Interplay between dihydrogen and alkali–halogen bonds: Is there some covalency upon complexation of ternary systems?

Boaz G. Oliveira *

Universidade Federal da Bahia, Instituto de Ciências Ambientais e Desenvolvimento Sustentável, Barreiras, BA 47801-100, Brazil

ABSTRACT

In this study, a theoretical investigation of traditional dihydrogen bonds and novel alkali–halogen bonds was performed in relation to the formation of $NaH \cdots HCF_3$ and $NaH \cdots HCCl_3$ binary and $NaH \cdots 2(HCF_3)$ and $NaH \cdots 2(HCCl_3)$ ternary complexes. The B3LYP/6-311++G(3df,3pd) level of theory was used to determine the optimized geometries of these complexes, mainly in order to examine the most important structural deformations. In addition to the infrared harmonic spectrum from which the red- and blue-shift effects were interpreted following NBO analysis, intermolecular energies (BSSE and ZPE included), dipole moment variations, quantification of charge transfer through the CHELPG and Mulliken approaches, and the Bader topology were considered in the modeling of the intermolecular covalence through the measurement of the kinetic and potential electronic energy densities.

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1. Introduction

Recently, a noteworthy increase in the number of new intermolecular interaction types has been observed [1]. According to Rzepa [2], there is a multifarious bonding zoo since so many atoms are involved in the formation of chemical bonds. Based on this insight, the interface between proton donors and acceptors plays a crucial role whether the bonding zoo displays an intermolecular profile incorporated into a well-known hydrogen bond model referred to as Y···H—X [3]. Hydrogen bond is one of most important intermolecular interactions existing in nature, which led Fellet to declare: "*Without them, life as we know it could not exist, yet the exact definition of the hydrogen bond*" [4]. As such, it should be highlighted that the electronegativities of Y and X are limited because the intermolecular contact Y···H is often noncovalent [5], whereas the moiety H—X is conceived as purely covalent. In a section of the journal Nature called "News and Views" Martin and Derewenda [6] provided a review of the historical background of the hydrogen bond, whose content rightly delineated the covalent character of this interaction. Dealing with this in depth, in a preliminary paper [7] and later in a review [8], Grabowski and collaborators presented a global profile adjusted to predict covalency in every interaction type known up to the present time, in which the hydrogen bond is one of the most contemplated in this regard.

Some time ago, however, Crabtree's research group [9] introduced a new idea of intermolecular contacts, wherein the

electronegative element Y became dispensable. Thus, would two hydrogen atoms interact one with one another? Although the "hydrogen···hydrogen" is a plausible interaction [10], the dihydrogen bond M—H···H—X (with M = alkaline earth metal) is the new intermolecular cornerstone to be considered [11]. Nowadays, dihydrogen bonds are drawing scientific interest from many researches centers, mainly those whose leaders are chemists and physicists, and through their studies on crystal structures obtained by means of X-ray crystallography, it is clear that the solid state of the matter, biochemical processes involving enzymes or proteins, and proton transfer reactions are greatly supported by the dihydrogen bond properties [12].

In a recent publication, we have detailed a theoretical investigation of dihydrogen bonds in systems whose spectroscopy characteristics are quite particular; some of them displaying red- and blue-shifts in the stretch frequencies of their proton donors [13]. However, since blue is a spectroscopy signal inherent to the C—H bond of the fluoroform (HCF_3), the existence of an uncommon red-shift for this bond has been found upon the formation of the dihydrogen-bonded complex $NaH \cdots HCF_3$ [13]. This occurs because weakly bound complexes are formed in hydrides (M—H) derived from lithium (M = Li), beryllium (M = Be), and magnesium (M = Mg), whereas the complexes with the strongest bonds are stabilized by sodium. Nevertheless, it is not mandatory that intermolecular complexes are formed via only one hydrogen bond [14]. Bifurcate hydrogen bonds or even those possessing multiple sites with donors (Lewis acid) and acceptors (lone-electron pairs or π clouds) of protons can lead to the formation of ternary systems [15–19], whose stability is arguably improved. In this context,

* Tel.: +55 77 3614 3152.
E-mail address: boazgaldino@gmail.com

the aim of this study was to investigate the formation of ternary dihydrogen-bonded complexes [20], such as $NaH\cdots2(HCF_3)$ and $NaH\cdots2(HCCl_3)$, and a comparative analysis of their properties with those obtained for the binary complexes $NaH\cdots HCF_3$ and $NaH\cdots HCCl_3$ [13] was carried out.

In addition to fluoroform, chloroform ($HCCl_3$) was also considered in this study, since a red-shift is the only vibrational event observed in the H—C bond of $HCCl_3$. In practice, it is very important to ascertain whether the appearance of a red- or blue-shift is occasioned by the interaction strength or by the specific oscillator of the proton donor type. Moreover, it should be emphasized that NaH is being extensively tested as a powerful Lewis base because the formation of the ternary bound systems requires a high charge density concentration, otherwise the simultaneous interaction with two proton donors, either HCF_3 or $HCCl_3$, cannot occur. If this is the case, the overall goal of this study can only be reached through a computational chemistry strategy for studying intermolecular systems [21]. Initially, a standard calculation level was chosen according to its accuracy in determining the intermolecular structures precisely in a deep potential energy surface. According to the theoretical literature, the application of the Density Functional Theory (DFT) [22] in studies on dihydrogen-bonded systems is a routine task which provides satisfactory results on the structure [23], interaction energy [24], infrared stretching frequencies [25], and topological sites formed by high and low concentrations of charge density [26]. In line with this, the B3LYP popular hybrid was used herein, but in association with 6-311++G(3df,3pd), specifically chosen for its capacity to minimize the overlap errors in the region of intermolecular contact beyond the basis set limit [27,28]. In agreement with the studies of Kaczor et al. [29] and Louis et al. [30], B3LYP/6-311++G(3df,3pd) represents the appropriate level of theory to be used in the investigation of the dihydrogen-bonded complexes, and a good performance in predicting a parameter series: structural, electronic, vibrational, and topological, is expected.

In addition to the structure, spectroscopic characteristic and interaction energy determined through the arguments of the supermolecule approach [31], there are some electronic parameters inherent to intermolecular systems that need to be analyzed. One of them is the charge transfer between the orbital frontier of HOMO and LUMO, which are the channels mimicking the Lewis concept of base and acid [32], respectively. In this case, these species correspond to sodium hydride and fluoroform or chloroform. In order to explore intermolecularly the electronic fluxes between the orbitals of these molecules, the charge transfer analysis will be performed through the Charge from Electrostatic Potentials using a Grid-based algorithm (CHELPG) [33]. Several atomic charge approaches are available [34], and the CHELPG was selected because its computational effort required to compute the one-electron integral of the Molecular Electrostatic Potential (MEP) is very low, and its efficiency in studies on intermolecular systems is widely established [35,36], in particular in the interpretation of the vibrational red- and blue-shifts of hydrogen-bonded complexes [37]. Nevertheless, it was assumed that a comparative study with traditional atomic charge partitions would be useful, mainly Mulliken population analysis, which was performed [38]. It is widely established that the Mulliken approach is highly basis-set dependent [39], which is very promising because a complete Pople algorithm is applied herein [40]. It is essential that the intermolecular nature is revealed, particularly with regard to the orbital configuration of the donating proton (H—X) and hydride (M—H). It is due to the applicability and efficacy of the Natural Bond Orbital (NBO) [41] that the interaction zoo of M—H⋯H—X can be modeled in terms of polarization and electronic delocalization at the overlapping wave function.

Besides the computation of the charge transfer, through which, indirectly, slight intermolecular electronic densities can be found

for the interaction between NaH and HCF_3 or $HCCl_3$, it is vital to determine quantitatively the charge density, and thereby verify the existence of the dihydrogen-bonded system [13]. This scenario can only be attained by using the application of the Quantum Theory of Atoms in Molecules (QTAIMs) [42], through which the intermolecular systems are characterized by means of the pure charge density (ρ) and the second derivative or differential operator of its gradient, namely the Laplacian (∇^2_ρ) calculated at the Bond Critical Point (BCP), and through the virial theorem incorporating the kinetic and potential energies:

$$2G + U = \left(\frac{\hbar^2}{4m}\right)\nabla^2\rho \qquad (1)$$

Furthermore, the overall goal of the QTAIM is not only to model intermolecular systems or electronic structures as a whole, but ideally the chemical bond and its covalent profile. In other words, if the noncovalence on Na—H⋯H—X (with Y = Na—H) or even the covalence on H—X (with X = CF_3 or CCl_3) are preserved after complexation of the binary systems $NaH\cdots HCF_3$ and $NaH\cdots HCCl_3$, such trends must be examined in the ternary systems $NaH\cdots2(HCF_3)$ and $NaH\cdots2(HCCl_3)$ because their stabilization energies are presumably lowest since strongest intermolecular strengths with higher covalence are often observed.

2. Computational details

The optimized geometries of the $NaH\cdots HCF_3$, $NaH\cdots HCCl_3$, $NaH\cdots2(HCF_3)$ and $NaH\cdots2(HCCl_3)$ complexes were determined at the B3LYP/6-311++G(3df,3pd) level of theory with all calculations carried out in the GAUSSIAN quantum package version 03 [43]. The calculations of the CHELPG atomic charges, Mulliken and NBO population analysis were determined applying the routine of GAUSSIAN 03, but the balances of the charge transfers from HOMO (NaH) to LUMO (HCF_3 or $HCCl_3$) were computed as follows: molecular or total charge transfer: $\Delta Q = Q_{(Na-H)complex} - Q_{(Na-H)monomer}$. The measurement of the intermolecular energies (ΔE) was carried out with the supermolecule approach as follows: $\Delta E_{binary} = E_{(Na-H\cdots H-X)} - E_{(Na-H)} - E_{(H-X)}$ and $\Delta E_{ternary} = E_{[Na-H\cdots2(H-X)]} - E_{(Na-H)} - 2E_{(H-X)]}$ with X = CF_3 or CCl_3. The refinement of these bonding energies (ΔE_{binary} and $\Delta E_{ternary}$) was carried out in accordance with the counterpoise correction from the Boys and Bernardi Basis Sets Superposition Error (BSSE) [44] together with the contribution of the Zero Point vibrational Energy (ZPE) [45], such that: $\Delta E^C = \Delta E + BSSE + \Delta ZPE$ for each individual binary and ternary system. The topological integrations of the QTAIM formalism were processed through the GAUSSIAN 03 program, although some additional calculations were performed in the versions 11.12.19 and 1.0 of the AIMAll [46] and AIM2000 [47] academic programs, respectively.

3. Results and discussion

3.1. Structures and vibrational spectra

Fig. 1 illustrates the optimized geometries of the binary complexes $NaH\cdots HCF_3$ (**I**) and $NaH\cdots HCCl_3$ (**II**), as well as the ternary complexes $NaH\cdots2(HCF_3)$ (**III**) and $NaH\cdots2(HCCl_3)$ (**IV**). In Table 1 these values are presented again together with the most important deformations of the structures of the sodium hydride, fluoroform, and chloroform, such as those which occurred in the Na—H and H—C bonds. A slight reduction in the bond length of the sodium hydride was computed, with δr(Na—H) values for **I** and **II** of −0.0006 Å and −0.0020 Å, respectively. On the other hand, the variations of 0.0046 Å and 0.0166 Å calculated for H—X (X = CF_3 or CCl_3) of **I** and **II**, respectively, cannot be considered slight

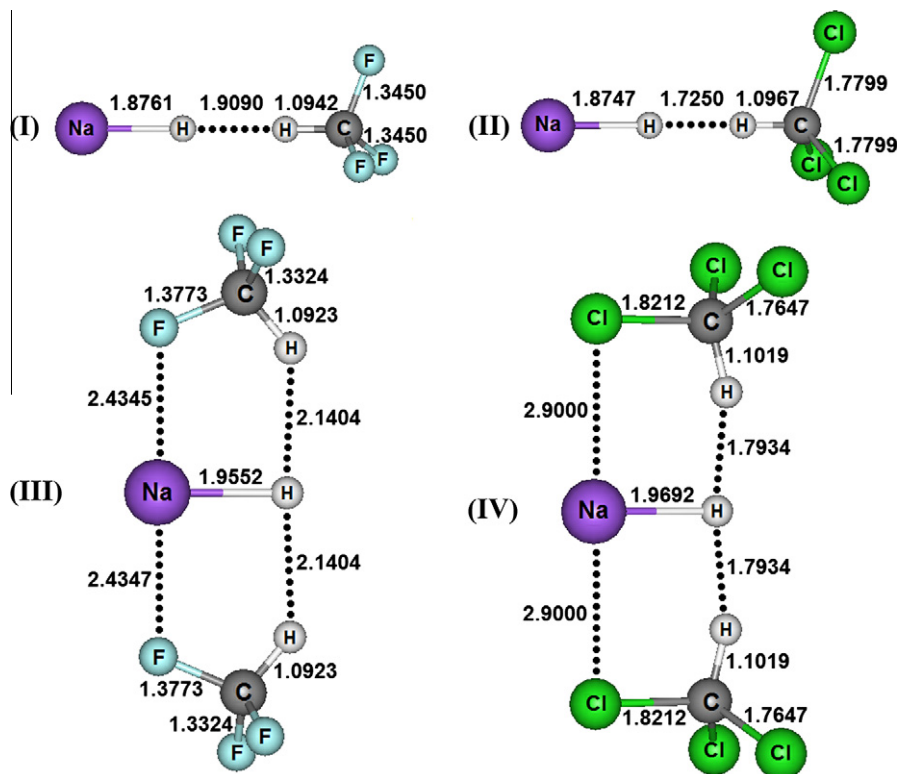**Fig. 1.** Optimized geometries of the binary NaH···HCF$_3$ (**I**) and NaH···HCCl$_3$ (**II**), as well as of the ternary complexes NaH···2(HCF$_3$) (**III**) and NaH···2(HCCl$_3$) (**IV**) obtained from B3LYP/6-311++G(3df,3pd) calculations.

Table 1
Structural and vibrational parameters of the **I** and **II** binary dihydrogen complexes, as well as for of the **III** and **IV** ternary alkali–halogen complexes obtained through the B3LYP/6-311++G(3dp,3df) calculations.

Parameters	Complexes			
	I	**II**	**III**	**IV**
$\delta r_{(Na-H)}$	−0.0006	−0.0020	0.0785	0.0925
$\delta r_{(H-X)}$	0.0046	0.0166	0.0027	0.0218
$\delta r_{(C-W)}$	0.0063	0.0048	0.0386	0.0461
$R_{(H\cdots H)}$	1.9090	1.7250	2.1404	1.7934
$R_{(Na\cdots W)}$	–	–	2.4345	2.9000
$\upsilon_{(Na-H)}$	1245.80	1265.62	1079.76	1031.31
$I_{(Na-H)}$	351.7	539.35	565.80	233.62
$\delta\upsilon_{(Na-H)}$	+77.87	+97.69	−88.17	−136.62
$I_{(Na-H),c}/I_{(Na-H),m}$	1.63	2.49	2.62	1.08
$\upsilon_{(H-X)}$	3039.01	2929.71	3080.95	2848.7
$I_{(H-X)}$	57.52	510.93	52.47	1228.03
$\delta\upsilon_{(H-X)}$	−82.65	−257.77	−40.71	−338.77
$I_{(H-X),c}/I_{(H-X),m}$	2.13	305.94	1.94	735.34
$\upsilon_{(C-W)}$	686.51	366.74	683.46	361.29
$I_{(C-W)}$	20.91	0.68	43.60	0.61
$\delta\upsilon_{(C-W)}$	−6.69	+1.03	−9.74	−3.42
$I_{(C-W),c}/I_{(C-W),m}$	1.70	4.53	3.55	4.06
$\upsilon_{(H\cdots H)}$	91.71	97.68	69.16	81.28
$I_{(H\cdots H)}$	0.02	0.12	0.34	0.00(1)
$\upsilon_{(Na\cdots W)}$	–	–	47.54	35.89
$I_{(Na\cdots W)}$	–	–	1.06	0.65

Values of υ and I are given in cm^{-1} and km mol^{-1}, respectively; values of R and r are given in Å; X = CF$_3$ or CCl$_3$; W = F or Cl; values of $\upsilon_{(Na-H)}$ and $I_{(Na-H)}$ for the sodium hydride monomer are 1167.93 cm^{-1} and 215.93 km mol^{-1}, respectively; values of $\upsilon_{(H-X)}$ and $I_{(H-X)}$ for the fluoroform monomer are 3121.66 cm^{-1} and 26.95 km mol^{-1}, respectively; values of $\upsilon_{(H-X)}$ and $I_{(H-X)}$ for the chloroform monomer are 3187.48 cm^{-1} and 1.67 km mol^{-1}, respectively.

enhancements. It can be seen that the differences between the bond length variations of **II** in comparison with **I** are enormous. On the other hand, the C—W bond lengths are moderately to highly varied, and the respective values are 0.0063 Å and 0.0048 Å for the binary systems **I** and **II**. Up to now, variations in C—W (W = F or Cl) should not be preferential since the dihydrogen bond strength is directly influenced by the Na—H and H—C bonds and vice versa. As such, the values of 1.9090 Å and 1.7250 Å for the dihydrogen bond distances indicate that chloroform provides a more strongly bound interactive complex, and therefore more accentuated changes were verified in the following bonds: Na—H and H—C.

Regarding the ternary dihydrogen complexes **III** and **IV**, their dihydrogen bond distances are longer in comparison with the binary complexes. In a contrasting reflection on this, it is well-known that ternary hydrogen complexes formed by π or lone-electron pairs as proton acceptors are much more stable than binary complexes in terms of their intermolecular distances [14–19]. This observation is not proven here, but it is common because increases in double or bifurcate dihydrogen bond distances are well-known [48,49], e.g., dihydrogen-bonded systems formed by ethyl cation and beryllium hydride [50]. From the structural viewpoint, it can be seen that the values of 2.1404 Å (**III**) and 1.7934 Å (**IV**) for H···H are shorter than the sum of the van der Waals radii for the hydrogen atom, whose tabulated datum is 1.09 Å [51]. Moreover, a novel interaction so-called alkali–halogen bond (the alkali being sodium) occurs between sodium and fluorine (Na···F) or chlorine (Na···Cl). This statement is supported by the van der Waals radii of Na (2.27 Å), F (1.47 Å), and Cl (1.75 Å), whose summed values of 3.74 Å (Na + F) and 4.02 Å (Na + Cl) are longer than the corresponding results of 2.4345 Å (**III**) and 2.9000 Å (**IV**) shown in Fig. 1. Corroborating these findings, significant variations of 0.0386 Å and 0.0461 Å in the C—W bonds can be noted, which was not observed in the binary systems. On comparing binary with ternary complexes, a change in the sodium hydride can be noted. In **I** and **II**, the Na—H bond shows a reduction in its length whereas an increase in the Na—H bond length was detected in the ternary systems **III** and **IV**. These contrasting structural profiles certainly
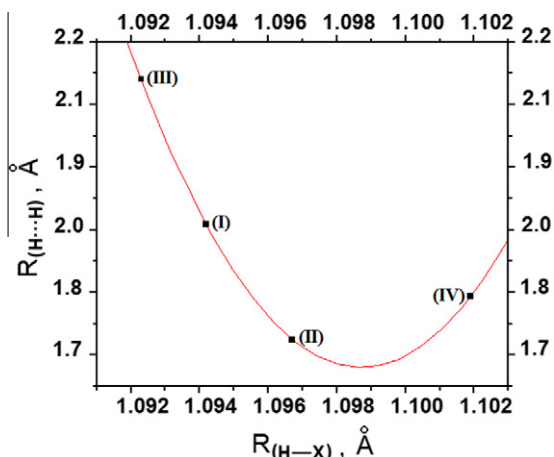
Fig. 2. Relationship between the values of the distances $R_{(H\cdots H)}$ and $R_{(H-X)}$ obtained from B3LYP/6-311++G(3df,3pd) calculations.

lead to very distinct vibrational effects, which are the spectroscopy cornerstone for identifying the formation of intermolecular interactions, that is, hydrogen bonds [52], dihydrogen bonds [53], or even the alkali–halogen bonds introduced herein.

In order to obtain accurate structural correlations in intermolecular systems, some time ago Grabowski [54] presented an interesting relationship between the dihydrogen bond distances and bond lengths of proton donors according to the Bond Valence model [55]. The results reported herein were collected through the application of the B3LYP/6-311++G(3df,3pd) level of theory, but the profile featured in Fig. 2 seems to be very similar to those generated by the BV model. An extremely close relationship between $R_{(H\cdots H)}$ and $R_{(H-X)}$ is established by means of the polynomial coefficient R^2 of 0.99:

$$y(R) = 11,190(R)^2 - 24,590(R) + 13,510, \quad R^2 = 0.99 \quad (2)$$

There is a trend toward weakness in the bonds of the proton donors (H—X) of HCCl$_3$ from **II** up to the formation of **IV**. Thus, the stretch frequency of the oscillator $\upsilon_{(H-X)}$ is downward readjusted by -81.00 cm^{-1} ($\delta\upsilon_{(H-X)IV} - \delta\upsilon_{(H-X)II}$) followed by an absorption intensity ratio of 2.4, which together are red-shift signals in the vibrational spectrum, whose theoretical values are also given in Table 1. On the other hand, HCF$_3$ behaves as a blue-shifted proton donor because the value of its stretch frequency $\upsilon_{(H-X)}$ is upward shifted by $+42$ cm^{-1} ($\delta\upsilon_{(H-X)III} - \delta\upsilon_{(H-X)I}$), which is a widely-established spectroscopic characteristic for fluoroform [56]. In total corroboration with recent investigations [57], it is demonstrated that intermolecular complexes with shorter distances such as those observed in **IV** are identified by red-shift events on the stretch frequencies of their proton donors. In contrast to this, stretch frequencies of longer intermolecular distances are shifted to blue, e.g., complex **III**.

Besides the chemical shifts, Table 1 also lists the values for the new vibrational modes, commonly referred as intermolecular infrared stretch frequencies $\upsilon_{(H\cdots H)}$ and their absorption intensities $I_{(H\cdots H)}$ for the systems **I**, **II**, **III**, and **IV** investigated in this study. Applying the same comparative procedure of analysis used for the binary systems to the ternary systems, blue-shifts in sodium hydride were determined, whose values for **I** and **II** were $+77.87$ cm^{-1} and $+97.69$ cm^{-1}, respectively. In contrast, red-shifts were identified in the H–X oscillator for which, although the value of -257.7 cm^{-1} in **II** is large, the result of -82.65 cm^{-1} for **I** is unusual because fluoroform is a standard proton donor model with blue-shift characteristic [57]. Hence, some chemical shifts, such as the red of -6.69 cm^{-1} and the blue of $+1.03$ cm^{-1}, are inconsis-

tent with the observation of the systematic increase in the C—F and C—Cl bond lengths of **I** and **II**. Although the C—F and C—Cl bond lengths are those with the largest variations in the ternary complexes, their stretch frequencies are slightly downward shifted, corresponding to lower red-shift values of -9.74 cm^{-1} and 3.42 cm^{-1} for **III** and **IV**, respectively. These red shifts are associated with those observed for Na—H, in which the computed values of -88.17 cm^{-1} and -136.62 cm^{-1} for **III** and **IV** are surprising because blue-shift effects of $+77.87$ cm^{-1} and $+97.69$ cm^{-1} have been previously observed for this oscillator upon the formation of the binary systems **I** and **II**. All of these red- and blue-shift effects can be explained through structural analysis, i.e., elongation and reduction of the corresponding bond length. For both sodium hydride and halocarbon bonds (C—F or C—Cl) it should be noted that no correlation between the magnitude of the red- and blue-shifts and the absorption intensity ratios was found. Besides the downward shift in the stretch frequencies, the specialized literature reports that red-shift effects for proton donors are often characterized by an increase in the absorption intensities [58], which in this study may also occur in the case of blue-shift effects. In other words, there is no tendency for chemical shifts, of red or blue origin, according to the absorption intensity.

In relation to the stretch frequencies $\upsilon_{(H\cdots H)}$ of the dihydrogen bonds, their values are in good agreement with the intermolecular distances. Note that $R_{(H\cdots H)}$ is shorter in **II**, although its $\upsilon_{(H\cdots H)}$ value of 97.68 cm^{-1} is slightly higher than the 91.71 cm^{-1} of **I**. In satisfactory agreement with traditional bound complexes [59], the stretch frequencies $\upsilon_{(H\cdots H)}$ presented extremely low absorption intensities, which is spectroscopically inherent to any intermolecular interaction type. In conformity with the results of the intermolecular distances debated elsewhere, the ternary complexes presented weak dihydrogen bond stretch frequencies, whose values of 69.16 cm^{-1} (**III**) and 81.28 cm^{-1} (**IV**) are accompanied by the lowest results for absorption intensity. With regard to the stretch frequencies of the alkali–halogen bonds, their values calculated by the B3LYP/6-311++G(3df,3pd) level show a direct correlation with the bond lengths, as can be seen by the linear coefficient R^2 of 0.95 graphically illustrated in Fig. 3.

$$y(\upsilon) = -52.5(R) + 183.5, \quad R^2 = 0.96 \quad (3)$$

Since $\upsilon_{(Na\cdots F)}$ and $\upsilon_{(Na\cdots Cl)}$ are modes containing low absorption intensities in the range of 0.65–1.06 km mol^{-1}, their localizations on the vibrational spectrum could only be obtained following preliminary structural identifications. Thus, although both alkali–halogen bonds Na$\cdots$F and Na$\cdots$Cl have been discovered, they are
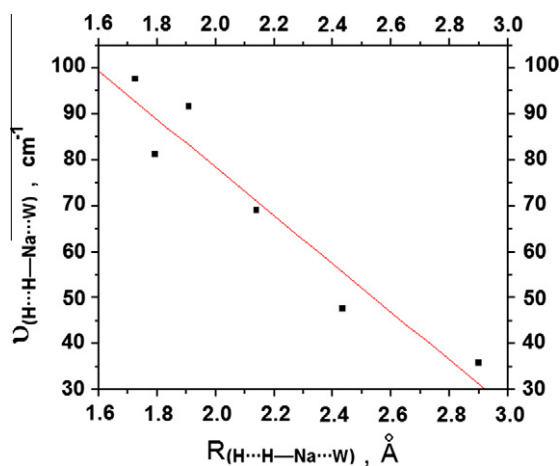

Fig. 3. Relationship between the values of the $\upsilon_{(H\cdots H)}$ and $R_{(H\cdots H)}$ obtained from B3LYP/6-311++G(3df,3pd) calculations.

not sufficiently strongly bound to overestimate the stabilization of the ternary complexes. Therefore, the H···H dihydrogen bonds are still predominant in this regard.

3.2. Stabilization energy, dipole moment, and charge transfer

In this study, the stabilization energy is referred as the intermolecular energy. However, henceforth they will be interpreted as dihydrogen bond energies in **I** and **II**, where the intermolecular cooperativity between dihydrogen bonds versus alkali–halogen bonds in **III** and **IV** should be taken into account. Thus, the energy values for the pure dihydrogen bonds $\Delta E^C_{(H\cdots H)}$, as well as the cooperative energies of the dihydrogen–alkali–halogen bonds $\Delta E_{(H\cdots H-Na\cdots W)}$, are listed in Table 2. Besides the structural and vibration results, the corrected values for $\Delta E^C_{(H\cdots H)}$ of -19.67 kJ mol^{-1} and -23.10 kJ mol^{-1} clearly verify that the binary complex **II** is more strongly bound than **I**. Indeed, it has been established that chloroform provides a higher degree of stabilization in comparison with fluoroform upon formation of the dihydrogen bond. In ternary systems, however, the corrected values for $\Delta E_{(H\cdots H-Na\cdots F)}$ of -46.88 kJ mol^{-1} and $\Delta E_{(H\cdots H-Na\cdots Cl)}$ of -63.15 kJ mol^{-1} also sustain the systematic stabilization discussed above, wherein **IV** with the HCCl$_3$ proton donor is more strongly stabilized than **III** bound with HCF$_3$. For this discussion, a brief comment should be made with regard to the values for $\Delta E_{(H\cdots H-Na\cdots F)}$ and $\Delta E_{(H\cdots H-Na\cdots Cl)}$, which reflect the contribution of four interactions, two of them being dihydrogen bonds (H···H) and the others the alkali–halogen bonds (Na···F and Na···Cl) introduced herein. This is a typical cooperative example [60,61] and, as such, it is not possible to compute accurately the strength of each isolated interaction because one uniform energy distribution occasioned by the symmetry of the ternary complexes is rooted in their electronic structures. Such cooperative energy diffusion leads to a weakness of the interaction mainly with regard to the dihydrogen

bonds in ternary systems, as discussed in this paper. This is an unlikely behavior because hydrogen complexes formed by multiple [62,63] interactions often provide intermolecular strengthening and, once again, this does not occur in the case of dihydrogen bonds.

A simple procedure to account for each cooperative energy value of $\Delta E_{(H\cdots H)}$, $\Delta E_{(Na\cdots F)}$, and $\Delta E_{(Na\cdots Cl)}$ is by taking into account the linear relationship between the intermolecular energy and chemical shifts of the proton donors, particularly when compared with the new vibrational modes. This coupling of the properties successfully predicts the interaction strength of hydrogen-bonded complexes. In this study, the cooperative energy incorporated into **III** and **IV** is not equally distributed along the $\Delta E_{(H\cdots H)}$ dihydrogen bonds or the $\Delta E_{(Na\cdots Cl)}$ and $\Delta E_{(Na\cdots F)}$ alkali–halogen bonds computed from the supermolecule (subtracting the total energy from the subsystems of interest) [31]. Even with the linear relationship between the structure and the spectrum plotted in Fig. 3, the highest interaction energies relate to the shortest bonding distances in a partially covalent zone, which has been highlighted by Szatyłowicz [64]. In Fig. 4, two profiles should be analyzed, which reflect the linear relationship (y_1) between the interaction energies and the new vibrational modes of the H···H dihydrogen bonds in **I–IV**. Nevertheless, if the contributions of the alkali–halogen bond energies are included, a parabolic relationship (y_2) is conceived, such as that obtained by Jabłoński and Solà [65]. It can be seen that although the Na···Cl and Na···F interaction strengths are extremely low, the energy distribution is considerably changed by them.

$$y_1(\Delta E^C) = -0.39(\upsilon) + 16, \quad R^2 = 0.99 \tag{4}$$

$$y_2(\Delta E^C) = -0.004(\upsilon)^2 + 0.03(\upsilon) - 12, \quad R^2 = 0.99 \tag{5}$$

Another important parameter often used to predict the intermolecular strength is the variation in the dipole moment ($\Delta\mu = \mu_{supermolecule} - \Sigma\mu_{monomers}$) computed from monomers ($\Sigma\mu_{monomers}$) up to the formation of the supermolecule entity ($\mu_{supermolecule}$). Motivated by induced effects, it is widely known that the more deformed the intermolecular systems the more strongly bonded they are [25,66]. Thus, the $\Delta\mu$ values of 1.26D and 1.82D (see Table 2) show that **II** is more deformed by the complexation, which leads to the affirmation that its interaction strength is overestimated. Upon formation of the ternary complexes, however, the polarizabilities of $-5.53D$ (**III**) and $-3.62D$ (**IV**) are lower in comparison with the isolated monomers, such as NaH, HCF$_3$, and HCCl$_3$. This finding is similar to the observations

Table 2
Values of the interaction energies of the **I** and **II** binary dihydrogen complexes, as well as the estimated ones of the **III** and **IV** ternary alkali–halogen complexes obtained through the B3LYP/6-311++G(3dp,3df) level of theory. Dipole moment changes ($\Delta\mu$), charges transfer amounts (ΔQ), and NBO parameters are also presented.

Parameters	Complexes			
	I	**II**	**III**	**IV**
$\Delta E_{(H\cdots H)}$	−25.15	−29.54	–	–
$\Delta E^C_{(H\cdots H)}$	−19.67	−23.10	−11.72	−15.78
$\Delta E_{(H\cdots H-Na\cdots W)}$	–	–	−58.72	−72.10
$\Delta E^C_{(H\cdots H-Na\cdots W)}$	–	–	−46.88	−63.15
$\Delta E_{(Na\cdots W)}$	–	–	−8.05	−6.97
ΔZPE	3.34	3.03	6.93	5.41
BSSE	2.14	3.41	4.91	3.53
$\Delta\mu$	1.26	1.82	−5.53	−3.62
$\Delta Q^{CHELPG}_{(H\cdots H)}$	−0.002	−0.024	–	–
$\Delta Q^{CHELPG}_{(H\cdots H-Na\cdots W)}$	–	–	0.002	−0.043
$\Delta Q^{Mull}_{(H\cdots H)}$	0.159	0.222	–	–
$\Delta Q^{Mull}_{(H\cdots H-Na\cdots W)}$	–	–	−0.087	−0.557
$\Delta Q^{NBO}_{(H\cdots H)}$	0.029	0.053	–	–
$\Delta Q^{NBO}_{(H\cdots H-Na\cdots W)}$	–	–	0.028	0.092
$p_{(H-X)}$	60.39	66.52	60.63	67.40
$s_{(H-X)}$	32.63	32.94	32.72	33.97
$\Delta E^2 \sigma_{(M-H)}-\sigma^*_{(H-X)}$	42.34	63.62	29.28	78.49
$\Delta E^2 n_{(C-W)}-\sigma^*_{(Na-X)}$	–	–	16.88	33.72

Values of $\Delta\mu$ are given in Debye (D); values of ΔE, ΔZPE, and BSSE are given in kJ mol^{-1}; values of ΔQ are given in electronic units (e.u.); W = F or Cl; about the ternary systems, their values of $\Delta E_{(Na\cdots W)}$ and $\Delta E^C_{(H\cdots H)}$ were not corrected by the BSSE approach, although their amounts were estimated from the corrected results, $\Delta E^C_{(H\cdots H)}$; p and s represent the polarization and s-character of the H—X bond, whose values are given in %.
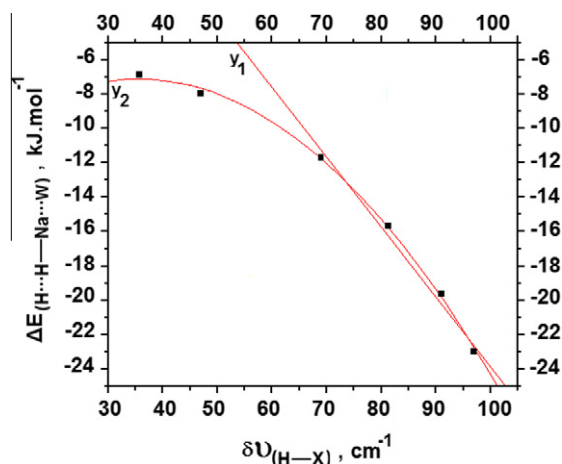

Fig. 4. Relationship between the values of the interaction energies and new vibrational modes obtained from B3LYP/6-311++G(3df,3pd) calculations.

documented by Parra and Zeng [67]. Note that **IV** is not as sensitive to the dipole moment variation as **III**. This again indicates the reduced stability of **III** and **IV**, in which the distributive energy per interaction is quite low. According to several reports [68–70], one of the most efficient criteria to validate the variations in the dipole moment is the computation of the charge transfer (ΔQ) via distinct available approaches, and the CHELPG values for **I**, **II**, **III** and **IV** are given in Table 2. As explained previously, $\Delta Q_{(H \cdots H)}^{CHELPG}$ is associated with the electronic quantity lost by sodium hydride to HCF_3 and $HCCl_3$. For the binary complexes, the higher value of -0.024 a.u. indicates that **II** is much more strongly bound than **I**. Nevertheless, a positive balance of charge transfer would be expected since hydride sodium must transfer electrons either to HCF_3 or $HCCl_3$, which was not observed. In contrast, a loss of charge density is observed for these halocarbons, which can be treated as typical Lewis bases instead of acids. With regard to ternary complexes, unfortunately neither correlation could be obtained, but the variation of charge density in **IV** is also consistent with hydride sodium being a Lewis acid, in which case both the fluoroform and chloroform would be bases.

The charge transfer from sodium hydride to halocarbons may explain the interaction strength. In this regard, the values obtained in the Mulliken analysis given in Table 2 successfully describe this scenario. In the binary systems, the greater charge transfer loss of 0.222 e.u. for NaH occurs due to its stronger interaction with $HCCl_3$, which corroborates the higher dihydrogen bond energy computed for **II**. It is worth noting that the weaker interaction strength in **I** is associated with its smaller charge transfer of 0.159 e.u. In the ternary systems, both the **III** and **IV** accumulate charge on NaH, whose values are -0.087 e.u. and -0.557 e.u., respectively. This means that a retroactive charge transfer occurs in NaH caused by its mutual interaction with two proton donors, either HCF_3 or $HCCl_3$. In other words, the charge is concentrated by $\Delta Q_{(H \cdots Na - Na \cdots W)}^{Mull}$ and simultaneously depleted by $\Delta Q_{(Na \cdots F)}^{Mull}$ or $\Delta Q_{(Na \cdots Cl)}^{Mull}$, respectively. It can be seen that the greatest charge transfer of -0.557 e.u. was computed for **IV**, so a good agreement with its stronger interaction strength in comparison with **III** is demonstrated. In fact, it is not usual that the charge transfer measurement based on the Mulliken protocol provides efficient interpretations involving the intermolecular parameters. Herein, the results for $\Delta Q_{(H \cdots H)}^{Mull}$ show good interpretation and satisfactory correlations with the interaction strengths. Regarding NBO, the values of $\Delta Q_{(H \cdots H)}^{NBO}$ and $\Delta Q_{(H \cdots H - Na \cdots W)}^{NBO}$ must be interpreted carefully. For example, the charge transfer values of 0.029 e.u. and 0.028 e.u. indicate similar interaction strength between **I** and **III**, which is an inconsistency because the results of $\Delta E_{(H \cdots H)}^{C}$ are extremely distinct. The same profile is not observed between **II** and **IV** but, particularly among binary and ternary systems, the NBO charge transfer is the only one that characterizes NaH as Lewis base. Moreover, a clear explanation for the strength of the interaction between **I** and **II** is conceived, as well as that between **III** and **IV**.

Table 2 not only shows the charge transfer but also other NBO values. One of these is the polarization p of the H–X bond, which is in good agreement with the values of $\Delta Q_{(H \cdots H)}^{NBO}$ and $\Delta Q_{(H \cdots H - Na \cdots W)}^{NBO}$ and is well correlated with the interaction energy. This means that considerable polar deformations in the proton donors are caused by the higher dihydrogen bond energy of **II** (-23.10 kJ mol^{-1}) in comparison with **I** (-19.67 kJ mol^{-1}), and later the dihydrogen–alkali–halogen from **III** (-46.88 kJ mol^{-1}) rather than **IV** (-63.15 kJ mol^{-1}). Additionally, it is not only through the NBO analysis that the interaction strength between candidates for Lewis acids or bases can be revealed, but also in the light of electronic delocalization in the overlapping wave functions, such as $\sigma(M-H) - \sigma^*(H-X)$ for the dihydrogen bonds

(M–H$\cdots$H–X) and $n(C-W) - \sigma^*(Na-H)$ for the alkali–halogen ones (C–W$\cdots$Na–H). This is well-known as the second-order (ΔE^2) perturbation theory energy, calculated according to the donor orbital occupancy (q), the orbital energy difference between donor (d) and acceptor (a), and the Fock matrix element (F) [71]:

$$\Delta E_{\sigma(MH) \to \sigma^*(HX)} = q_{\sigma(MH)\sigma^*(HX)} \frac{\langle \sigma(MH)|F|\sigma^*(HX)\rangle^2}{[\varepsilon_{\sigma(MH)} - \varepsilon_{\sigma^*(HX)}]} \quad (6)$$

$$\Delta E_{n(CW) \to \sigma^*(NaH)} = q_{n(CW)\sigma^*(NaH)} \frac{\langle n(CW)|F|\sigma^*(NaH)\rangle^2}{[\varepsilon_{n(CW)} - \varepsilon_{\sigma^*(NaH)}]} \quad (7)$$

From these equations, the electronic delocalization values presented in Table 2 corroborate well with the dihydrogen bond energies computed through the application of the traditional supermolecule approach [31], and chloroform provides the formation of a stronger intermolecular bonded system (**II**). With regard to the total interaction strength (H$\cdots$H–Na$\cdots$W) in the ternary complexes, the value of 78.49 kJ mol^{-1} for $\Delta E \sigma_{(M-H)}^2 - \sigma_{(H-X)}^*$ agrees satisfactorily with the result of -63.15 kJ mol^{-1} for $\Delta E_{(H \cdots H - Na \cdots W)}^{C}$. In fact, there was a predominant contribution of the halogen bond, which was quantified by the results of 16.88 kJ mol^{-1} and 33.72 kJ mol^{-1} for $\Delta E^2 n_{(C-W)} - \sigma_{(Na-H)}^*$ in the **III** and **IV** systems, respectively. It is worth mentioning that the lone-electron pair of the chlorine yields not only a high NBO perturbation energy, but also a definitive stabilization for the ternary complex **IV**. These findings are partially in line with those reported for strongly bound systems with covalent character, such as $H_2O \cdots OH^-$, $NH_3 \cdots NH_4^+$, and $NH_3 \cdots HF$ [8], although the partial covalence is unapproachable via NBO at this current time.

3.3. QTAIM modeling: atomic radii, charge density concentration, virial theorem and comparative covalence

The pioneering Bader [72] elaborated the QTAIM foundation, engendered in accordance with a quantum mechanical formalism projected on the molecular surface of molecular systems [73], and subsequently of intermolecular systems [74]. From the equations of Schrodinger and Schwinger [75], an elegant set of equations rule an intrinsic QTAIM protocol through the connection between electronic cooperativity and the momentum of open systems with macroscopic chemical properties [76]. Nowadays, the QTAIM applicability reaches beyond the pure theoretical context, as reported by Abramov [77], Matta and Arabi [78], and others [79,80]. One of them is the spectroscopic nature of the harmonic vibrational modes previously discussed herein. Grabowski [81] idealized an interpretation for the chemical shifts (red or blue) of proton donors (H–X with X = CF_3 or CCl_3) based on BCPs localized along their bonds. It was established that variations in the atomic radii of carbon and hydrogen are the reason for the red- and blue-shift effects as follows: $\delta rX > \delta rH$ means red-shift while $\delta rX < \delta rH$ means blue-shift. Based on the results listed in Table 3, all red-shift values for the H–X oscillator are explained by the increase in the carbon radius in comparison with hydrogen because the carbon s-character (see Table 2) of 30.52% is not considerably enhanced in comparison with the results of 32.63% (**I**), 32.94% (**II**), 32.72% (**III**), and 33.97% (**IV**). Moreover, the carbon polarization of 56.78% is increased to 60.39% (**I**), 66.52% (**II**), 60.63% (**III**), and 67.40% (**IV**). In other words, higher polarization values are associated with larger atomic radii, and hence are the cornerstone to explaining the red-shift events in relation to the H–X bond. The blue-shifts in Na–H occur with $\delta rNa > \delta rH$, which is unusual since the very slight increase in the s-character from 99.18% (NaH monomer) to 99.48% in the **I** and **II** complexes cannot be associated with a significant decrease in polarization (% Na) in ranges of 13.23%

Table 3
Values of the atomic radii determined from the location of the BCP of the monomers, binary dihydrogen complexes, and ternary alkali–halogen systems.

Systems	Atomic radii					
	$r\text{Na}_{(Na-H)}$	$r\text{H}_{(Na-H)}$	$r\text{C}_{(C-W)}$	$r\text{W}_{(C-W)}$	$r\text{C}_{(C-H)}$	$r\text{H}_{(C-H)}$
NaH	0.8772	0.9969	–	–	–	–
HCF$_3$	–	–	0.4571	0.8816	0.7144	0.3563
HCCl$_3$	–	–	0.7790	0.9965	0.7043	0.3567
I	0.9965 (0.1192)	0.8796 (−0.1172)	0.4586 (0.0014)	0.8865 (0.0048)	0.7360 (0.0216)	0.3581 (0.0017)
II	0.9963 (0.1191)	0.8783 (−0.1185)	0.7751 (−0.0039)	1.0049 (0.0084)	0.7388 (0.0345)	0.3577 (0.0010)
III	1.0188 (0.1408)	0.9343 (−0.0625)	0.8963 (0.0171)	1.7065 (0.0187)	0.7373 (0.0229)	0.3347 (−0.0216)
IV	1.0239 (0.1467)	0.9432 (−0.0537)	0.7838 (0.0047)	1.0375 (0.0410)	0.7463 (0.0420)	0.3359 (−0.0208)

All values are given in Å; the atomic radii variations are listed in parentheses.

Table 4
QTAIM (BCP) topological descriptors of the binary dihydrogen complexes (**I** and **II**), as well as of the ternary alkali–halogen ones (**III** and **IV**) obtained through the Bader's calculations routine.

Parameters	Complexes			
	I	**II**	**III**	**IV**
$\rho_{(Na-H)}$	0.0341	0.0340	0.0301	0.0290
$\nabla^2\rho_{(Na-H)}$	0.1304	0.1307	0.1094	0.1068
$G_{(Na-H)}$	0.0314	0.0315	0.0263	0.0254
$U_{(Na-H)}$	−0.0303	−0.0304	−0.0252	−0.0241
$-G_{(Na-H)}/U_{(Na-H)}$	1.0380	1.0399	1.043	1.0526
$\rho_{(H-X)}$	0.3104	0.2978	0.3118	0.2943
$\nabla^2_{\rho(H-X)}$	−1.2660	−1.1610	−1.2834	−1.1386
$G_{(H-X)}$	0.0228	0.0307	0.0224	0.0301
$U_{(H-X)}$	−0.3622	−0.3507	−0.3657	−0.3450
$-G_{(H-X)}/U_{(H-X)}$	0.0630	0.0863	0.0613	0.0874
$\rho_{(C-W)}$	0.2817	0.1916	0.2576	0.1744
$\nabla^2_{\rho(C\cdots W)}$	−0.4129	−0.2553	−0.3959	−0.1979
$G_{(C-W)}$	0.3229	0.0658	0.0270	0.0600
$U_{(C-W)}$	−0.7491	−0.1956	−0.0639	−0.1695
$-G_{(C-W)}/U_{(C-W)}$	0.4311	0.3364	0.4225	0.3540
$\rho_{(H\cdots H)}$	0.0165	0.0240	0.0136	0.0243
$\nabla^2_{\rho(H\cdots H)}$	0.0328	0.0423	0.0244	0.0374
$G_{(H\cdots H)}$	0.0078	0.0114	0.0058	0.0104
$U_{(H\cdots H)}$	−0.0075	−0.0122	−0.0054	−0.0115
$-G_{(H\cdots H)}/U_{(H\cdots H)}$	1.047	0.9333	1.056	0.9036
$\rho_{(Na\cdots W)}$	–	–	0.0131	0.0101
$\nabla^2\rho_{(Na\cdots W)}$	–	–	0.0775	0.0452
$G_{(Na\cdots W)}$	–	–	0.0163	0.0092
$U_{(Na\cdots W)}$	–	–	−0.0132	−0.0071
$-G_{(Na\cdots W)}/U_{(Na\cdots W)}$	–	–	1.2200	1.2885

Values of ρ and $\nabla^2\rho$ are given in e/a$_o^3$ and e/a$_o^5$, respectively; values of G and U are given in atomic units (a.u.); X = CF$_3$ or CCl$_3$; W = F or Cl.

(monomer) to 9.95% (**I**) and 9.23% (**II**). Therefore, the blue-shift effect and length reduction are clearly evident for the Na—H bond.

The values for the topography descriptors computed following the QTAIM procedure for the **I–IV** systems are listed in Table 4. In agreement with the positive Laplacian values of 0.0328 e/a$_o^5$ and 0.0423 e/a$_o^5$ for the H···H dihydrogen bonds of the **I** and **II** binary systems, the Na—H bonds also present the same closed-shell character, whose ∇^2_ρ values are 0.1304 e/a$_o^5$ and 0.1307 e/a$_o^5$. There are, thus, two simultaneous noncovalent interactions in **I** and **II**, namely H···H and Na—H. Moreover, this contact leads to depletions in the electronic density, with values of 0.0165–0.0341 e/a$_o^3$ which are very low. In a recent paper, Grabowski et al. [82] predicted the covalent character of several binary and ternary system types by assuming a relationship (−G/U) between the positive values of the kinetic electronic energy density (G) and negative values of the potential electronic energy density (U) computed by the QTAIM routine through the BCP localization. Not surprisingly, considering the high dihydrogen bond energy of −23.10 kJ mol^{-1} and the shortest intermolecular distance of 1.7250 Å, it should be expected that the covalence partially dominates the intermolecular zoo of H···H in **II** instead of a noncovalent profile. Thus, it is stated that the dihydrogen bond systems formed by chloroform are not only more stable or strongly bound, but their intermolecular frameworks belong to the selective class of partially covalent systems.

In the case of the ternary complexes, an extension of the parameters discussed in relation to the binary complexes is carried out, although there are four interactions of which two are dihydrogen bonds and two alkali–halogen bonds. In practice, one analysis is performed for the dihydrogen bonds and other to the alkali–halogen bonds. The H···H dihydrogen bonds were identified by means of the intermolecular electronic density values $\rho_{(H\cdots H)}$ of 0.0136 e/a$_o^3$ (**III**) and 0.0243 e/a$_o^3$ (**II**) accompanied by their corresponding positive Laplacians $\nabla^2\rho_{(H\cdots H)}$ of 0.0244 e/a$_o^5$ (**III**) and 0.0374 e/a$_o^5$ (**IV**). In structural analysis, the presence of the Na···F and Na···Cl alkali–halogen bonds has been estimated empirically based on the van der Waals radii [83]. Herein, these interactions are quantum-mechanically validated through the $\rho_{(Na\cdots F)}$ and $\rho_{(Na\cdots Cl)}$ quantities of 0.0131 e/a$_o^3$ and 0.0101 e/a$_o^3$, as well as the positive $\nabla^2\rho_{(Na\cdots F)}$ and $\nabla^2\rho_{(Na\cdots Cl)}$ values of 0.0775 e/a$_o^5$ and 0.0452 e/a$_o^5$, respectively. The Na—H bonds remain noncovalent, as can be seen by the $\rho_{(Na-H)}$ values of 0.0301 e/a$_o^3$ (**III**) and 0.0290 e/a$_o^3$ (**IV**). In addition, the Laplancian fields are positive, which suggests noncovalence in Na—H. Generally, if the −G/U relationship is taken into account, the interactions of dihydrogen bonds or sodium hydride bonds seem to be noncovalent in nature. As an exception to this, the H···H dihydrogen bond in **IV** is partially covalent given the $-G_{(H\cdots H)}/U$ value of 0.9036. Even if dihydrogen bond pairing is formed in a hydride, its intermolecular partial covalent character is not lost in comparison with the binary system (**II**). Comparing the $-G_{(H\cdots H)}/U_{(H\cdots H)}$ values of 0.9333 (**II**) and 0.9036 (**IV**), clearly NaH···2(HCCl$_3$) is intermolecularly more covalent than NaH···HCCl$_3$, i.e., the contribution of the potential electronic energy density is greater in the dihydrogen bonds of the ternary complex. If the bound distances are evaluated, it can be affirmed that $R_{(H\cdots H)}$ of **II** < $R_{(H\cdots H)}$ of **I**. For the alkali–halogen bonds, a similar tendency was observed, which is mainly related to the high noncovalent character. The −G/U values of 1.2200 (**III**) and 1.2885 (**IV**) indicate a definitive weakness for Na···F and Na···Cl. In this regard, Fig. 5 plots a linear relationship between the −G/U results and the intermolecular distances computed at the B3LYP/6-311++G (3df,3pd) level of theory.

$$y(-G/U) = 0.32(R) + 0.37, \quad R^2 = 0.96 \qquad (8)$$

Although the interactions investigated herein presented very distinct energy values, individual examinations should be performed in order to verify their strengths. Some time ago, a new measure of the interaction strength based on structural data in association with the QTAIM topology was proposed [84]. Subsequently, we have suggested that good relationships can also be modeled through spectroscopic parameters instead of structural ones [85]. An equation to predict the interaction strength is con-
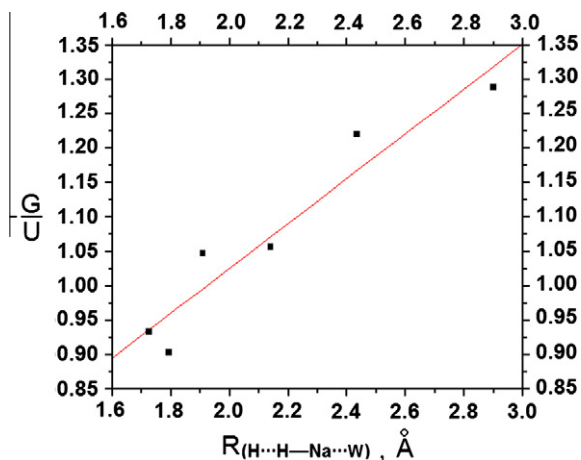
Fig. 5. Relationship between the $-G/U$ ratios and intermolecular distances obtained from B3LYP/6-311++G(3df,3pd) calculations.
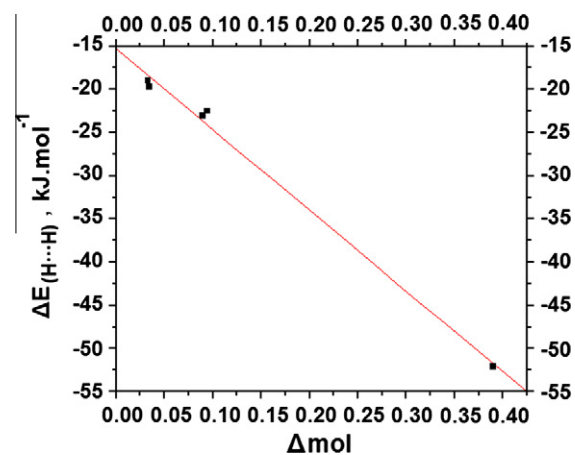

Fig. 6. Relationship between the values of the estimated intermolecular energies and molecular parameter (Δmol).

ceived by means of the variation in the bond length or in the chemical shift (red or blue) of the proton donor (HX) combined with ρ and ∇_ρ^2.

$$\Delta\text{mol} = \left[\left(\frac{\delta_{v\text{HX}}}{v_{o\text{HX}}}\right)^2 + \left(\frac{\delta_{\rho\text{HX}}}{\rho_{o\text{HX}}}\right)^2 + \left(\frac{\delta\nabla_{\rho\text{HX}}^2}{\nabla_{\rho o\text{HX}}^2}\right)^2 \right]^{1/2} \quad (9)$$

The molecular complex parameter (Δmol) can be fitted by structural (δr) or spectroscopy (δv) data. Besides the QTAIM parameters ($\delta\rho_{\text{HX}} = |\rho_{o\text{HX}} - \rho_{\text{HX}}|$ and $\delta\nabla^2\rho_{\text{HX}} = |\nabla^2\rho_{o\text{HX}} - \nabla^2\rho_{\text{HX}}|$), it can be noted that Δmol was estimated via vibrational chemical shifts ($\delta v = |v_{o\text{HX}} - v_{\text{HX}}|$). Up to now, the interaction energies estimated herein can be considered indirect values, but this equation can validate them all. Fig. 6 illustrates the relationship between the values for the dihydrogen bond energies of **I**, **II** and others, such as the dihydrogen-bonded complexes LiH···HCF$_3$, LiH···HCCl$_3$, and NaH···HF [86,87].

$$y(\Delta E^C) = -93.6(\Delta\text{mol}) - 15.3, \quad R^2 = 0.99 \quad (10)$$

Although the ternary complexes are formed by a symmetrical (cooperative) energy distribution, the simultaneous presence of dihydrogen bonds and alkali–halogen leads to the quantification of their interaction energies through the application of Eq. (9)

being unapproachable. Thus, the binary systems are more suitable in this regard because their intermolecular energies are directly incorporated into a single interaction strength and, as such, other systems were inserted with the purpose to reinforcing the statement debated herein. As is well-known, the dihydrogen complex NaH···HF is strongly bonded and almost covalent, either based on its intermolecular energy of -52.15 kJ mol^{-1} or even the $-G/U$ ratio of 0.5350. Among the complexes examined in this study, only those formed by chloroform yielded partial covalent character, and therefore they are much less stabilized than NaH···HF. In other words, the covalent character is not systematic in terms of interaction energy, and a careful examination of the QTAIM topological parameters is mandatory in this situation. In summary, it can be reported that the remaining bonds (F—C, Cl—C, and C—H) are covalent or topologically shared. The Laplacian values are negative and vary between -0.3959 e/a$_o^5$ and -1.2834 e/a$_o^5$ in **III**, and -1.1386 e/a$_o^5$ and -0.1979 e/a$_o^5$ in **IV**. In line with this, the $-G/U$ values are significantly lower, thus indicating the pure covalence of these bonds. Finally, for the high and low electronic density centers located in BCPs along the intermolecular surfaces examined in this study, it may be necessary to discuss another topological descriptor, namely the Ring Critical Point (RCP), whose values for the ternary complex **IV** are shown in Fig. 7. The algebraic difference between BCP and RCP is related to the Poincaré–Hopf relationship [42] in terms of non-zero curvatures of ρ at the critical point, yielding the coordinates (3,−1) and (3,+1). According to the QTAIM framework, BCP is an interatomic pathway containing electronic density without chemical bond characteristics and RCP is defined by an intersection of interatomic surfaces that form a ring. According to Castillo et al. [88], from the lowest G values of 0.0049 a.u.
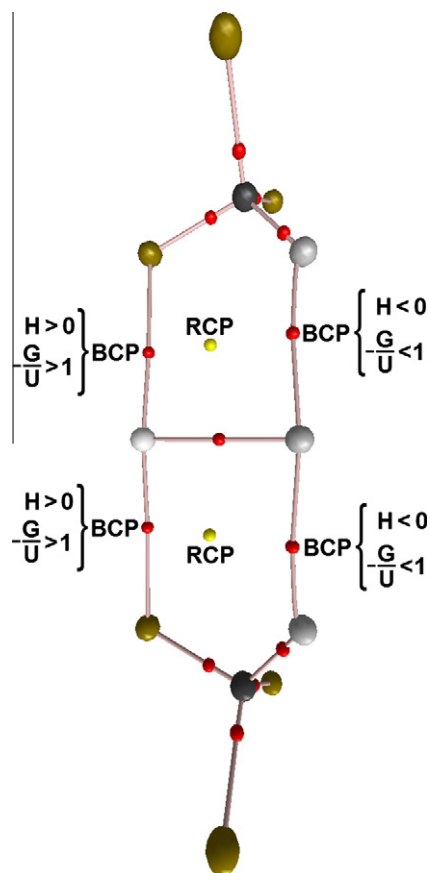

Fig. 7. Bond paths, BCP, RCP, and covalent characterization by means of H = G + U for the **IV** complex.

and 0.0043 a.u. it can be easily noted that a slower charge density flux is observed for RCP compared with BCPs. Moreover, the electronic densities of 0.0070 e/a_o^3 and 0.0067 e/a_o^3 are smaller and the Laplacian fields tend toward annulment, i.e., $\rho_{BCP} > \rho_{RCP}$ and $\nabla^2\rho_{BCP} > \nabla^2\rho_{RCP}$.

4. Concluding remarks

A theoretical investigation of the interaction strength and covalent tendency in systems formed by dihydrogen bonds and new alkali–halogen bonds was presented herein. From the structural point of view, the intermolecular distances behave well. These values are in agreement with the tabulated van der Waals radii for Na$\cdots$W dihydrogen bonds and for the H$\cdots$W (with W = F and Cl) of the alkali–halogen bonds. Upon the formation of the NaH$\cdots$HF$_3$ and NaH$\cdots$HCCl$_3$ complexes, chloroform (HCCl$_3$) provides the strongest bond with a difference in the intermolecular energy in range of 4 kJ mol^{-1}. Vibrational events inherent to red- and blue-shifts were identified for these binary systems and also for the ternary complexes NaH$\cdots$2(HCF$_3$) and NaH$\cdots$2(HCCl$_3$). As is well-known, red-shift effects were verified for the more strongly bound complexes whereas the blue-shifts of weaker ones were caused by variation in the polarization of the carbon atom of the proton donor, either HCF$_3$ or HCCl$_3$, as well as through the estimation of the atomic radii. As such, and in agreement with the QTAIM foundations, the H$\cdots$H dihydrogen bonds revealed partially covalent intermolecular profiles with strongly bonded complexes, such as NaH$\cdots$HCCl$_3$ and NaH$\cdots$2(HCCl$_3$) and, although being less stable than a pure intermolecular covalent complex like NaH$\cdots$HF, the covalence described qualitatively by the kinetic and potential electronic energy densities plays a decisive role in the rationalization of the interaction strength.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.comptc.2012.07.031. These data include MOL files and InChiKeys of the most important compounds described in this article.

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