond strength (II-$HOClO_3\cdots CO$ and I-$HOClO_3\cdots H_2O$). Finally, the HB strength in trimers is influenced by relevant dimers.

An excellent linear correlation [Eq. (1)] was found between the frequency shifts and interaction distances as shown in Fig. 2. Furthermore a good linear relationship [Eq. (2)] between stretching frequency red shifts in O-H bond and density of the intermolecular LCP in HB complexes was found in Fig. 3.

$$\Delta v_{str} = -19815\Delta r + 1.6776 \qquad R^2 = 0.9998 \qquad (1)$$

$$\rho - 7E - 05\Delta v_{str} + 0.0115 \qquad R^2 = 0.9949 \qquad (2)$$

Energy Analysis of the Complexes

The values of the corrected stabilization energies ΔE^C, ($\Delta E_{uncorrected} = E_{supermolecule} - E_{isolated\ monomers}$, $\Delta E^C = \Delta E_{uncorrected} + BSSE$) are listed in Table 2. The energy results reveal that the stabilization of complexes is in the order IV > III > II > I. This trend shows that the stability of cyclic triads is more than linear ones. This finding

Table 1: Variation of bond stretching frequencies (Δvstr, cm-1) and bond length (Δr, Å) of O-H bond upon complexation.

Configuration	Complex					
	HOClO₃···CO		HOClO₃···H₂O		CO···HOClO₃···H₂O	
	Δv^{str}	Δr	Δv^{str}	Δr	Δv^{str}	Δr
I	-10.28	0.0008	2.38	-0.0002	-9.46	0.0008
II	1.59	-0.0002	-472.96	0.0238	-450.77	0.0228
III	-10.02	0.00081	-473.32	0.0240	-518.47	0.0263
IV	-159.29	0.0078	-473.32	0.0240	-606.24	0.0308

v^{str} and r of OH in isolated HOClO₃ are 3736.43 cm-1 and 0.97152 Å respectively.
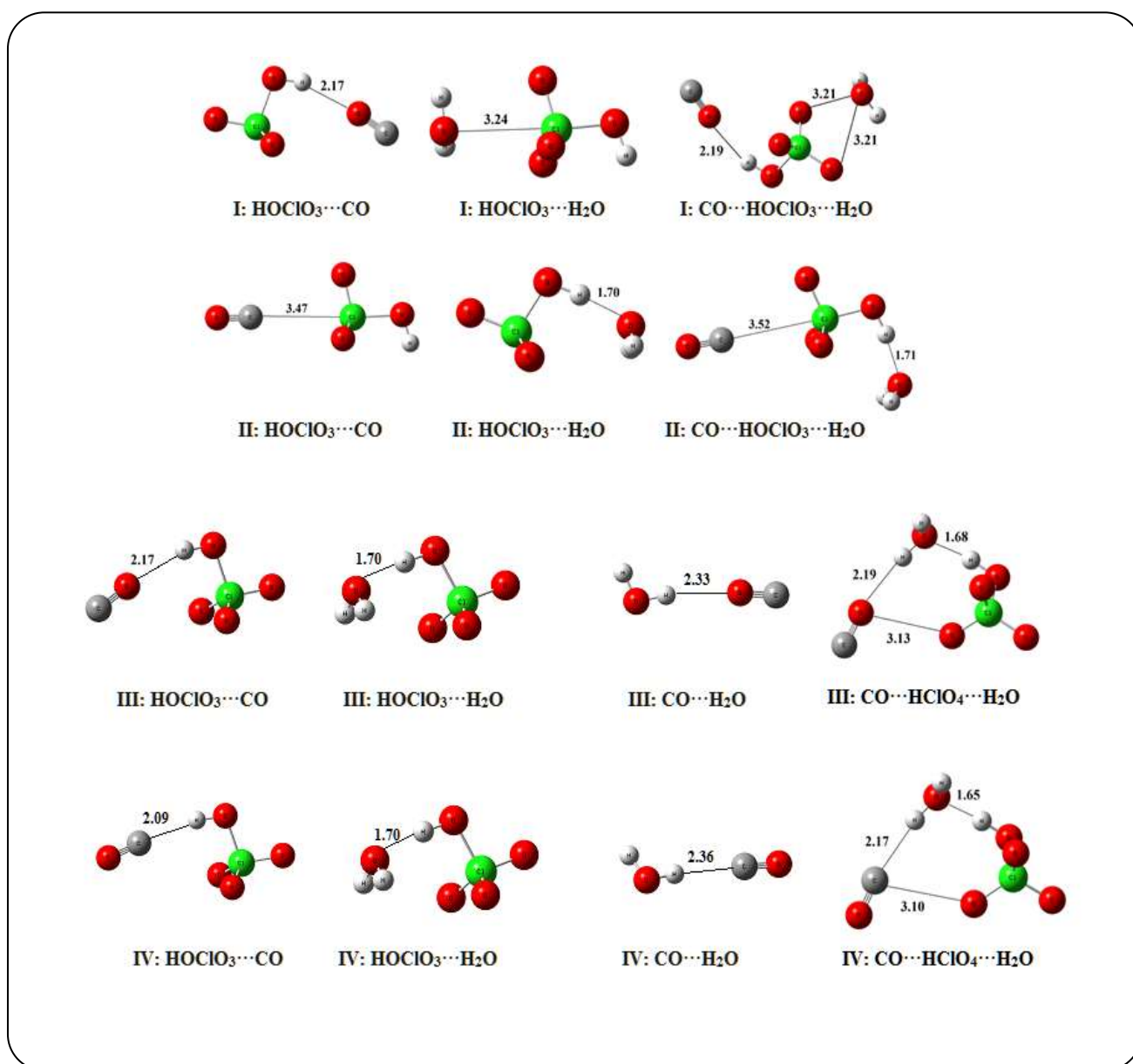

Fig. 1: Optimized geometries of the studied triads in all probably configurations and respective dimers.

***Table 2: Corrected stabilization energy ΔECint (kJ/mol) and cooperative energy values Ecoop in the studied dyads
and triads complexes.***

Complex (A···B···C) CO···HOClO₃···H₂O	ΔE_{AB}	ΔE_{BC}	ΔE_{AC}	ΔE_{ABC}	ΔE^{*}_{AC}	E_{coop}
configuration I	-5.73	-5.29	–	-11.00	-0.10	0.12
configuration II	-2.65	-41.16	–	-42.77	-0.12	1.16
configuration III	-5.73	-41.16	-2.33	-46.60	–	2.62
configuration IV	-17.15	-41.16	-6.63	-55.11	–	9.83

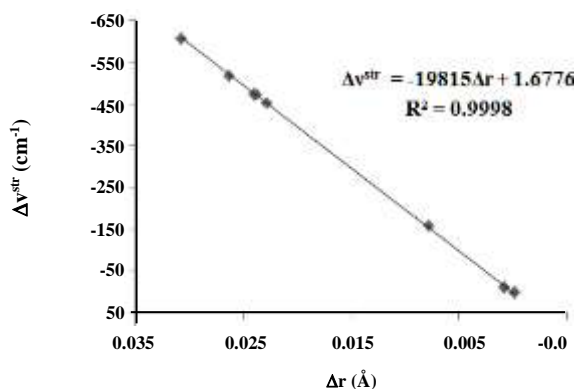*ΔE*: The values obtained from dyads frozen in the geometry of the triads.*

Fig. 2: Correlation between stretching frequency shifts and distances in all interactions of all studied complexes.

Fig. 3: Correlation between electron densities of the intermolecular LCP in HB complexes and stretching frequency red shifts in O-H bond.

is to be expected because the cyclic ones have one more intermolecular contact. But the interesting point is the high amount of stabilization energy (-42.77 kJ/mol) in configuration II that it is closeness to the trimer number III (-46.60 kJ/mol) although its structure is linear. This means that the nature of atoms involved in the interactions is a determinant factor in addition to the linear or cyclic shape of the structure. With comparisons of the energy values, it was well understood that difference in energy values, depends on the interaction site of the CO donor species, O side or C side, and monomers position in addition to the number of interactions. As can be seen, AB (CO···HOClO₃) dimers have the most stability when perchloric acid and carbon act as HB donors and acceptor, respectively (configuration IV). As the same way, when oxygen acts as HB acceptor the stabilization energy gets lower values (configurations I and III). This finding is in agreement with previous theoretical results for the complexes of carbon monoxide with hypohalous acids [6]. Finally,
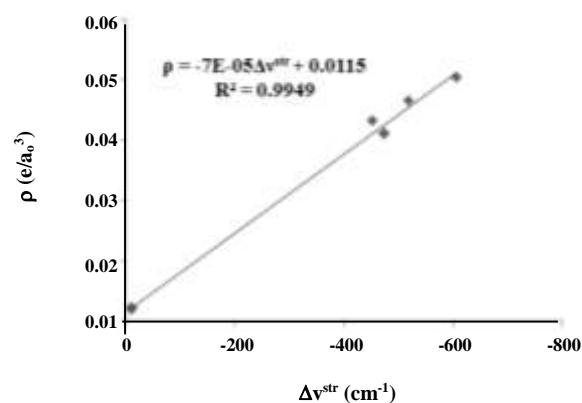
the lowest stabilization energy value of dimers is related to configuration II that perchloric acid acts as an XB donor. With similar comparisons in the case of BC dimers (HOClO₃···H₂O), there are considerable energy differences depending on the HOClO₃ role. Actually when HOClO₃ acts as HB donor the energy value is -41.16 kJ mol⁻¹ while its value decreases to -5.29 with the change of role from HB to XB donor.

In general, from these results can be concluded that more significant differences in the stabilization energy are related to the type of coordination, HB, XB, or van der Waals vdW. The HB complexes are the most stable minima, and vdW complexes are the least.

An energetic cooperativity parameter was calculated using Eq. (3) and Eq. (4) for linear and cyclic triads respectively.

$$E_{coop} = \Delta E^{C}_{ABC} - \Delta E^{C}_{AB} - \Delta E^{C}_{BC} - \Delta E^{C*}_{AC} \qquad (3)$$

$$E_{coop} = \Delta E^{C}_{ABC} - \sum \Delta E^{C}_{dimmers} \qquad (4)$$

Research Article

Table 3: Decomposition of stabilization energy [kJ/mol] of the studied triads using the geometry within the triads.

CO···HOClO$_3$···H$_2$O (A···B···C)	$\Delta E^2_{A\text{-}B}$	$\Delta E^2_{B\text{-}C}$	$\Delta E^2_{A\text{-}C}$	$\Delta E^3_{A\text{-}B\text{-}C}$	E$_S$
configuration I	-5.69	-5.34	-0.10	-0.01	0.14
configuration II	0.97	-44.40	-0.12	-2.47	3.25
configuration III	-1.80	-45.43	-1.47	-2.27	4.38
configuration IV	-3.97	-46.04	-5.11	-5.62	5.62

Where $\Delta E^{C^*}_{AC}$ term is the interaction energy of AC dimer frozen in the geometry of the triad.

In the studied CO···HOClO$_3$···H$_2$O complex, diminutive effects are observed in all configurations with values as shown in Table 2. As shown as results no significant correlation found between the cooperative values and stabilities. Indeed the cooperativity and anti-cooperativity effects are mainly attributed to the charge transfer [40].

Many-Body Interaction Analysis

The results in Table 2 described that CO···HOClO$_3$···H$_2$O in geometry IV and geometry I have maximum and minimum stabilization energy among studied complexes respectively.

As seen in Table 3 the main contribution of stabilization energy except for the cases of geometry I is obtained by the two-body interaction $\Delta E^2_{B\text{-}C}$. This means that the OClO$_3$H:OH$_2$ interaction contributes more to the stabilization energy of triads than other present interactions.

In the all studied systems the two-body $\Delta E^2_{A\text{-}B}$, $\Delta E^2_{B\text{-}C}$, $\Delta E^2_{A\text{-}C}$, and three-body $\Delta E^3_{A\text{-}B\text{-}C}$ interactions have negative (attractive) values. The only case of two-body with the positive value is $\Delta E^2_{A\text{-}B}$ in configuration II that contributes to HO$_4$Cl:CO interaction.

The strain energy (E$_S$) can be defined as a measure of the degree of strain that drives the distortion of the ternary system. Equation (5) describes how to calculate the E$_S$. As seen in Eq. (5), E$_S$ calculate by the sum of the monomers energies froze in the geometry of the triads minus sum of the optimized monomers energies.

$$E_S = \left(E_A + E_B + E_C\right)_T - \left(E_A + E_B + E_C\right) \qquad (5)$$

So, the total binding energy of the triad is obtained using Eq. (6):

$$\Delta E^C_{ABC} = \Delta E^2_{A-B} + \Delta E^2_{B-C} + \Delta E^2_{A-C} + \Delta E^3_{A-B-C} + E_S \quad (6)$$

According to values in Table 3, the strain energy is positive, that it makes a destabilizing contribution to the total stabilization energy of the triads.

Energy decomposition analysis

The Energy-Decomposition Analysis (EDA) was performed to obtain insight into the source of the interaction energy using Eq. (7) [41].

$$E_{int} = E_{elst} + E_{exch-rep} + E_{pol} + E_{disp} \qquad (7)$$

E$_{elst}$, E$_{exch-rep}$, E$_{pol}$ and E$_{disp}$ correspond to electrostatic, exchange-repulsion, polarization and dispersion terms respectively.

Table 4 lists the energy decomposition analysis results for perchloric acid complexes. The results reveal that electrostatic effects make the main contribution to the interaction energies (48.19% - 74.33%). This reveals that electrostatic interactions are essentially responsible for the stability of all studied complexes. Based on the energy decomposition results for dimers it is apparent that the polarization component in complexes with the presence of hydrogen bonding interactions represents more values in comparison with the rest complexes. Also, the electrostatic term for CO···HOClO$_3$ dimers shows larger values in configurations with oxygen interaction side (configuration I and III) of the CO than carbon interaction side (configuration II and IV).

Electron Density Analysis

Table 5, lists the results of the QTAIM topological parameters, as electronic density (ρ), Laplacian (∇^2) and the ratios between the kinetic (G) and potential (V) electron energy.

The topological analysis of the electron density displays the presence of intermolecular line critical point (LCP) in all of the complexes, HB, XB, and vdW.

In all cases, these LCPs show small values of the electron density and small positive Laplacians,

Table 4: EDA of perchloric acid complexes in kJ/mol.

complex	E_{elst}	$E_{exch-rep}$	E_{pol}	E_{disp}	E_{MP2}
$CO \cdots HOClO_3$ (I)	-12.68 (71.32%)	11.05	-5.10 (28.68%)	0.92	-5.82
$HOClO_3 \cdots H_2O$ (I)	-14.18 (74.01%)	13.64	-1.72 (8.98%)	-3.26 (17.01%)	-5.48
$CO \cdots HOClO_3 \cdots H_2O$ (I)	-25.31 (74.33%)	22.93	-6.36 (18.68%)	-2.38 (6.99%)	-11.13
$CO \cdots HOClO_3$ (II)	-6.57 (54.93%)	9.25	-0.75 (6.27%)	-4.64 (38.80%)	-2.68
$HOClO_3 \cdots H_2O$ (II)	-82.26 (69.40%)	73.51	-35.06 (29.58%)	-1.21 (1.02%)	-45.02
$CO \cdots HOClO_3 \cdots H_2O$ (II)	-86.69 (68.61%)	80.37	-34.48 (27.29%)	-5.19 (4.11%)	-46.02
$CO \cdots HOClO_3$ (III)	-12.59 (71.66%)	10.92	-4.98 (28.34%)	0.88	-5.77
$HOClO_3 \cdots H_2O$ (III, IV)	-82.42 (69.37%)	73.81	-35.23 (29.65%)	-1.17 (0.98%)	-45.02
$CO \cdots HOClO_3$ (IV)	-24.52 (48.19%)	33.01	-14.56 (28.62%)	-11.80 (23.19%)	-17.87
$CO \cdots HOClO_3 \cdots H_2O$ (III)	-93.93 (67.76%)	87.61	-42.43 (30.61%)	-2.26 (1.63%)	-51.00
$CO \cdots HOClO_3 \cdots H_2O$ (IV)	-106.57 (61.69%)	111.96	-53.01 (30.68%)	-13.18 (7.63%)	-60.75

Table 5: Computed values of the QTAIM topological parameters at the LCP.

complex	configuration	interaction	Interaction distance	ρ	∇^2	G/|V|	|V|/G
$HOClO_3 \cdots CO$	I	$OClO_3H:OC$	2.17	0.0123	0.0509	1.22	0.82
$HOClO_3 \cdots H_2O$	I	$HO_4Cl:OH_2$	3.24	0.0075	0.0328	1.24	0.81
$CO \cdots HOClO_3 \cdots H_2O$	I	$O_3ClOH:OC$	2.19	0.0119	0.0490	1.23	0.81
$CO \cdots HOClO_3 \cdots H_2O$	I	$HClO_3O:OH_2$	3.21	0.0067	0.0264	1.22	0.82
$CO \cdots HOClO_3 \cdots H_2O$	I	$HClO_3O: OH_2$	3.21	0.0066	0.0266	1.24	0.81
$HOClO_3 \cdots CO$	II	$HO_4Cl:CO$	3.47	0.0045	0.0224	1.59	0.63
$HOClO_3 \cdots H_2O$	II	$O_3ClOH:OH_2$	1.70	0.0411	0.1319	0.94	1.06
$CO \cdots HOClO_3 \cdots H_2O$	II	$HO_4Cl :CO$	3.52	0.0046	0.0209	1.59	0.63
$CO \cdots HOClO_3 \cdots H_2O$	II	$O_3ClOH :OH_2$	1.71	0.0433	0.1212	0.89	1.12
$HOClO_3 \cdots CO$	III	$O_3ClOH:OC$	2.18	0.0121	0.0500	1.22	0.82
$HOClO_3 \cdots H_2O$	III, IV	$O_3ClOH:OH_2$	1.70	0.0413	0.1323	0.94	1.06
$CO \cdots HOClO_3 \cdots H_2O$	III	$O_3ClOH:OH_2$	1.68	0.0465	0.1257	0.87	1.15
$CO \cdots HOClO_3 \cdots H_2O$	III	$CO:HOH$	2.19	0.0109	0.0469	1.26	0.79
$CO \cdots HOClO_3 \cdots H_2O$	III	$HClO_3O:OC$	3.13	0.0049	0.0186	1.15	0.87
$HOClO_3 \cdots CO$	IV	$O_3ClOH:CO$	2.09	0.0224	0.0600	1.00	1.00
$CO \cdots HOClO_3 \cdots H_2O$	IV	$OClO_3H:OH_2$	1.65	0.0504	0.1300	0.85	1.18
$CO \cdots HOClO_3 \cdots H_2O$	IV	$OC:HOH$	2.17	0.0180	0.0539	1.09	0.92
$CO \cdots HOClO_3 \cdots H_2O$	IV	$HClO_3O:CO$	3.10	0.0062	0.0209	1.23	0.81

Values of ρ and $\nabla^2 \rho$ are given in $e.a_o^{-3}$ and $e.a_o^{-5}$, respectively.
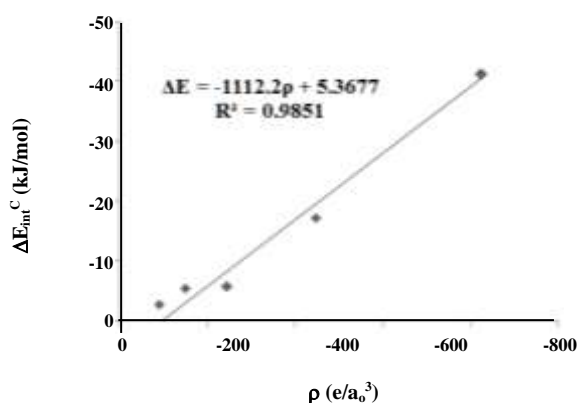
Research Article

Fig. 4: Correlation between electron densities of the LCP in dimer complexes and stabilizaton energy.

an indication of the closed-shell characteristics of the interaction, similar to those found in weak interactions [42-47]. Furthermore, with the comparison of dimer complexes, a good linear correlation was found between electron density of LCPs and stabilization energy showing in Fig. 4 and Eq. (8). This represents that more stable complexes have larger values of electron density.

$$\Delta E = -1112.2\rho + 5.3677 \qquad R^2 = 0.9851 \qquad (8)$$

The G/|V| value is indicating interaction nature as covalent or non-covalent [48]. The G/|V| values are higher than 1, between 1 and 0.5 and lower than 0.5 indicating interaction with non-covalent, partial covalent and covalent characteristics, respectively. So the values in Table 5 illustrate that OClO₃H:OC and O₃ClOH:OH₂ interactions are non-covalent and partial covalent interactions, respectively.

On the other hand |V|/G ratio exhibits the electrostatic characteristic. So that, interactions which have the values of |V|/G ratio in about |Vb|/Gb < 1 and 1 < |Vb|/Gb < 2 exhibit dominant electrostatic and partially covalent-electrostatic properties, respectively [49]. According to the data, the electrostatic properties are dominant in the studied complexes which are in line with energy decomposition analysis results.

CONCLUSIONS

Theoretical study of the 1:1 HOClO₃···CO and HOClO₃···H₂O dyad complexes as well as 1:1:1 H₂O···HOClO₃···CO triad complex was investigated

by quantum chemical calculations at the MP2/6-311++G(2d,2p) level. The triad systems were located in 4 configurations, 2 linear and 2 cyclic.

The vibrational analysis of the studied complexes revealed that HB formation has been led to a red shift in the stretching frequency of the O-H in the perchloric acid molecule. The positive values of E_coop indicate diminutive effects in all studied complexes.

Many body analyses indicated that HOClO₃···H₂O interaction contributes more to the stabilization energy of triads than other present interactions.

Based on the Energy Decomposition Analysis (EDA), it can be seen that the electrostatic interactions are essentially responsible for the stability of all studied complexes.

We hope that the results of the present study could be useful for understanding the diminutive and competitive role of hydrogen and halogen bonding in biological systems, molecular recognizing and crystal engineering.

REFERENCES

[1] Desiraju G., Steiner T, "The Weak Hydrogen Bond: In Structural Chemistry and Biology", Oxford University Press, Oxford (1999).

[2] Jeffrey G.A., "An Introduction to Hydrogen Bonding", Oxford University Press, New York (1997).

[3] Scheiner S., "Molecular Interactions: From van der Waals to Strongly Bound Complexes", John Wiley & Sons, Inc., Chichester, UK (1997).

[4] Gilli G., Gilli P., "The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory", Oxford University Press, New York (2009).

[5] Grabowski S. J., "Hydrogen Bonding: New Insights", Springer, The Netherlands (2006).

[6] Blanco F., Alkorta I., Solimannejad M., Elguero J., Theoretical Study of the 1:1 Complexes between Carbon Monoxide and Hypohalous Acids, *The Journal of Physical Chemistry A (J. Phys. Chem. A.),* **113** (13): 3237–3244 (2009).

[7] Rozas I., On the Nature of Hydrogen Bonds: An Overview on Computational Studies and a Word About Patterns, *Physical Chemistry Chemical Physics* (*Phys. Chem. Chem. Phys.*), **9**(22): 2782-2790 (2007).

[8]   Albernaz A. F., Aquilanti V, R. P. Barreto P., Caglioti C., Claudia P. S. Cruz A., Grossi G., Lombardi A., Palazzetti F., Interactions of Hydrogen Molecules with Halogen-Containing Diatomics from Ab Initio Calculations: Spherical-Harmonics Representation and Characterization of the Intermolecular Potentials *The Journal of Physical Chemistry A* (*J. Phys. Chem. A*.), **120**(27): 5315–5324 (2016).

[9]   Li Q., Lin Q., Li W., Cheng J., Gong B., Sun J. , Cooperativity between the Halogen Bond and the Hydrogen Bond in $H_3N\cdots XY\cdots HF$ Complexes (X, Y=F, Cl, Br), (*ChemPhysChem*), **9**(15):2265–2269 (2008).

[10] Zhao G.M., Liu Y.C., Shi W.J., Chai T., Qin Sh.D., A Theoretical Investigation into the Cooperativity Effect Involving Anionic Hydrogen Bond, Thermodynamic Property and Aromaticity in $Cl^-\cdots$benzonitrile$\cdots H_2O$ Ternary Complex, *Computational and Theoretical Chemistry* (*Comp. Theor. Chem.*), **1035**: 76-83 (2014).

[11] Hobza P., Havlas Z., Blue-Shifting Hydrogen Bonds, *Chemical Reviews* (*Chem. Rev.*), **100** (11): 4253-4264 (2000).

[12] Jabłoński M., Palusiak M., Nature of a Hydride–Halogen Bond. A SAPT-, QTAIM-, and NBO-Based Study, *The Journal of Physical Chemistry A* (*J. Phys. Chem. A*.), **116**(9): 2322-2332 (2012).

[13] Lipkowski P., Grabowski S.J., Leszczynski J., Properties of the Halogen−Hydride Interaction: An ab Initio and "Atoms in Molecules" Analysis, *The Journal of Physical Chemistry A (J. Phys. Chem. A.)*, **110**(34): 10296-10302 (2006).

[14] Solimannejad M., Hosseini S. M., Zabardasti A., Cooperative and Diminutive Interplay between Halogen, Hydride and Cation-σ Interactions, *Physical Chemistry Research* (*Phys. Chem. Res.*), **4**(4): 583-589 (2016).

[15] Solimannejad M., Rezaei Z., Esrafili M. D., Interplay and Competition between the Lithium Bonding and Halogen Bonding: $R_3C\cdots XCN\cdots LiCN$ and $R_3C\cdots LiCN\cdots XCN$ as a Working Model (R = H, CH_3; X = Cl, Br), *Molecular Physics (Mol. Phys.)*, **112**(13): 1783-1788 (2014).

[16] Auffinger P., Hays F. A., Westhof E., Shing Ho P., Halogen Bonds in Biological Molecules, *National Acad Sciences* (*Acad. Sci. U. S. A.*), **101**(48):16789-16794 (2004).

[17] Hardegger L. A., KuhnL A., Spinnler B., Anselm B., Ecabert L., Stihle R., Gsell M., Thoma B., Diez R., Benz J., Plancher J., Hartmann J. M., Banner G., Haap D. W., Diederich W., Systematic Investigation of Halogen Bonding in Protein–Ligand Interactions, (*Angew. Chem. Int. Ed.*), **50**(1): 314-318 (2011).

[18] Metrangolo P., Resnati G., Halogen Bonding: A Paradigm in Supramolecular Chemistry, *Chemistry: A European Journa* (*Chem. Eur. J.*), **7**(12):2 511-2519 (2001).

[19] Solimannejad M., Orojloo M., Amani S., Effect of Cooperativity in Lithium Bonding on the Strength of Halogen Bonding and Tetrel Bonding: $(LiCN)_n\cdots ClYF_3$ and $(LiCN)_n\cdots YF_3Cl$ (Y = C, Si and n = 1-5) Complexes as a Working Model, *Journal of Molecular Modeling* (*J. Mol. Model.*), **21**: (7)183 (2015).

[20] Solimannejad M., Bayatmanesh E., Esrafili M. D., Interplay Between Lithium Bonding and Halogen Bonding in $F_3CX\bullet\bullet\bullet YLi\bullet\bullet\bullet NCCN$ and $F_3CX\bullet\bullet\bullet NCCN\bullet\bullet\bullet LiY$ Complexes (X = Cl, Br; Y = CN, NC), *Physical Chemistry Research (Phys. Chem. Res.)*, **2**(2):171-178 (2014).

[21] Solimannejad M., Malekani M., Alkorta I., Substituent Effects on the Cooperativity of Halogen Bonding, *The Journal of Physical Chemistry A (J. Phys. Chem. A.)*, **117**(26):5551-5557 (2013).

[22] Solimannejad M., Malekani M., Cooperative and Diminutive Interplay between the Hydrogen Bonding and Halogen Bonding in Ternary Complexes of HCCX (X = Cl, Br) with HCN and HNC, *Computational and Theoretical Chemistry (Comp. Theor. Chem.)*, **998**: 34-38 (2012).

[23] Solimannejad M., Malekani M., Alkorta I, Cooperativity between the Hydrogen Bonding and Halogen Bonding in F3CX ··· NCH(CNH) ··· NCH(CNH) Complexes (X=Cl, Br), *Molecular Physics (Mol. Phys.),* **109**: (13)1641-1648 (2011).

[24] Molina M. J., Rowland F. S., Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom-Catalysed Destruction of Ozone, (*Nature*), **249**: 810-812 (1974).

[25] Francisco J. S., Ab Initio Characterization of $HOClO_3$ and HO_4Cl: Implications for Atmospheric Chemistry, *The Journal of Physical Chemistry (J. Phys. Chem.)*, **99**(36): 13422-13425 (1995).

[26] Riley K. E., Hobza P., Assessment of the MP2 Method, Along with Several Basis Sets, for the Computation of Interaction Energies of Biologically Relevant Hydrogen Bonded and Dispersion Bound Complexes, *The Journal of Physical Chemistry A* (*J. Phys. Chem. A.)* **111**: (33) 8257-8263 (2007).

[27] Sponer J., Leszczynski J., Hobza P., Hydrogen Bonding, Stacking and Cation Binding of DNA Bases, *Journal of Molecular Structure: THEOCHEM*, **573**:(1-3) 43-53 (2001).

[28] Riley K. E., Pitonak M., Cerny J., Hobza P., On the Structure and Geometry of Biomolecular Binding Motifs (Hydrogen-Bonding, Stacking, X−H···π): WFT and DFT Calculations, *Journal of Chemical Theory and Computation, J. Chem. Theory Comput.*, **6**(1): 66-80 (2010).

[29] Simonaitis R., Heicklen J., Perchloric Acid: A Possible Sink for Stratospheric Chlorine, *Planetary and Space Science (Planet. Space Sci.)*, **23**(11): 1567-1569 (1975).

[30] Harrison J.F., Relationship between the Charge Distribution and Dipole Moment Functions of CO and the Related Molecules CS, SiO, and SiS, *The Journal of Physical Chemistry A (J. Phys. Chem. A.)*, **110** (37): 10848-10857 (2006).

[31] Dyer P. J., Hydrogen Bonding and Induced Dipole Moments in Water: Predictions from the Gaussian Charge Polarizable Model and Car-Parrinello Molecular Dynamics, Cummings P. T. *The Journal of Chemical Physics (J. Chem. Phys.)*, **125**(14): 144519 (2006).

[32] Bucher D., Kuyucak S., Polarization of Water in the First Hydration Shell of K⁺ and Ca²⁺ Ions, *The Journal of Physical Chemistry B (J. Phys. Chem. B.)*, **112**(35): 10786-10790 (2008).

[33] Frisch M.,Trucks G., Schlegel H., Scuseria G., Robb M., Cheeseman J., Montgomery Jr. J., Vreven T., Kudin K., Burant J., Pittsburgh P. A., Pople J. A., (2009) Gaussian 09, Revision A02. Gaussian Inc., Wallingford.

[34] Schmidt M. W., Baldridge K. K., Boatz J. A., Elbert S., Gordon M. S., Jensen J. H., Koseki S., Matsunaga N., Nguyen K. A., Su S. J., Windus T. L., Dupuis M., Montgomery J. A., General Atomic and Molecular Electronic Structure System, *Journal of Computational Chemistry (J. Comput. Chem.)*, **14**: 1347-1363 (1993).

[35] Frisch M.J., Pople J.A., Binkley J.S., Self-Consistent Molecular Orbital Methods 25. Supplementary Functions for Gaussian Basis Sets, *The Journal of Chemical Physics (J. Chem. Phys.)*, **80**(7): 3265 (1984).

[36] Boys S. F., Bernardi F. D., The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors, *Molecular Physics* (*Mol. Phys.)*, **19**(4): 553-566 (1970).

[37] Bader R. F. W., "Atoms in Molecules: A Quantum Theory", Oxford University Press, Oxford (1990).

[38] Popelier P.L.A., "Chemical Modelling: Applications and Theory, Atoms in Molecules, Introduction", Pearson Education Limited, Prentice Hall, London, England (2000).

[39] Gu Q. Y., Lou S. C., "Table of Chemical Materials", Jiangsu Science and Technology Press: Jiangsu, China (1998).

[40] Glendening E. D., Natural Energy Decomposition Analysis: Extension to Density Functional Methods and Analysis of Cooperative Effects in Water Clusters, *The Journal of Physical Chemistry A* (*J. Phys. Chem. A.)*, **109** (51): 11936-11940 (2005).

[41] Su P., Li H., Energy decomposition analysis of covalent bonds and intermolecular interactions, *The Journal of Chemical Physics (J. Chem. Phys.)*, **131**(1):014102 (2009).

[42] Alkorta I., Elguero J., Non-conventional Hydrogen bonds, *Chemical Society Reviews (J. Chem. Soc. ReV.)*, **27**(2): 163-170 (1998).

[43] Bone R. G. A., Bader R. F. W., Identifying and Analyzing Intermolecular Bonding Interactions in van der Waals Molecules, *The Journal of Physical Chemistry* (J. *Phys. Chem.)* **100**(26): 10892-10911 (1996).

[44] Rozas I., Alkorta I., Elguero J., Behavior of Ylides Containing N, O, and C Atoms as Hydrogen Bond Acceptors, *Journal of the American Chemical Society* (*J. Am. Chem. Soc.)* **122**: 11154-11161 (2000).