REVIEW

Hydrocarbons as Proton Receptors and Evidences of Unconventional and Unusual π···H, p-π···H and C···H Hydrogen Bonds

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Abstract:

In this current work, a brief historical narrative of the most popular theories that decisively aid in the comprehension of the hydrogen bond formation is presented. As is well-known, the valence bond theory was efficiently suitable to certify the electronic structure of Lewis acids/bases, in particular the fluorine, oxygen and nitrogen as high charge density sources, and as such the homodimers of 2(HF), 2(H_2O) and 2(NH_3) were framed as reference systems. Regarding the π bonds of acetylene and ethylene as well as the p-π (pseudo unsaturated bond) clouds of cyclopropane, these compounds belong to a distinct group of proton receptors by which the π···H, p-π···H and C···H hydrogen bonds are formed.

Keywords: acetylene, ethylene, cyclopropane, hydrogen bond

1. Introduction

As it is widely known, a clear comprehension concerning the basic entity of chemistry, the atom, reveals a quite direct relationship with one of the benchmark points in experimental or theoretical researches for the electronic structure, the chemical bonding [1-4]. In 1916, the first proposition idealized by Lewis aligned well with the Valence Bond Theory (VBT) [5-6], which handles the way by which the atoms interact with each other [7]. At that time, the course of several studies and the advent of important lines of research were guided by the VBT, such as, the characterization of acid/bases components in chemical equilibrium [8-10]. However, some researchers, for instance Latimer and Rodebush in the early of 20s decade [11] as well as Winhill and Moore [12] deservedly recognized only years later [13], they declared that the acid/base dissociation phenomenon is essentially electrostatic.

Two decades after publication of these works, precisely in 1937 during a Faraday Conference hosted at the Edinburg city, Scotland, Hildebrand [14] presented a lecture about the hydrogen bond highlighting it as being a special case of dipole-dipole interaction [15]. The hydrogen bond is then treated as a classical molecular interaction [16] potentialized by the contributions of the Fluorine, Oxygen and Nitrogen atoms (F.O.N.) [17-18]. As contemporaries, the experimental studies performed by Brockway and Pauling [19] revealed the existence of hydrogen bonds in carboxylic acids, and amazingly, this discovery also corroborates with the results already reported by Latimer and Rodebush [11]. At that moment, it is worthy pointing out that Pauling has introduced the concept of atomic electronegativity [20], which has been largely used by years, decades, and notoriously up to the more recent days in chemical bond studies. In this type of importance, the Pauling's electronegativity scale has been also adopted in investigations of intermolecular systems framed in the context of the hydrogen bonds [21-24], what led Pauling to declare [25]:

"*Under certain conditions an atom of hydrogen is*

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attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond."

Meanwhile, the first half of the 20th century was noteworthy by the consolidation of quantum mechanics [26]. Among the most honored names in this scientific area, the contributions of Schrödinger, Heisenberg and Dirac [27], besides the interpretation of Born for the wave function as well as Roothaan for the molecular orbital [28], all of them were decisive to compose the foundations for those whom have became the quantum chemical methods applied for the studies of electronic structure [29], and precisely also those ones from intermolecular nature [30]. In 1954, Coulson and Danielson [31] divulged the first quantum study of hydrogen bond. For the water dimer, they interpreted the noncovalent profile of (O)⋯(H–O), and even the ionic form symbolized as (O–)⋯(+H–O). In this context and by taking into account the charge transference and interaction strength, once if both are determined at light of the wave function, it has been reported that hydrogen bonds and the computation of interaction energy are often embodied by electrostatic effects [32]. In this same year, Tsubomura [33] was other researcher that aggrandized the use of quantum formalism for investigating the events of hydrogen bonds in the water. In opposition to the hybrid formalism of the valence bonding proposed by Coulson [34], Tsubomura carried out its research based on the molecular orbital. These works signed by Coulson, Danielson and Tsubomura [31, 33] for the intermolecular structure of the $H_2O⋯H_2O$ complex should be unified as a special starting point for the hydrogen bonds in researches of the chemistry, physics and biology [35-36] and other areas subsequently developed [37-39].

On the basis of the archives of the International Pure and Applied Chemistry (IUPAC) reported in 1994, the hydrogen bond is defined as an associative interaction between the hydrogen atom and one electronegative element [40-42], e.g., those embodied by F.O.N. [43]. Moreover, because the aforementioned Coulombic nature of the hydrogen bond, the arising of dipole moment and partial charges yield values of binding energy in range of 20 and 25 $KJ.mol^{-1}$ [44]. Previously to the studies already documented by Coulson, Danielson and Tsubomura [31, 33] for the $H_2O⋯H_2O$ dimer, the hydrogen bond model is framed by the O⋯H–O interaction between two electronegative atoms, the oxygen, although being intermediated by the hydrogen. Actually, the understanding for F.O.N. is also feasible for the F⋯H–F e N⋯H–N hydrogen bonds in the complexes of fluoride acid [45] and ammonia [46]. Not exclusively idealized on the basis of theoretical chemistry by means of the molecular orbital calculations either by taking into account the *ab initio* formalism or even the hybrid functional of the Density Functional Theory (DFT) [47], but the evolution of the hydrogen bond studies was also supported by experimental evidences, mainly those based on the infrared and microwave spectroscopy [48-49]. These techniques evidences the most lowermost vibration changes in the oscillators of the chemical bonds, essentially the stretch frequencies and absorption intensities [50] and, in addition, at light of the knowledge of the rotational constants as well as the moment of inertia, it is possible to unveil the intermolecular structure of any system stabilized via hydrogen bond [51]. Among the reliable perspectives and frontier horizons inherent to the phenomenology of hydrogen bonds [52-54], it is worthy to be noted that all of this wide scope in the experimental and theoretical areas are not exclusive of the chemists, but also of physicists and biologists [55], and as such, the hydrogen bond has been considered one of the foundations in several research lines, by which led to Jeffrey and Saenger to affirm [56]:

"*The discovery of the hydrogen bond could have won someone the Nobel prize, but it didn't.*"

2. Classical complexes

"The name is bond – Hbond" was an adapted sentence by Martin and Derewenda [57] for the universal recognition of weakly bound systems by the hydrogen bond formation. Despite the water historically explored, all other intermolecular structures whose proton receptor centers

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encompassing F.O.N., certainly reaffirm that the systems represented by hydrogen fluoride (HF···HF) [58], water (H₂O···H₂O) [59], and ammonia (H₃N···H₃N) [60] are Hbond standard examples. On these structures, the F···H, O···H and N···H hydrogen bonds present a direct relationship with intermolecular geometry, mainly regarding the angular profile along the axis in the F-H-X and O-H-X bonds [61]. Amazingly before the primary investigation signed by Coulson, Danielson and Tsubomura [31, 33], in 1948 the intermolecular structure of the hydrogen fluoride was already known by means of a classical electrostatic study signed by Evans and Glocker [62]. So, the developments and advances about the interaction of the hydrogen fluoride have become widely known, and in this regard, the cyclic ternary structure framed by three HF subunits was elucidated [63]. Nevertheless, it is also recommended to revisit the second half of the 20th century, wherein Pimentel was one of the researchers that exercised a clear leadership in investigations of intermolecular systems [64-66]. By using the cryogenic matrix to isolate structures at extremely low temperatures, three propositions were elected examine the dimer of water [67]. In accordance with Kollman, Allen and Buckingham [68-69], some results from theoretical calculations point out that the linear structure is more stable by -22 KJ.mol⁻¹ in an absolute deep minimum of energy, by which, 5.4 and 3.4 KJ.mol⁻¹ are more favorable in comparison with the cyclic and bifurcate geometries, respectively. From the VBT point of view, the discussion about the dissociation or the intermolecular contact between acid/base point out that the charge densities of the lone electron pairs of F.O.N. are the driving forces to overestimate the interaction strength, and by which, it becomes one of the cornerstones to unveil the intermolecular stabilization [70-73].

3. The standard intermolecular model

In the 30s, since the electronegativity theory divulged by Pauling *et al*. [19-20, 25] that a new understanding about the formation of hydrogen bond interactions was established [74-75]. By taking into account the center of high electronic density (Y), the molecular proton donor (HX), and the hydrogen bond ruled by the electronegativities of Y and HX, the intermolecular scaffold at light of

sharing of electronic densities may be summarized as follows [41-42]:

$$Y\cdots H–X \tag{1}$$

In his own research work, Huggins investigated the structures of amino acids at light of the C=O···H–N or O–H···N hydrogen bonds [76]. By assuming the carbonyl group as the proton receptor, it must be worthy to notice that the resulting atomic electronegativity encompasses this functional group not singly but wholly (C=O). By assuming these arguments, the hydrogen bond model must evolve to [77]:

$$W–Y\cdots H–X \tag{2}$$

where, the summed electronegativity for the W–Y bond must be higher than H–X. Regardless, even the weak hydrogen bonds should reveal a slight enhancement in the dipole moment, thus being one of the certifications of intermolecular stability. Decades after the announcement, the theory of Pauling was established in the intermolecular studies of Pimentel and McClellan [64]. In reverse, Huggins has observed some limitations about the use of the electronegativity scale in detriment of fundamental conceptions, e.g., the intermolecular distance for Y···H must be shorter than the sum of the van der Waals radii for Y and H [78].

At light of VBT, the conception of the lone electron pairs from Y must value how much of electron density concentration should be necessary to affirm the existence of the hydrogen bond [79]. Through the Molecular Orbital Theory (MOT), however, despite the HOMO-LUMO gap usually must agree with the magnitude of the interaction strength between Y and HX, there is no sense to assign the charge density of the lone electron pairs of Y to the HOMO orbital. Unfailingly, the argumentation proposed by Rzepa [80] titled "The importance of being bonded" exalts the most useful methodological approaches for investigating the hydrogen bond formation, although a set of criteria quite important are also highlighted in this regard.

4. The new charge source for unusual complexes

Regarding the molecular systems and all

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requirements that validates the existence of hydrogen bond, Rzepa [80] has put in evidence the challenge of explaining the complexity of this interaction and its phenomenology into a single citation:

> *"All chemists when asked would probably say that they know a bond when they see one, but they might be harder pressed to provide definitions for the current menagerie in the bonding zoo"*

The chemical bonding is a wide universe to be explored even though might be guided by the functionality of the "bonding zoo" [80] (F.O.N.) in the hydrogen fluoride dimer, water and ammonia. By the widely known conception on W–Y···H–X and the intermolecular profile governed by the molecular orbital once the electronic charge transfer is accounted, the theoretical analysis exposes the capability of systems deprived of lone pairs of electrons for interacting with donors of protons [36, 41-43, 52, 78]. Regardless, the interaction strength often reveals weakly bound supermolecules with low polarity results [32, 63]. This conception of bases unfitted with the Lewis theory has converged to a small number of hydrocarbons, namely as acetylene (C_2H_2), ethylene (C_2H_4) and cyclopropane (C_3H_6) [81-82]. To consider these compounds as proton receptors was a real challenge because the π clouds contain low charge density amounts for donating to monoprotic acids [83-84]. The π bonds of acetylene and ethylene contain a minimum density of electrons to be transferred up to the antibonding orbital (σ*) of the proton donor [85]. In C_3H_6, the occurrence of the ring strain is governed by the distortion of the *p* orbital, and as such, the C–C bond is designed as pseudo-π, or justly, p-π. In according with Cremer and Kraka [86], this disruption of the *p* orbital is translated as a high capability of C_3H_6 to grant electrons, or more precisely, just like a sharing of electrons between acid and base well understood as a charge transfer to a proton donor [16]. Regarding the hydrogen bond formation [87-90], the assumed model can be represented as follows:

$$\pi \cdots H–X \qquad (3)$$

$$p\text{-}\pi \cdots H–X \qquad (4)$$

Experimentally, intermolecular structures stabilized through the π···H–X and pseudo-π···H–X hydrogen bonds have been studied [91-97], precisely by means of the rotational spectroscopy technique [98], although not justly the π clouds, but other Lewis bases formed by F.O.N. still are targets of investigation by many scientific groups [99]. By analyzing the rotational transitions and moments of inertia, the preeminence of these studies is valued by structural parameters, i.e., the intermolecular bond lengths or the angles inherent to the attack of acid species to the bases ones [100]. In some aspects, indeed, not exclusively guided by experimental techniques, but, the use of *ab initio* calculations have also decisively contributed to the elucidation of hydrogen-bonded complexes [101-102]. The structural characterization of complexes formed by acetylene, ethylene and cyclopropane became known by the hydrogen fluoride as proton donor [103]. The π···H–F and p-π···H–F hydrogen bonds strength on the basis of the Pauling's scale of electronegativity [20, 25] has been one of the main goals despite only the value for fluorine is taken into account in this regard. In concordance with this scenario, certainly some other requirements shall be necessary to furnish a detailed explanation for these interactions.

5. $C_2H_2\cdots HF$, $C_2H_4\cdots HF$ and $C_3H_6\cdots HF$ complexes

Concerning the studies of rotational spectroscopy of intermolecular systems reported in the early years of the 80s, Read and Flygare [104] have elucidated the structure with T-shape geometry of the $C_2H_2\cdots HF$ complex. Really, this supermolecule presents a C_{2v} symmetry operation [105] because the interaction is orthogonally arranged between the internuclear axis of the hydrogen fluoride and acetylene (see structure I in Figure 1). In this context, the hydrogen bond π···H–F occurs exactly in the middle of the π cloud of the acetylene, and as already aforementioned, the charge density of the π clouds is transferred to the anti-bonding orbital σ*(HF) of the hydrogen fluoride [106].

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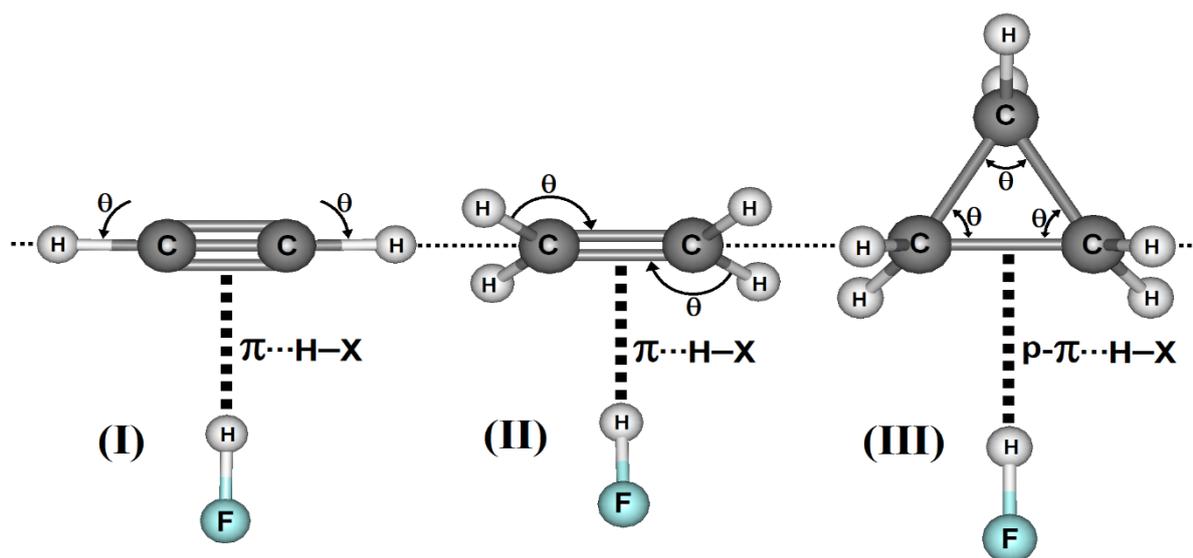
Figure 1. Structures of the $C_2H_2 \cdots HF$ (**I**), $C_2H_4 \cdots HF$ (**II**) and $C_3H_6 \cdots HF$ (**III**) complexes.

Well, Wojtulewski and Grabowski [104] called $\pi \cdots H$ of "unconventional" hydrogen bonding whereas Rozas and co-workers [107] have chosen another designation, "unusual". The structure of the complex formed by ethylene ($C_2H_4 \cdots HF$) was experimentally elucidated by Shea and Flygare [108]. Once again, the hydrogen fluoride is orthogonally oriented with respect to the internuclear axis of ethylene, such as have been also verified by Aldrich and collaborators [109] in studies involving the hydrochloride acid. Finally, Buxton and its colleagues have already presented the geometry of the complex with cyclopropane, $C_3H_6 \cdots HF$ [110]. In this complex, the acid attack is aligned in the same planar orientation of the homocyclic structure, precisely in the center of the p-π cloud. Additionally, it can be seen that the hydrogen bonds formed by hydrocarbons are in line with the regioselective reaction vastly known by halogenation mechanisms of vinyl compounds [111], wherein the electrophilic attack occurs into whatever carbon of the unsaturated bonds. Thus, it is worthy to notice, the main modifications in the structures of C_2H_2 and C_2H_4 are the HĈC angles (θ) [112] that corroborate with the changes in the $sp \rightarrow sp^2$ hybridizations in the carbons, although in the C_3H_6, this parameter is recognized by the ring strain energy. Even being very similar to the halogenation mechanisms, the ring-opening reaction on cyclic structures examined via hydrogen bond theories reveals a good concordance with the SN_2 nucleophilic substitution mechanism, either in gaseous or in aqueous phase [113].

6. Intermolecular parameters and quantum mechanical contributions

In studies of intermolecular systems stabilized by means of hydrogen bond formation, the spectral analysis, peculiarly in the infrared region [114-115], it is admittedly vital, and the structure must represent a global minimum in the potential energy surface [116]. This theme became clearly relevant along the decades, and as such, the data informed by Gorman [117] as well as those by Frayer *et al.* [118] and Bolkova *et al.* [119] should be cited as reference data for further researches. Once the hydrogen bond strength often ranges between low and moderate, in 1988 Nesbitt [120] signed a revision work regarding the application of high resolution of infrared spectroscopy in studies of weakly-bound systems. Among many considerations, it was dedicated a great emphasis to the equilibrium cell methods and supersonic molecular beam used for studies of haloacids, rare gases, carbonyl compounds and oxides [120], but for the $C_2H_2 \cdots HF$ and $C_2H_4 \cdots HF$ complexes, a suitable discussion of the values of the stretch frequencies and corresponding shifts observed after the complexation [120]. For the monomer of the hydrogen fluoride, the

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experimental value of the stretch frequency of 3961.42 cm^{-1} is shifted to 3794.36 and 3781.73 cm^{-1} due to the formation of the (**I**) and (**II**) complexes [120], respectively. Once the shifts means the appearing of stretching frequencies at lower energy values in the electromagnetic spectrum, these events are well known as red-shifts rather than the bathochromic effect widely cited [120]. On the theoretical viewpoint, once the researches of intermolecular complexes carried out at light of *ab initio* or DFT calculations, Figure 2 exhibits the theoretical simulations of the infrared spectra for (**I**), (**II**) e (**III**) [97].

Thus, at the B3LYP/6-311++G(d,p) level of theory [17, 85, 121], the values of the shifting frequencies for the hydrogen fluoride in the (**I**), (**II**) and (**III**) complexes are -224, -254.50 and -222,0 cm^{-1}, respectively. These are uncontested features about the formation of hydrogen bonds, and to characterize as well as to interpret them jointly with their effects, the quantum chemical calculations play a significant role in this regard [122-124]. In comparison with the data revisited by Nesbitt [118], the computed results of the red-shifts could be well reproduced by this level of electronic structure composed by the B3LYP hybrid funtional and the Pople split-valence [125-126]. This kind of spectral shift is one of the most important effects that better demonstrates the formation of the hydrogen-bonded complexes, although, the enhancements in the absorption intensities are also one overwhelming event in the spectral line. By considering the value of absorption intensity of 130.13 Km.mol^{-1} for the monomer of the hydrogen fluoride, the results of 730, 796 and 548.6 yield the respective ratios of 5.6 (**I**), 6.1 (**II**) and 4.2 (**III**), which as can be noted they are quite similar. So, these data cannot be used to discuss the interaction strength among the **I**, **II** and **III** systems. The nature of these increases in the absorption intensity can be interpreted by theoretical calculations of the molecular orbital, or in other words, the charge transfer stated between the frontier orbitals, HOMO and LUMO [127]. Ideally, the Figure 2 must be carefully analyzed because not only the stretching frequencies when shifted to low spectral energies, but many other modes may be erroneously interpreted as noise signed by the experimental equipment caused by thermal instability, such as the new vibrational modes or the hydrogen bond frequencies for π···H–F (**I** and

II) and p-π···H–F (**III**).

In 1997, Araújo *et al.* [128] developed a pioneering study of π···H and p-π···H hydrogen bonds formed by hydrocarbons as proton receptors, namely the acetylene as well as ethylene and cyclopropane. Firstly, Araújo and co-authors [127] have performed Hartree-Fock calculations followed by perturbation levels at second order, and, on the structural viewpoint, deformations in the HĈC angle of the acetylene were presented and discussed (Figure 1.**III**). Through the several routine tests performed at the MP2/6-311++G(d,p) level of theory, the interaction strength was indirectly unveiled by means of the value of 180.55º (or $\theta = 0.55º$) for HĈC. Furthermore, the bond length structure of the π clouds (base centers for binding with proton donors) and H–F subunits, the remarkable variations of 0.0013 and 0.0066 Å are clear evidences upon the complexation. This same systematic tendency was also observed in complexes formed by acetylene with other proton donors, namely HCN and HNC [129]. A lot of atomic charge algorithms have been used in the comprehension of the red-shift phenomenon, e.g., the Mulliken charges [130-131], the Bader partition [132] supported by the formalism of the Quantum Theory of Atoms in Molecules (QTAIM) [133], Charges from a Electrostatic Potentials using a Grid-Based (ChElPG) [134], or even the Natural Bond Orbitals (NBO) [135]. Through the DFT calculations, Vianna and co-workers [121] have used the computation of the atomic charges derived from Generalized Atomic Polar Tensors (GAPT) [136]. By determining the atomic contributions through the execution of the partial derivatives of the dipolar moments at x, y, and z coordinates (Equations 5 and 6), this method has been successfully applied in spectroscopy researches of red-shift effects manifested on proton donors.

$$P_x^\alpha = \begin{bmatrix} \dfrac{\partial \mu_x}{\partial x_\alpha} & \dfrac{\partial \mu_x}{\partial y_\alpha} & \dfrac{\partial \mu_x}{\partial z_\alpha} \\[2ex] \dfrac{\partial \mu_y}{\partial x_\alpha} & \dfrac{\partial \mu_y}{\partial y_\alpha} & \dfrac{\partial \mu_y}{\partial z_\alpha} \\[2ex] \dfrac{\partial \mu_z}{\partial x_\alpha} & \dfrac{\partial \mu_z}{\partial y_\alpha} & \dfrac{\partial \mu_z}{\partial z_\alpha} \end{bmatrix} \tag{5}$$

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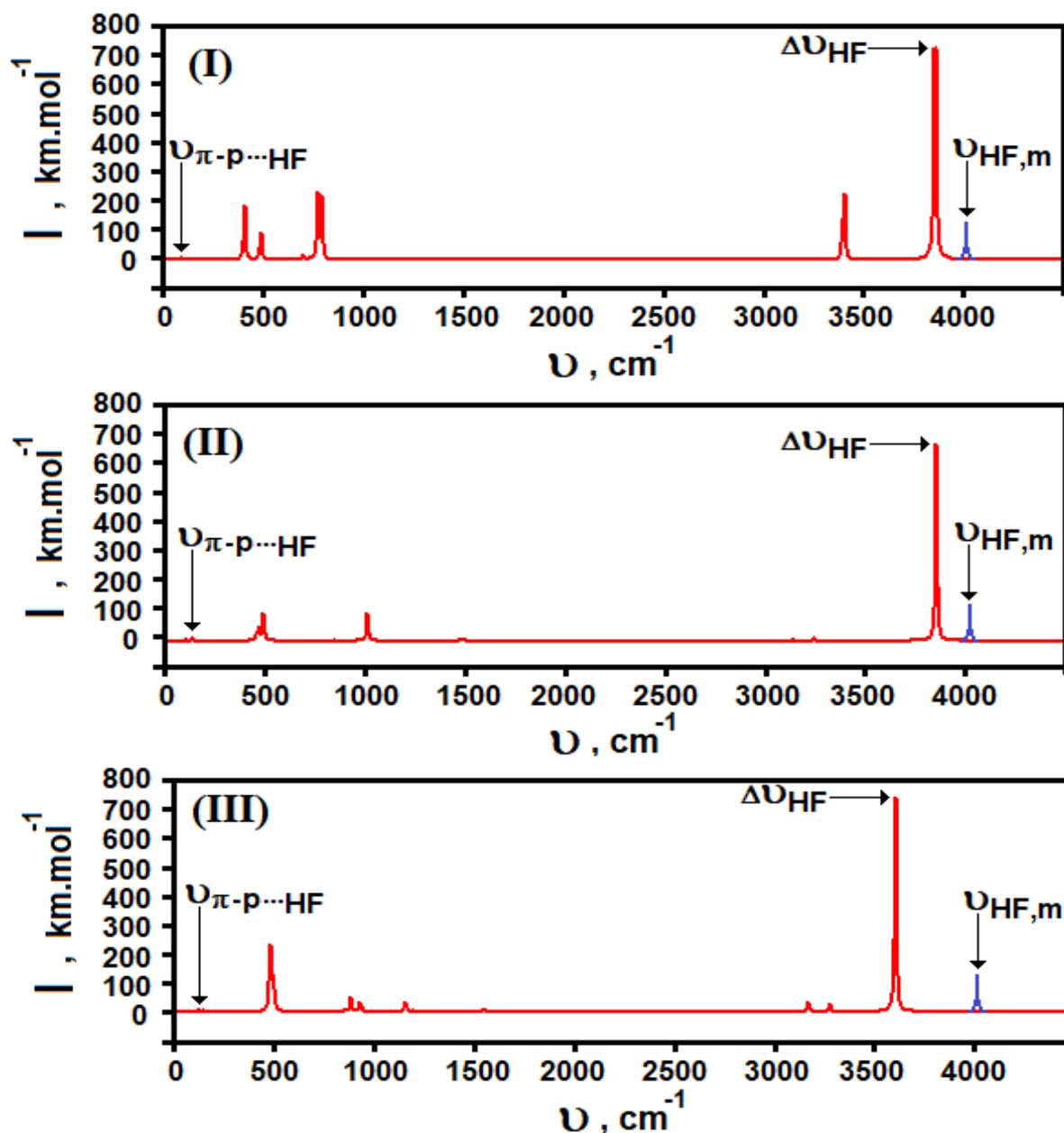
Figure 2. Theoretical infrared spectra of the $C_2H_2\cdots HF$ (**I**), $C_2H_4\cdots HF$ (**II**) and $C_3H_6\cdots HF$ (**III**) complexes. $\upsilon_{HF,m}$ and υ_{HF} represent the stretch frequency of the hydrogen fluoride as monomer and complexed with acetylene, ethylene and cyclopropane.

$$q_\alpha = \frac{1}{3}\left[\frac{\partial\mu_x}{\partial x_\alpha} + \frac{\partial\mu_y}{\partial y_\alpha} + \frac{\partial\mu_z}{\partial z_\alpha}\right] \quad (6)$$

Moreover, at the B3LYP/6-311++G(d,p) level of theory, the interaction strength of the $C_2H_2\cdots HF$ complex was also estimated through the charge flux from base center (Y) towards the proton donor HX (X = F) [121]. Thus, the atomic charge of the hydrogen is increased in association with the enhancement of the bond length, which is a typical event of the red-shifts observed in the harmonic infrared spectrum.

$$\left[\left(\frac{\partial qH}{\partial r_{HX}}\right)r_{HX}^o\right] \quad (7)$$

Comparing the results of MP2 and B3LYP routinely used with full basis sets composed by valence, diffuse and double-zeta polarized functions, the results obtained at light of the hybrid functional overestimated the interaction strength

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by 0.529 if compared with 0.423 determined by the Møller-Plesset approach, and therein, the red-shifts are more evident and clearly detected. Through the computation of corrected atomic charges or charge flux, both are used for estimating the theoretical values of absorption intensities (see Equation 8), whose MP2/6-311++G(d,p) results of 525.2 and 527.4 $Km.mol^{-1}$ are in disagreement of the already known efficiency of the DFT calculations. In this context, amazingly the largest shifted frequencies arisen through the formation of the $C_2H_2\cdots HF$ system were successfully interpreted by means of the intensity absorption ratios. Nevertheless, it is necessary to point out that a satisfactory description of the infrared modes must be in agreement with structural aspects, and particularly regarding the $C_2H_2\cdots HF$ complex, its planarity and symmetry are parameters taken into account.

$$I_{HX} = k\left[q_H^{corr} + \left(\frac{\partial qH}{\partial r_{HX}}\right)r_{HX}^o\right]^2 \quad (8)$$

In order to explore systems whose geometries reveal a stereochemistry of high complexity, the ChElpG and NBO algorithms are more frequently applied [137-139]. Even though by measuring the interaction strength on the basis of the supermolecule approach followed by the corrections of the Zero-Point Energy (ZPE) [140] as well as the Basis-Sets Superposition Error (BSSE) [141], the corrected values for the interaction energies correlate well with the intermolecular charge transference amount. Moreover, a set of linear models highly efficient is fitted through the relationship between the values of red-shifts and bonding energies determined via NBO calculations, E^{NBO} (Equation 9). Therefore, the difference between the energy of the orbital in the unsaturated bonds (π clouds between carbon-carbon) and the hydrofluoric acid in the context of the Fock operator (F), the E^{NBO} values brought new horizons for the interpretation of the interaction strength of the $C_2H_4\cdots HF$ complex [85], for instance.

$$E^{NBO}\pi(CC) \to \sigma^*(HF) = -2\frac{\langle\pi(CC)|F|\sigma^*(HF)\rangle}{[\varepsilon_{\pi(CC)}-\varepsilon_{\sigma^*(HX)}]} \quad (9)$$

The interpretation of the interaction strength by means of the red-shifts in the proton receptors still remains as an unsolved question. Briefly, it means that the variations in the charge density of the π clouds of acetylene, ethylene and cyclopropane may unveil the profile of the intermolecular energy, and thereby, the strongest bound system shall be revealed [142]. By the values of 23.05 (**I**), 25.25 (**II**) and 8.26 (**III**) $KJ.mol^{-1}$, the greatest charge densities, mainly in the double bond of the ethylene, ideally it promotes the formation of a stronger-bonded complex [106-107]. By comparing with the infrared spectrum analysis, wherein the slightly shortest frequency shift arises in the H–F bond of (**III**), amazingly the E^{NBO} energy reveals that $C_3H_6\cdots HF$ is the weakest bonded complex. As a contemporary of Araújo [126-127], Rozas and co-workers [107] have demonstrated the existence of π···H hydrogen bonds in some hydrocarbons. The mapping of the molecular electronic density shows a total concordance with the QTAIM quantum protocols [90, 130], as can be seen in Figure 3.
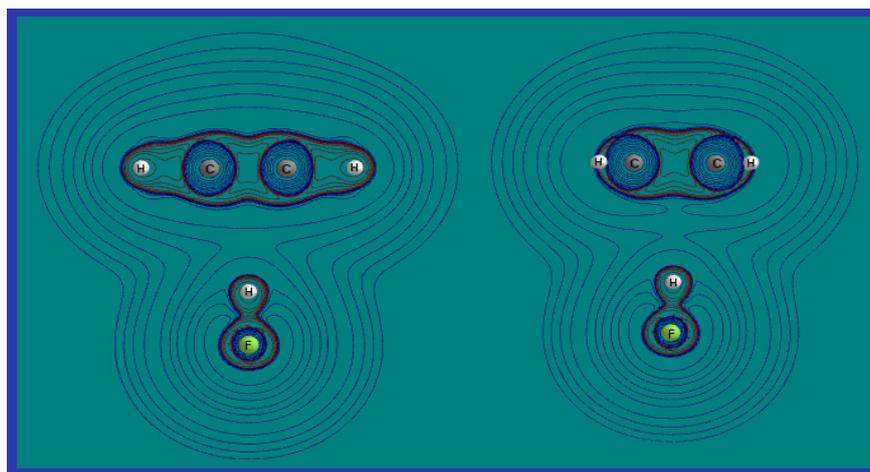
Figure 3. Isosurfaces of charge density [143] of the $C_2H_2\cdots HF$ and $C_2H_4\cdots HF$ complexes.

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The charge concentrations in the carbon-carbon bonds described by means of the electronic density (ρ) [144] converge to a consensus that, although ρ represents a physical parameter, the QTAIM routine calculations is poorly dependent from *ab initio* and DFT levels of theory [137]. Furthermore, the condition for measuring the bond order (n) by means of the ρ values (Equation 10) was defined by Bader [145]. It is established that, B = ρ for C_2H_6; and A varies according to n(C_2H_4) = 2.0 and n(C_2H_2) = 3.0. The values of 3.0 (**I**), 2.0 (**II**) and 0.9 (**III**) guarantee the characters of the double, triple and single bonds in the acetylene, ethylene and cyclopropane respectively, and reveal slight variations in comparison with the isolated structures.

$$n = e^{[A(\rho_C - B)]} \qquad (10)$$

7. Brief perspective for the $\pi\cdots$H–F and p-$\pi\cdots$H–F hydrogen bonds

The reasoning of Rzepa [80] about the evolutionary growing of intermolecular systems in the conjecture of the "bonding zoo" is inspiringly comprehensive and corroborates with the interpretation of Dobrzańska *et al.* [146] for the Au$\cdots$H–X gold contact, which behaves as a similar interaction to the $\pi\cdots$H–F and p-$\pi\cdots$H–F hydrogen bonds revisited in this current work. In according with Grabowski [147], the accounting of a singular microcosm of chemical interactions is unreal because not only the hydrogen bond, but a lot of intermolecular contacts have emerged, among which, it is noteworthy the participation of hydrides, metals and halogen [148-149] (Figure 4). Regardless, the unrelenting criterion for examining each one of these interactions is always the sharing of charge density and the electronic flux between the HOMO/LUMO frontier molecular orbitals. Among these interactions, the reasoning debated by Metrangolo and Resnati *et al.* [150] for the Y$\cdots$Hal$^{+\delta}$–C$^{-\delta}$ halogen bond revealed that either nucleophilic (**A**) or electrophilic (**B**), both these centers may be suitable to form one single interaction even if ruled by distinct theorems, such as is depicted in Figure 5.

It was through these local moieties of charge density that a new approach for the chemical bond was formulated: the π-hole and σ-hole deformations on unsaturated or saturated bonds

[151]. In practice are molecular centers of the electronic structure with a positive electrostatic potential, by which the Hal$^{+\delta}$–C$^{-\delta}$ bond becomes able to interact with highly charged density centers or any Lewis base, for instance. The preeminence of the hydrogen bonds has been demonstrated in studies of molecular modeling for drug discovery with location of QSAR multidimensional fields and virtual screening for docking simulations [152-154].
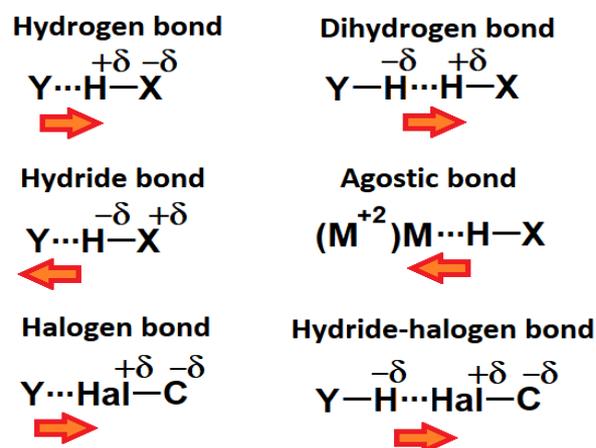
Figure 4. Screen of the main intermolecular interactions.
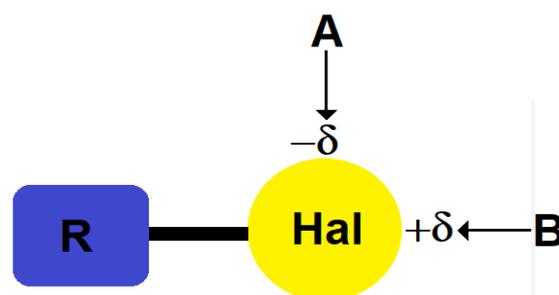
Figure 5. Halogen bond scheme [149].

It means that the experimental activities for a set of biocompounds might be explained by the identification of halogen bonds rather than the hydrogen bond in the form of hydrophilic interactions [155]. Notwithstanding the halogen bonds, but this is one of the most innovative intermolecular fields for exploring perspectives concerning the formation of the $\pi\cdots$H–F and p-$\pi\cdots$H–F hydrogen bonds with haloacids or halohydrocarbons. For hydrogen bonds formed by π clouds as charge donating, then Grabowski [156] has declared:

"*There are only few*

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studies on halogen bonds with the π-electron species as the Lewis bases."

Nevertheless, Li *et al.* [157] presented an intermolecular study of complexes formed by borazine and halogen compounds, e.g, FCN, BrCCH and ICF$_3$, wherein the T-shape structures match to those formed by the complexes of acetylene and ethylene. In addition, Riley and co-authors [158] have investigated the possibility of interactions between halogen centers and the π cloud resonance in the benzene ring. It was by this context that Grabowski [159] elucidated the intermolecular structures of C$_2$H$_2$···BF$_3$ and C$_2$H$_4$···BrF$_3$ with the formation of π···Br halogen bonds. Computed at the MP2/aug-cc-pVTZ level of theory, the interaction energies for these systems are -24.68 and -26.77 kJ.mol^{-1}. It must be highlighted that these values encompass only corrections based on the BSSE scheme [141, 159], although by comparing with the values of -5.92 and -10.58 kJ.mol^{-1} of the analogous C$_2$H$_2$···HF and C$_2$H$_4$···HF whose geometries were

modeled at the B3LYP/6-311++G(d,p) level of calculation [121], the acetylene and ethylene are more efficient halogen bond receptors instead of hydrogen bond proton donors.

Some decades ago, when the T-shape benzene dimer was first studied, the term "anti hydrogen bond" was introduced by Hobza *et al*. [160]. This designation was clearly disseminated in the whole scientific community over the fact of opposite observations to some already known for the hydrogen bonds, specifically regarding the proton donor structure [70-73, 78, 90, 111, 120, 161-162]. Regardless of the phenomena, effect or event, the "anti hydrogen bond" may be attributed to the amphoteric donor/receptor of protons and/or its sources of charge density. In this manner, on the contrary of the electronic clouds that make the structure avid by proton donors, in past years the possibility of vinyl cation, such as the ethyl cation (C$_2$H$_5$$^+$) illustrated in Figure 6-**VI**, behave as proton donor to form an ionic π···H+ hydrogen bond [163-164] was enthusiastically examined.

Figure 6. Structures and redistribution of electronic density to stabilize the ethyl cation (**VI**).

Similar to **I**, **II** and **III**, the structures of the C$_2$H$_5$$^+$···C$_2H_2$, C$_2H_5$$^+$···C$_2H_4$ and C$_2$H$_5$$^+$···C$_3H_6$ complexes are formed by ionic π···H$^+$ and p-π···H hydrogen bonds with the natural advent of red-shifts in the resonant double bond, then becoming it the most evident proton donor center in the C$_2$H$_5$$^+$ subunit. The interaction energies of -33.7, -32.34 and -34.48 kJ.mol^{-1} and the respective QTAIM densities of 0.028, 0.027 e 0.032 e.a$_o$$^{-3}$ point out the stability and higher interaction strength rather than those determined for **I**, **II** and **III** [165-166]. Besides the hydrogen bonds and halogen bonds depicted in Figure 4, the overall notion of charge-sharing makes the π···H hydrogen bonds reproduce in parts the functionality of the dihydrogen bond H$^{-δ}$···H$^+$ ~
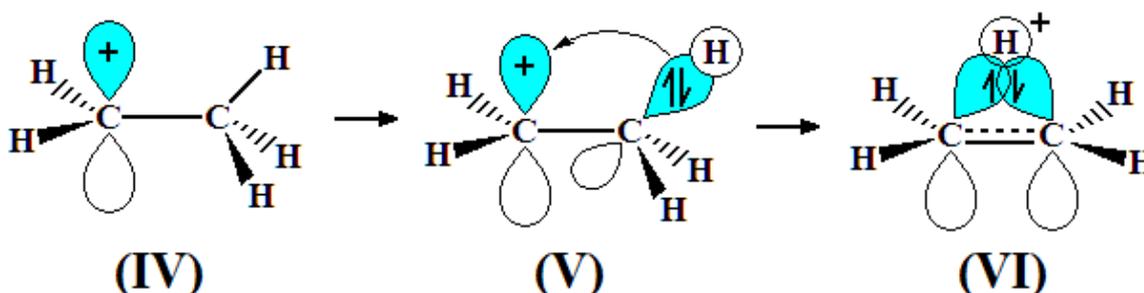
π···H.

8. The C···H hydrogen bond beyond the electronegativity

Throughout the last decades, the knowledge gained by exploring the universe of the intermolecular interactions [18, 167], in particular the hydrogen bonds, extends beyond of hitherto known systems [168-172]. In the framework of the proton donor-acceptor association, thermodynamic relationships for predicting the binding free energies through the interaction strength led to nominal designations for hydrogen bond [173-174]. Regardless and as

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aforementioned, the hydrogen bonds have been explored and interpreted on the basis of electronegativity of the atoms embodied in the W–Y···H–X model. So, the ionic and neutral π···H⁺ and p-π···H hydrogen bonds have been revisited here, but the condition of electronegativity of the bases is challenged due to the formation of the C···H interaction [174-175] which has been also considered a hydrogen bond. In comparison with halogen or chalcogen, it is important to bear in mind the tiny ability of the carbon for donating electrons, even though the existence of C···H was verified and valued by theoretical calculations and experimental analyses [176]. The occurrence of a C···H hydrogen bond is not so rare, and it happens in the dimer formed by methane and water just as documented by Isaev [177]. According to Silva and Oliveira [63] as well as Carvalho *et al.* [85], from a small dimer of "hydrocarbon:proton-donor" up to a supramolecular configuration embodied by five acid molecules, the frame of the π···H and p-π···H hydrogen bonds may change to C···H with variations in the interaction strength. This tendency not matches with the intermolecular behavior observed in the cyclic hydrocarbons formed by three and four members when Grabowski [177] signed a theoretical study of the C_3H_6···HF, C_4H_8···HF and C_5H_{10}···HF complexes. Ideally that the enlargement of the cyclic chain minimizes the ring strain [86, 178], although the energy of -5.0 Kcal.mol⁻¹ for the p-π···H hydrogen bond in the cyclopropane is twice the amount of -2.5 Kcal.mol⁻¹ which is higher than -1.9 Kcal.mol⁻¹ in comparison with the respective complexes of cyclobutane and cyclopentane whose interaction is C···H rather than p-π···H.

9. Conclusions

The historical background of the hydrogen bond documented in two important timeless contexts, hosting firstly the electronegativity idea, and then followed by the intermolecular distances and charge transfer ruled by the concentrations of electronic density. The second and more recent conception concerns the profiles of the receptor/donor of protons, although, even so without evident electronic densities, the identity of these intermolecular subparts were revisited here. Indeed, this statement is allusive to the nonpolar hydrocarbons, such as acetylene, ethylene and cyclopropane, being all of them

considered revolutionary molecules for the evolution of the hydrogen bond model. As such, for long time experimentalists and theoreticians have studied the structures of C_2H_2···HF, C_2H_4···HF, C_3H_6···HF as well as others from cationic nature $C_2H_5^+$···C_2H_2, $C_2H_5^+$···C_2H_4, $C_2H_5^+$···C_3H_6, $C_2H_5^+$···BeH_2 and $C_2H_5^+$···MgH_2. As the prime focus is the infrared spectrum, in which, the stretch frequencies are shifted to upward and downward values followed by the enhancements in the absorption intensities, these are the unfailing effects that characterize any intermolecular system, and in this context, several computational approaches and quantum calculation levels have been successfully used. In more recent years, the π···H–F and p-π···H–F hydrogen bonds were definitively consolidated as one of the main chemical contacts. Notwithstanding these interaction types, the nonpolar structures of the hydrocarbons provide the appearing of another interaction, also recognized as a new hydrogen bond, namely C···H. Even though the carbon and hydrogen present very similar values of electronegativity, the C···H is a weaker hydrogen bond than p-π···H, and obviously, π···H.

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