



**THE ELECTRONIC STRUCTURE OF THE C<sub>2</sub>H<sub>3</sub>Cl···HX (X = Cl,  
CN, NC AND CCH) VINYLCHLORIDE COMPLEXES  
EVALUATED VIA TOPOLOGICAL PARAMETERS AND DFT  
CALCULATIONS**

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**Abstract**

The optimized geometries of the C<sub>2</sub>H<sub>3</sub>Cl···HX vinylchloride complexes with X = Cl, CN, NC and CCH were obtained at B3LYP/6-311++G(d,p) level of theory. In a first analysis, the (Cl···HX) hydrogen bonds were examined by taking into account their distances, intermolecular interaction energies and CHELPG charge transfer, as well as charge densities obtained through the calculations of theory of Atoms In Molecules (AIM). Moreover, a (X···H) secondary interaction between the hydrogen atoms of vinylchloride and fluorine of HF, nitrogen of both HCN and HNC molecules, and  $\pi$  bond of HCCH was also a target of investigation. This secondary interaction was studied not only in terms of topological criteria or by results of structural and electronic parameters, but it was also analyzed the stretch modes in the infrared spectrum. At last, as far as the vibrational red-shifts of the HX molecules were characterized, the stretch frequencies and absorption intensities of the (X···H) secondary interactions were also identified, but only for the C<sub>2</sub>H<sub>3</sub>Cl···HCCH complex.

## Resumen

Las geometrías del  $C_2H_3Cl \cdots HX$  vinylchloride complejos con  $X = Cl, CN, NC$  y  $CCH$  fueron obtenidas en el nivel de teoría B3LYP/6-311++G(d,p). En un primer análisis, el ligaciones de hidrógeno ( $Cl \cdots HX$ ) fueron examinadas teniendo en cuenta sus distancias, energías de interacción intermoleculares y transferencia de carga CHELPG, así como las densidad de electróns obtenidas por los cálculos de la teoría de Atoms in Molecules (AIM). Además, una interacción secundaria ( $X \cdots H$ ) entre los átomos de hidrógeno de vinylchloride y el flúor de HF, nitrógeno de HCN como de las moléculas de HNC, y la ligacion  $\pi$  de HCCH fueron también un objetivo de investigación. Esta interacción secundaria fue estudiada no sólo en términos de criterios topológicos o por resultados de parámetros estructurales y electrónicos, pero también fue analizado los modos de extensión en el espectro infrarrojo. Por fin, por lo que los cambios rojos vibrational de las moléculas HX fueron caracterizados, las frecuencias y intensidades de absorción del las interacciones secundarias ( $X \cdots H$ ) también fueron identificadas, pero sólo para el complejo  $C_2H_3Cl \cdots HCCH$ .

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## Introduction

Nowadays, it has been manifested a great interest by studies of non-covalent intermolecular phenomena, in which the hydrogen bonding is one of the most important types because there is a large number of biological, physical and chemical systems formed through the interaction between a proton donor and a rich charge density site. One important charge density center is the halide species, which in some situations interacts with hydrocarbons and produces the halide hydrocarbons. As example, vinylhalide or more specifically vinylchloride ( $C_2H_3Cl$ ), which is a chloride hydrocarbon containing a carbon-carbon double bond formed by attack of hydrochloric acid to acetylene [1-2], properly the formation of  $C_2H_3Cl$  is ruled by the interaction of the hydrochloride acid aligned with  $\pi$  bond of acetylene, what leads at formation of an intermolecular system characterized by a typical ( $\pi \cdots H$ ) interaction [3]. After this, other hydrochloride acid molecule interacts with the n lone electron pair (Cl) of vinylchloride and thereby a ( $n \cdots H$ ) hydrogen bond is formed [4].

Some years ago, geometries and related parameters of  $\pi$  intermolecular systems formed by acetylene and proton donors have been detailed studied [3]. Recently, coexistence of theoretical and experimental observations about the electronic structures of the  $C_2H_3Cl \cdots HCl$  and  $C_2H_3Cl \cdots HF$  complexes has been reported by Herrebout and van der Veken [5-7]. Experimentally, by using the pulsed-nozzle Fourier Transform Microwave Spectroscopy (FTMS) [8], Legon and co-workers have documented several studies about the equilibrium geometry of hydrogen complexes constituted by vinylhalide and monoprotic acids [9-11]. From these works, it has been established that the interaction between vinylhalide ( $Y = Cl$  or  $F$ ) and acid species ( $HX$ ) are characterized by a distortion on its ( $Y \cdots HX$ ) hydrogen bonds, as already observed in other hydrogen-bonded species [12]. Specifically, the ( $Y \cdots HX$ ) hydrogen bond is non-linear because is supposed the formation of a secondary interaction between the halogen and hydrogen atom of vinylhalide. For  $C_2H_3Cl \cdots HCl$  and  $C_2H_3F \cdots HF$  complexes, in fact this secondary interaction is based on experimental evidences, which says that Cl and F interacts with the H atom ( $=CH_2$  group) of the  $C_2H_3Cl$  and  $C_2H_3F$  molecules, respectively [11]. By taking into account the  $C_2H_3Cl \cdots HX$  with  $X = Cl, CN, NC$  and  $CCH$  set of complexes, however, we alert the importance for studying the nature of the secondary interaction in these systems. In practice, we expect to obtain theoretical informations that corroborates with the FTMS experimental results, as well as lead us to predict new insights about this interaction phenomenon.

### Computational strategy

However, by projecting a theoretical study of the  $C_2H_3Cl \cdots HX$  vinylchloride complexes and their hydrogen bonds and secondary interactions, we should mention that a quantumchemical description of charge density and molecular topology seems to be essential. The objective of determination and evaluation of molecular surface parameters from charge density can be naturally associated to theory of Atoms in Molecules (AIM) [13] of Bader. In this work, the contribution of AIM calculations will be performed by localization of Bond Critical Points (BCP) between chloride of vinylchloride and hydrogen atom of acid species, as well as if possible between Cl, CN, NC and CCH groups and hydrogen atoms of the vinylchloride, what properly characterizes the  $(Cl \cdots X)$  hydrogen bonds and  $(X \cdots H)$  secondary interactions, respectively. In this insight, we would like to emphasize that the choice of computational method must be evaluated critically. As well-known, the addition studies of hydrogen halides to alkenes [14] have been effectuated successfully by using the Density Functional Theory (DFT) [15]. In terms of DFT calculations, the B3LYP [16] hybrid was chosen because a lot of hydrogen-bonded systems have been successfully studied through this popular functional [17-23]. For *ab initio* basis sets, during all these years the choice for split-valence and/or correlation consistent types still yields intense discussion among the theoreticians. Thereby, we admit some traditional concepts, i.e., the description of “heavy” (C, N and Cl) and “soft” (H) atoms will be developed through the application of “d” and “p” polarization functions within the 6-31G Pople’s split-valence wave function. Fundamentally, the inclusion of diffuse functions (++) is also important, mainly for BSSE correction.

### Theoretical procedure

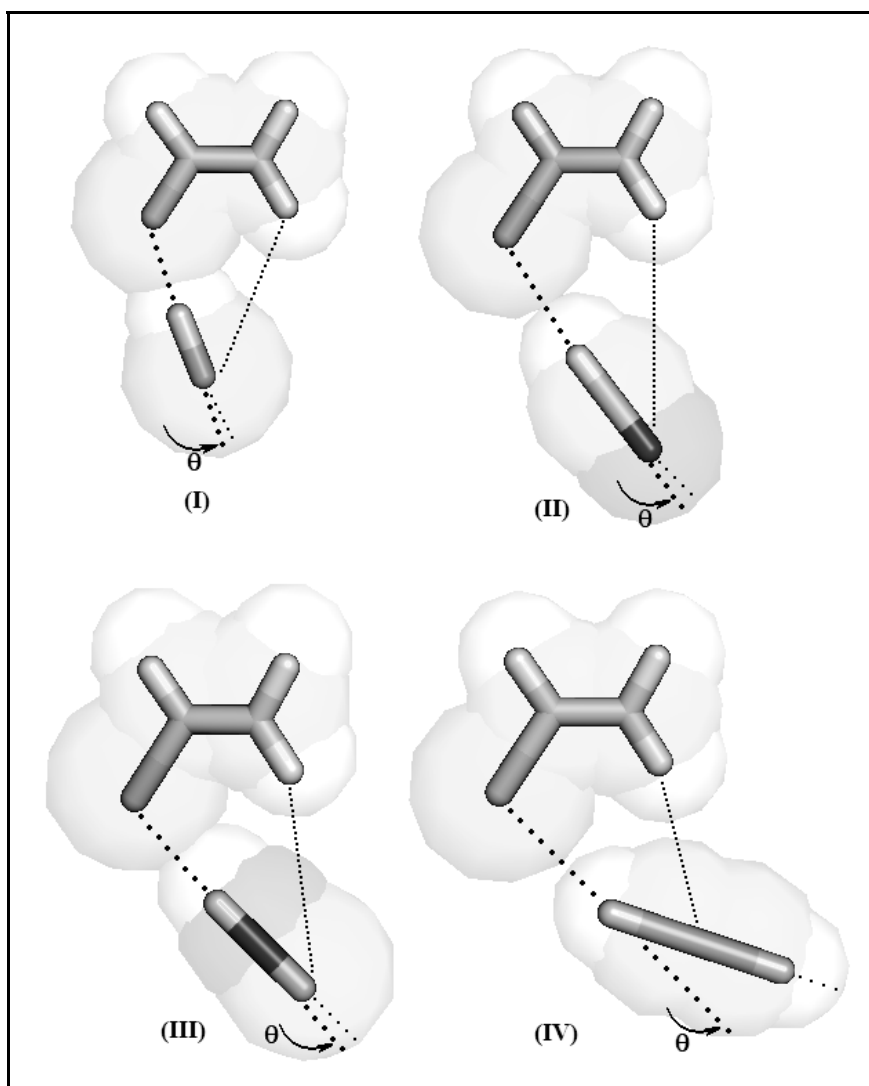
The optimized geometries of the  $C_2H_3Cl \cdots HX$  with  $X = Cl, CN, NC$  and CCH vinylchloride complexes were processed by using the GAUSSIAN 98W program [24] through the execution of the B3LYP/6-311++G(d,p) calculations. Through the GAUSSIAN 98W, it was calculated the CHELPG atomic charges [16]. The  $\Delta Q^{CHELPG}$  quantities were determined by a balance of atomic charges on proton donor molecules. The topological analysis was performed by using the AIM 1.0 2000 program [25]. The results of  $\Delta E$  interaction energies were determined through the application of the supermolecule approach,  $\Delta E = E(AB) - [E(A) + E(B)]$  [26]. Furthermore, the  $\Delta E$  values were corrected by the BSSE [27] scheme of Boys and Bernardi.

## Results and discussion

### Optimized geometrical parameters

From the B3LYP/6-311++G(d,p) calculations, the optimized geometries of the  $C_2H_3Cl \cdots HCl$  (**I**),  $C_2H_3Cl \cdots HCN$  (**II**),  $C_2H_3Cl \cdots HNC$  (**III**) and  $C_2H_3Cl \cdots HCCH$  (**IV**) vinylchloride complexes are illustrated in Figure 1, whereas the results of the structural parameters are listed in Table 1. In this picture, the van der Waals surfaces are represented in background [28]. From a long time ago, more specifically since the first empirical studies of hydrogen complexes, the van der Waals fields have been taken as useful parameter to analyze intermolecular interactions and thereby some interesting conclusions were proposed [29-33]. For the vinylchloride complexes studied here, it was admitted that van der van Waals surface can contribute at least qualitatively with the study of the hydrogen bonds  $(Cl \cdots X)$  and secondary interactions  $(X \cdots H)$ . Thus, the van der Waals surfaces depicted in Figure 1 shows that  $(X \cdots H)$  secondary interactions are not formed, although almost all  $(Cl \cdots H)$  hydrogen bonds were identified, excepting in the  $C_2H_3Cl \cdots HCCH$  vinylchloride complex because the van der Waals surfaces of HCCH and vinylchloride does not overlaps. By assuming that van

der Waals surface is an parameter of current interest in studies of molecular modeling and intermolecular interactions [34], in practice the van der Waals radii based on this surface are the only criteria to certify the formation of an intermolecular contact, although if we consider the  $R(\text{Cl}\cdots\text{HX})$  distances of 2.5471 Å, 2.7704 Å, 2.464 Å and 3.035 Å for (I), (II), (III) and (IV) vinylchloride complexes, as well as their  $R(\text{X}\cdots\text{H})$  secondary interactions values of 3.3599 Å, 3.8470 Å, 3.249 Å and 3.1589 Å, excepting the  $\text{C}_2\text{H}_3\text{Cl}\cdots\text{HCCH}$  whose  $R(\text{Cl}\cdots\text{HX})$  and  $R(\text{X}\cdots\text{H})$  results are longer than sum of van der Waals radii [H (1.40), C (1.70), O (1.50), and Cl (1.76)], all remaining complexes have typical intermolecular distance values.



**Fig. 1.** Illustration of the van der Waals surfaces and optimized geometries of the  $\text{C}_2\text{H}_3\text{Cl}\cdots\text{HCl}$  (I),  $\text{C}_2\text{H}_3\text{Cl}\cdots\text{HCN}$  (II),  $\text{C}_2\text{H}_3\text{Cl}\cdots\text{HNC}$  (III) and  $\text{C}_2\text{H}_3\text{Cl}\cdots\text{HCCH}$  (IV) vinylchloride complexes using B3LYP/6-311++G(d,p) calculations.

A natural consequence of secondary interactions for vinylchloride complexes is the non-linearity deviation ( $\theta$ ) on the  $(\text{Cl}\cdots\text{X})$  hydrogen bonds (35-36). From B3LYP/6-311++G(d,p) calculations, it was found a large  $\theta$  value of 28.7° for (IV), whereas smaller for (I), (II) and (III) complexes. Based on previous papers (37), the linearity deviation is

observed when the distances of the secondary interactions are compatible to van der Waals radii. Although all  $R(X \cdots H)$  values are longer than van der Waals radii, this distance criterion is not adequate for **(I)**, **(II)**, **(III)** and **(IV)** complexes. Regarding to molecular deformations, the slight  $\Delta r_{HX}$  value of 0.0014 Å for **(IV)** indicates how weakly bound is this intermolecular system. Moreover, for **(I)** and **(III)**, we can observe by  $\Delta r_{HX}$  results of 0.006 Å and 0.0063 Å that the hydrochloride acid and hydroisocyanic acid properly provokes substantial deformations on the structure of the vinylchloride complexes.

**Table 1.** Main structural parameters of the  $C_2H_3Cl \cdots HX$  vinylchloride complexes using B3LYP/6-311++G(d,p) calculations.

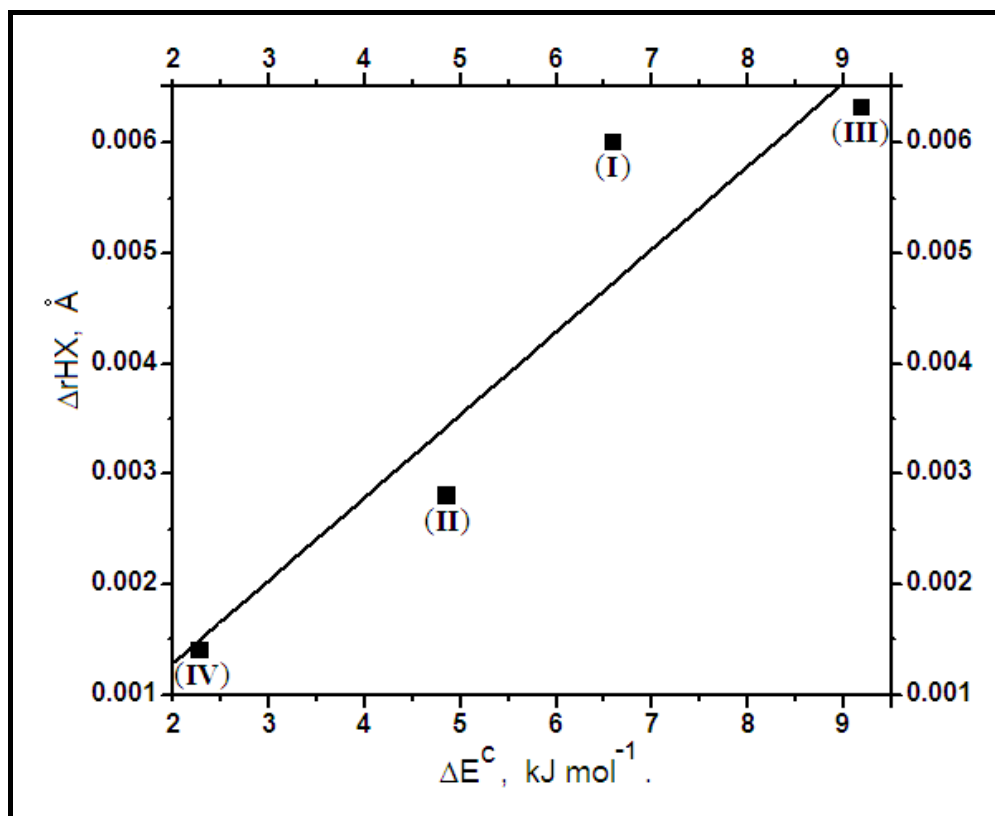
Parameters	$C_2H_3Cl \cdots HX$ vinylchloride complexes			
	<b>(I)</b>	<b>(II)</b>	<b>(III)</b>	<b>(IV)</b>
<b>R(Cl<math>\cdots</math>HX)</b>	2.5471	2.7704	2.4640	3.0350
<b>R(X<math>\cdots</math>H)</b>	3.3599	3.8470	3.2490	3.1579
<b><math>\Delta r_{HX}</math></b>	0.006	0.0028	0.0063	0.0014
<b><math>\theta</math></b>	9.7	6.7	7.3	28.7

\* Values of  $r$  and  $R$  are given in ångströms, Å;

\* Values of  $\theta$  angles are given in degrees.

### Interaction energies and charge transfers

The values of uncorrected intermolecular energies ( $\Delta E$ ), corrected intermolecular energies ( $\Delta E^C$ ), and BSSE correction amounts for the **(I)**, **(II)**, **(III)** and **(IV)** vinylchloride complexes are presented in Table 2. All  $\Delta E^C$  results obtained here corresponds to low energies, which can be associated to van der Waals interactions whose values are in range of 3.0-9.8 kJ mol<sup>-1</sup> [38]. In this sense, we can emphasize that these  $\Delta E^C$  results were obtained by small BSSE contributions, as in accord with data documented for  $\pi$  hydrogen-bonded complexes [39]. As debated here, the main structural changes ( $\Delta r_{HX}$ ) which occurs due to formation of hydrogen complexes is related to proton donor molecules. Such geometric parameter suggests systematic tendencies about the interaction strength by means of a direct relationship between  $\Delta r_{HX}$  results and  $\Delta E^C$  intermolecular energies, as shown by Figure 2. From this picture, a linear coefficient  $R^2$  of 0.96 was computed, what in fact, is a demonstration that stronger vinylchloride bound complexes are formed by intense changes on their molecular structures (40). In fact, by the interaction between HOMO orbital of proton acceptor and LUMO orbital of proton donor (41), electronically we can interpret the charge transfer between these frontier orbitals by means of the intermolecular CHELPG quantities ( $\Delta Q^{CHELPG}$ ). From  $\Delta Q^{CHELPG}$  values of -0.026 e.u. and -0.036 e.u. gathered in Table 2, we can verify the **(I)** and **(II)** complexes as the strongest bound systems, what corroborates with  $\Delta E^C$  analysis already debated here. For **(III)** and mainly the **(IV)** complex, the  $\Delta Q^{CHELPG}$  amounts of -0.014 e.u. and -0.012 e.u. indicates weak interaction strengths.



**Fig. 2.** Relationship between the values of the corrected intermolecular energies ( $\Delta E^C$ ) and increments of the proton donor bonds ( $\Delta rHX$ ) of the  $C_2H_3Cl \cdots HCl$  (I),  $C_2H_3Cl \cdots HCN$  (II),  $C_2H_3Cl \cdots HNC$  (III) and  $C_2H_3Cl \cdots HCCH$  (IV) vinylchloride complexes using B3LYP/6-311++G(d,p) calculations.

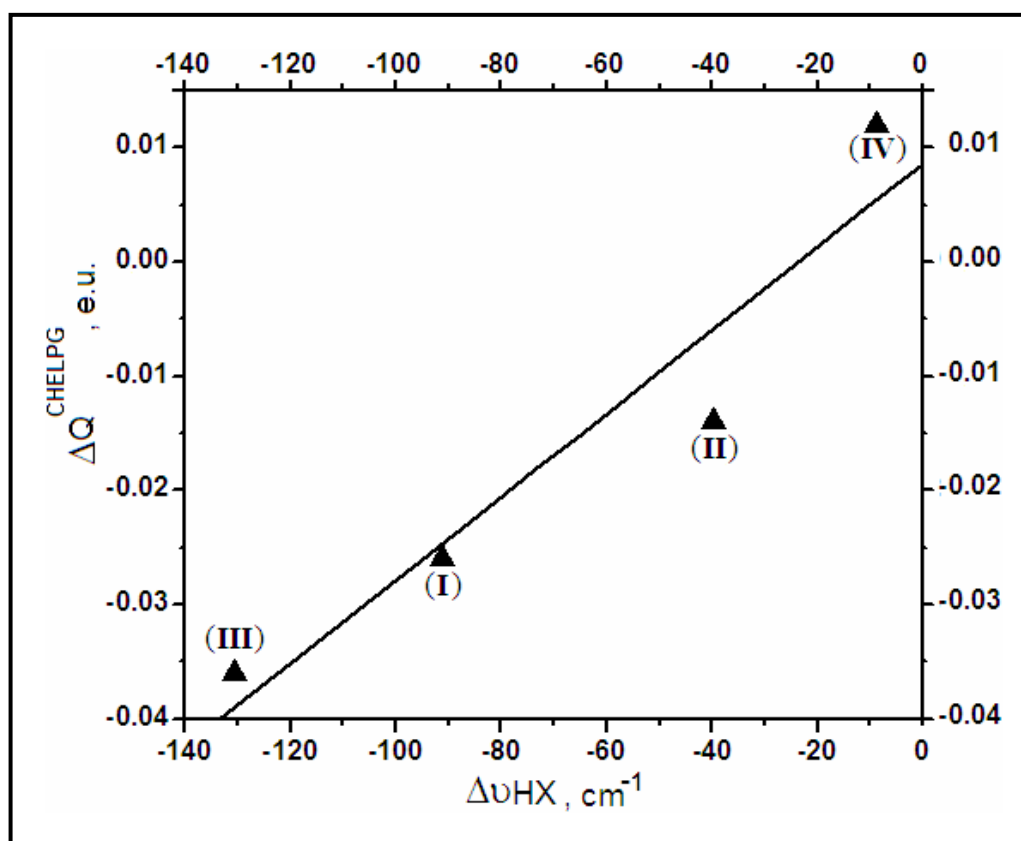
**Table 2.** Values of uncorrected ( $\Delta E$ ) and corrected intermolecular energies ( $\Delta E^C$ ), BSSE amounts and CHELP charge transfer ( $\Delta Q^{CHELPG}$ ) of the  $C_2H_3Cl \cdots HX$  vinylchloride complexes using B3LYP/6-311++G(d,p) calculations.

Parameters	$C_2H_3Cl \cdots HX$ vinylchloride complexes			
	(I)	(II)	(III)	(IV)
$\Delta E$	7.73	5.53	9.8	3.0
BSSE	1.73	0.67	0.40	0.72
$\Delta E^C$	6.6	4.86	9.4	2.28
$\Delta Q^{CHELPG}$	-0.026	-0.014	-0.036	-0.012

\* Values of  $\Delta E$ , BSSE and  $\Delta E^C$  are given in  $kJ mol^{-1}$ .

### Infrared spectra analysis

In terms of infrared spectrum parameters, the main vibrational modes of the (I), (II), (III) and (IV) vinylchloride complexes are presented in Table 3. As widely known, one of the most important vibrational phenomena upon the formation of hydrogen complexes is the red-shift effects on the proton donor [42], whose  $\nu(HX)_m$  frequency signal of isolated monomer is re-localized to a lower  $\nu(HX)_c$  region accompanied by a elevation on the absorption intensity,  $I(HX)_c/I(HX)_m$  (35). For the (I), (II), (III) and (IV) vinylchloride complexes, their  $\Delta\nu(HX)$  results were analyzed by  $\Delta Q^{CHELPG}$  amount data, whose relationship between them is in very good agreement, as can be seen in Figure 3. By analyzing this graph, a  $R^2$  linear correlation coefficient of 0.95 says that the red-shifts can be securely interpreted by quantification of the intermolecular charge transfer.



**Fig. 3.** Relationship between red-shift effects of HX proton donating and CHELPG charge transfer on  $C_2H_3Cl \cdots HCl$  (I),  $C_2H_3Cl \cdots HCN$  (II),  $C_2H_3Cl \cdots HNC$  (III) and  $C_2H_3Cl \cdots HCCH$  (IV) vinylchloride complexes.

Well, the excellent relationship for charge transfer is because the CHELPG algorithm has been implemented to calculate electronic populations near of outside of the van der Waals surface [43-45], which is illustrate on Figure 1. However, it was also verified the existence of weak vibrational modes, which in essence are named as hydrogen bond stretch frequencies. So, we can verify by the  $\nu(Cl \cdots HX)$  and  $I(Cl \cdots HX)$  values that all vinylchloride complexes are weak bound, mainly for (IV) whose result of absorption intensity of  $0.65 \text{ km mol}^{-1}$  is the lowest. However, it was found an interesting information for (IV) concerning to secondary interaction stretch frequency, whose results for  $\nu(X \cdots H)$  and  $I(X \cdots H)$  are  $21.1 \text{ cm}^{-1}$  and  $1.3 \text{ km}$

$\text{mol}^{-1}$ , respectively. In fact, the discovering of this secondary interactions is quite impressive, although we should notice that such observation was not verified on the (I), (II) and (III) complexes. In terms of the optimized geometric structure, the secondary interaction on (IV) was expected due the larger non-linearity deviation ( $\theta$ ) computed.

**Table 3.** Main vibrational modes of the  $\text{C}_2\text{H}_3\text{Cl}\cdots\text{HX}$  vinylchloride complexes using B3LYP/6-311++G(d,p) calculations.

Parameters	$\text{C}_2\text{H}_3\text{Cl}\cdots\text{HX}$ vinylchloride complexes			
	(I)	(II)	(III)	(IV)
$\Delta\nu(\text{HX})$	-91.0	-39.6	-130.6	-8.7
$I(\text{HX},c)/I(\text{HX},m)$	8.2	2.7	2.8	1.20
$\nu(\text{Cl}\cdots\text{HX})$	71.4	61.5	88.1	46.8
$I(\text{Cl}\cdots\text{HX})$	3.8	3.4	6.4	0.65
$\nu(\text{X}\cdots\text{H})$	—	—	—	21.2
$I(\text{X}\cdots\text{H})$	—	—	—	1.3

\* Values of  $\nu$  and  $I$  are given in  $\text{cm}^{-1}$  and  $\text{km mol}^{-1}$ , respectively;

\*  $\Delta\nu(\text{HX}) = \nu(\text{HX},c) - \nu(\text{HX},m)$ .

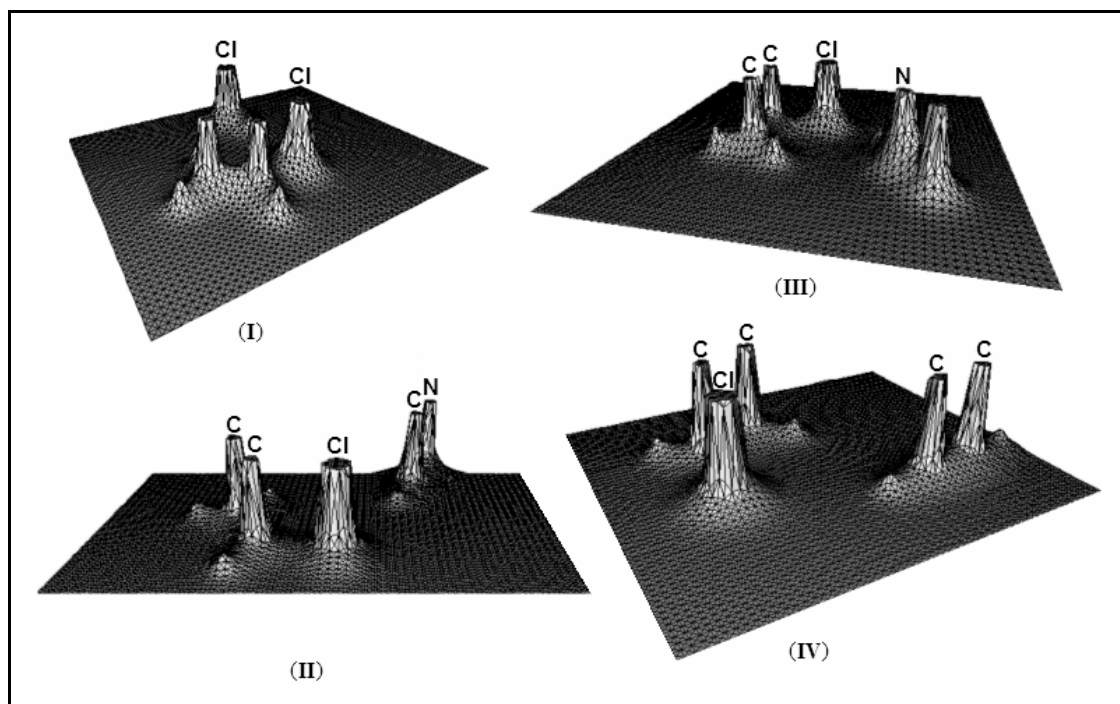
### Contribution of the AIM topology

Regarding to electronic parameters, we hope that an investigation of the molecular charge density can help us to understand the possibility to form the (Cl $\cdots$ H) hydrogen bonds and (X $\cdots$ H) secondary interactions. In this insight, the Table 4 presents the results of AIM calculations for the (I), (II), (III) and (IV) vinylchloride complexes, where the values of electronic densities ( $\rho$ ) and Laplacian ( $\nabla^2\rho$ ) are presented. According to inherent approaches of the AIM theory,  $\nabla^2\rho$  Laplacian is a topological parameter defined through the sum of the eigenvalues from diagonalization of Hessian matrix of  $\rho$ . Through the identification of Bond Critical Points (BCP) between two neighbouring atoms (46), Laplacian of  $\rho$  can be used to characterize the formation of hydrogen-bonded complexes when concentrations ( $\nabla^2\rho > 0$ ) and depletions ( $\nabla^2\rho < 0$ ) of the charge density are quantified. If take a look in our results, we can firstly perceive the high charge density concentration on HX bonds, whose values are defined in an average of  $0.190 \text{ e/a}_0^3$ . Moreover, the negative Laplacian values also indicates an electronic accumulation on proton donor bonds, what in terms of AIM theory, such elevated lumps of  $\rho$  is named as shared interactions. In other words, the charge concentration is localized within the atomic pathway, more specifically on BCP.

For the (Cl $\cdots$ HX) hydrogen bonds, however, the AIM result shows a slight concentration of charge density, consequence of an electronic separation on the atomic centers (Cl and H) revealed by negative values to  $\nabla^2\rho$  (47), as can be seen in relief maps of electronic density of the (I), (II), (III) and (IV) vinylchloride complexes pictured in Figure 4. Indeed, we can see a protuberance of charge density on Cl atom of vinylchloride and X (Cl, CN, NC and CCH) groups of the proton donors. Nevertheless, as previously debated about the possibility to form the secondary interaction between the hydrogen atoms of vinylchloride



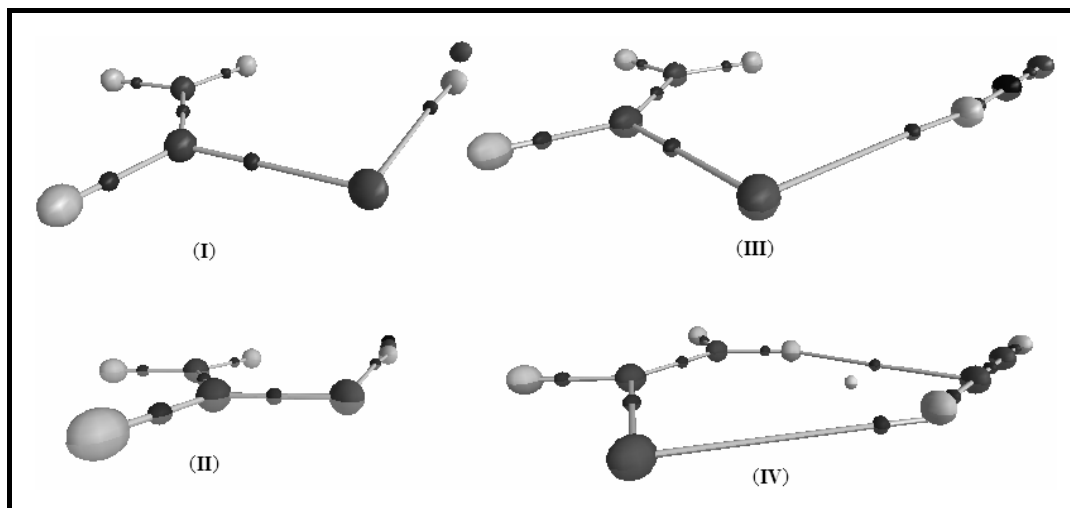
species and CN, NC and CCH groups of proton donors, as demonstrated in Table 4 the  $\rho(X \cdots H)$  and  $\nabla^2 \rho(X \cdots H)$  values of  $0.003 \text{ e/a}_0^3$  and  $0.008 \text{ e/a}_0^5$  obtained from AIM integrations identified such secondary interactions, but only on the  $C_2H_3Cl \cdots HCCH$  complex (IV), as demonstrated in Figure 5, where is illustrated their whole set of BCP.



**Fig. 4.** Relief maps of the electronic densities on the  $C_2H_3Cl \cdots HCl$  (I),  $C_2H_3Cl \cdots HCN$  (II),  $C_2H_3Cl \cdots HNC$  (III) and  $C_2H_3Cl \cdots HCCH$  (IV) vinylchloride complexes.

**Table 4.** Values of electronic densities ( $\rho$ ) and Laplacians ( $\nabla^2 \rho$ ) of the  $C_2H_3Cl \cdots HX$  vinylchloride complexes using AIM calculations.

Parameters	$C_2H_3Cl \cdots HX$ vinylchloride complexes			
	(I)	(II)	(III)	(IV)
$\rho(HX)$	0.190	0.190	0.189	0.192
$\nabla^2 \rho(HX)$	-2.664	-0.268	-0.264	-0.270
$\rho(Cl \cdots HX)$	0.012	0.007	0.012	0.004
$\nabla^2 \rho(Cl \cdots HX)$	0.034	0.022	0.040	0.013



**Fig. 5.** BCP (in small black spheres) and molecular pathways on the  $C_2H_3Cl \cdots HCl$  (I),  $C_2H_3Cl \cdots HCN$  (II),  $C_2H_3Cl \cdots HNC$  (III) and  $C_2H_3Cl \cdots HCCH$  (IV) vinylchloride complexes.

However, we make evidence that the secondary interaction is not formed between the hydrogen atom of vinylchloride and  $\pi$  bond of acetylene, by contrary, it was found that the hydrogen of vinylchloride interacts directly with carbon of acetylene instead of unsaturated bond [11]. As discussed in the structural parameters that even though the  $CCH \cdots H$  distance is longer than sum of van der Waals radii, but the AIM protocol was efficacious to identify a BCP between the C and H atoms, showing then the existence of the secondary interaction, which has been presumed by FTMS analysis [10]. By the way, it is not surprising that BCP are localized between near atoms, as in case of halogen interactions recently found and reported by Grabowski [49]. So, a direct consequence about the identification of the secondary interaction in (IV) is that, undoubtedly its interaction energy of  $2.28 \text{ kJ mol}^{-1}$  cannot be associated to  $Cl \cdots H$  primary hydrogen bond, but it must be also related to  $CCH \cdots H$ . Thereby, there is a limitation of the supermolecule approach for determination of the interaction energies, which cannot be performed by subtracting the energy of the complex ( $C_2H_3Cl \cdots HCl$ ,  $C_2H_3Cl \cdots HCN$ ,  $C_2H_3Cl \cdots HNC$  or  $C_2H_3Cl \cdots HCCH$ ) minus of its isolated monomers ( $C_2H_3Cl$  and  $HCl$ ,  $HCN$ ,  $HNC$  or  $HCCH$ ). This problem was recently debated in hydrogen-bonded complexes (alcohol  $\cdots$  water and heterocyclic  $\cdots$  hydrofluoric-acid) [49-50] wherein multiple hydrogen bonds were characterized on these structures.

### Concluding remarks

A theoretical study about the molecular structure of the  $C_2H_3Cl \cdots HX$  vinylchloride complexes with  $X = Cl, CN, NC$  and  $CCH$  was proposed through the B3LYP/6-311++G(d,p) calculations and topological integrations of the atoms in molecules theory. Through the structural and electronic parameters, the vinylchloride complexes were considered weakly bound systems because it was computed large  $R(Cl \cdots H)$  hydrogen bond distances and low  $\Delta E^C$  interaction energies.

Based on experimental assays documented in literature, it has been observed a ( $X \cdots H$ ) secondary interaction formed between the halogen atom (H) of vinylchloride specie and X group of the  $HCl$ ,  $HCN$ ,  $HNC$  and  $HCCH$  monoprotic acids. From B3LYP/6-311++G(d,p) calculations, this secondary interaction unlikely cannot be formed because the  $R(X \cdots H)$

distance is longer than sum of van der Waals radii. Still about this, it was showed by van der Waals surfaces that no secondary interactions might to exist. Indeed, by taking into account the van der Waals surface of the  $C_2H_3Cl \cdots HX$  set of complexes, as far as the  $(X \cdots H)$  secondary interactions is not observed, but for  $C_2H_3Cl \cdots HCCH$  system, the structure of its optimized geometry suggests that the formation of the  $(Cl \cdots H)$  primary hydrogen bonds also is not possible to be done.

By analyzing the infrared spectrum, however, we have observed that all  $\nu(Cl \cdots H)$  stretch frequencies and  $I(Cl \cdots H)$  absorption intensities were successfully identified, although the  $\nu(X \cdots H)$  signal of the secondary interaction on  $C_2H_3Cl \cdots HCCH$  complex was characterized and interpreted. In corroborating to that, AIM calculations also localized BCP between CCH group and vinyl hydrogen, although this contact is formed by a direct alignment of vinyl hydrogen to the carbon of acetylene instead of  $\pi$  bond.

### Acknowledgements

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### Supplementary information

Cartesian coordinates of optimized geometries and the values of the molecular energies (E) of the  $C_2H_3Cl \cdots HCl$  (I),  $C_2H_3Cl \cdots HCN$  (II),  $C_2H_3Cl \cdots HNC$  (III) and  $C_2H_3Cl \cdots HCCH$  (IV) vinylchloride complexes using B3LYP/6-311++G(d,p) calculations.

(I)				(III)			
C	0.185002	-2.040602	0.000000	C	-1.680956	0.870724	0.000000
H	0.676027	-3.003633	0.000000	H	-2.356666	1.714244	0.000000
C	-1.124734	-1.858287	0.000000	C	-2.050955	-0.398404	0.000000
H	-1.775117	-2.725192	0.000000	H	-3.108285	-0.635982	0.000000
H	-1.584809	-0.878320	0.000000	H	-1.347776	-1.221491	0.000000
H	0.000000	1.437311	0.000000	Cl	0.000000	1.396626	0.000000
Cl	1.350236	-0.722465	0.000000	C	2.427645	-2.544016	0.000000
Cl	-0.860689	2.402652	0.000000	N	1.888592	-1.507342	0.000000
				H	1.418177	-0.617842	0.000000
<b>E = -999.0770366 Hartree</b>				<b>E = -631.6753628 Hartree</b>			
(II)				(IV)			
C	-1.737372	1.155559	0.000000	C	-1.868648	0.530153	0.000000
H	-2.283466	2.088482	0.000000	H	-2.949309	0.565833	0.000000
C	-2.293243	-0.044413	0.000000	C	-1.080488	1.592867	0.000000
H	-3.373970	-0.124122	0.000000	H	-1.528319	2.579870	0.000000
H	-1.717276	-0.960951	0.000000	H	0.000000	1.523123	0.000000
H	1.542739	-0.878335	0.000000	H	1.751301	-0.823454	0.000000
Cl	0.000000	1.422739	0.000000	Cl	-1.268911	-1.120038	0.000000
C	2.030298	-1.830293	0.000000	C	2.630759	-0.223771	0.000000
N	2.547697	-2.856677	0.000000	C	3.618599	0.457160	0.000000
				H	4.496481	1.056819	0.000000
<b>E = -631.6966814 Hartree</b>				<b>E = -615.5978782 Hartree</b>			

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