

A Theoretical Study of Binary and Ternary Hydride-Bonded Complexes $N(\text{BeH}_2)\cdots X$ with $N = 1$ or 2 and $X = \text{K}^+$ or Ca^{+2}

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Abstract

A theoretical study of hydride bonds formed between beryllium hydride and alkaline earth metal cations is presented. B3LYP/6-311++G(d,p) calculations were used for determining the optimized geometries of the $\text{BeH}_2\cdots\text{K}^+$, $\text{BeH}_2\cdots\text{Ca}^{+2}$, $\text{BeH}_2\cdots\text{K}^+\cdots\text{BeH}_2$, and $\text{BeH}_2\cdots\text{Ca}^{+2}\cdots\text{BeH}_2$ hydride-bonded complexes, where among them the first are binaries, whereas the last ones are ternaries with the calcium (Ca^{+2}) and potassium (K^+) ions mediating the interactions with the beryllium hydride (BeH_2). A detailed structural analysis were performed, by which the yielded profiles are in good agreement with results of the infrared vibrational spectrum, mainly in regards to the existence of red-shifted modes followed by enlarged absorption intensity ratios of the B-H bonds of the binary complexes. The capability of either donating or accepting of protons among BeH_2 , K^+ , and Ca^{+2} , is currently treated in conformity with Lewis's acid/base theory, but is also interpreted through the application of the Quantum Theory of Atoms in Molecules (QTAIM), whose formalism consents in the molecular modeling of concentrations and depletions of charge density ruled by the Laplacian shapes, charge transference fluxes, as well as by the local virial theorem of the electronic density with quantification of the kinetic and potential energies along the bonds and interactions.

Keywords: Hydride Bonds, Vibrational Infrared Spectrum, B3LYP, QTAIM

1. Introduction

In nature, a lot of systems are formed due to a wide chemical diversity, as intrinsically present in biological organisms, chemical processes, physical phenomena, and ray diffractions in spectroscopy analysis, where all these systems and events produced by them are governed by any kind of molecular contact [1]. In fact, the stable contact between a site highly electronegative (lone-electron pairs or unsaturated bonds) and proton donors (Lewis acids) is a typical scheme of hydrogen bonds, which is considered the cornerstone for the intermolecular interactions [2], although there are other types very interesting in their own ways. Agostic interactions [3,4], halogen bonds [5-7], dihydrogen bonds [8,9] or even π stacking [10,11] are one of the unconventional interactions known beyond the hydrogen bond profile. In opposition to the hydrogen bonds [12], there is an additional interaction so-called hydride bond deriving from the contact be-

tween two positive centers, and it can be identified as $Y^{+\delta}-H^{-\delta}\cdots X^{+\delta}$ [13]. The apparent negative character of $H^{-\delta}$ is manifested due to the electropositivity of $Y^{+\delta}$ and $X^{+\delta}$, and thereby, $H^{-\delta}$ behaves as intermolecular mediator. Notwithstanding the positive character of $X^{+\delta}$ be partial, it can be a cationic species what leads to a most efficient or stronger interaction with $H^{-\delta}$. Thus, the great insight is dedicated to the negativity of $H^{-\delta}$, whose origin arises due to its bond with the highest electropositive atom $Y^{+\delta}$.

Recently, Yáñez *et al.* [14] have reported a theoretical study with analysis of electronic and spectroscopic parameters of intermolecular complexes formed at light of "Beryllium Bonds", whose main features are the non-linear configurations and interactions with lone-electron pairs of the Lewis base. Before of this, however, Grabowski [15] has already shown the ability of the beryllium hydride (BeH_2) as proton-accepting molecule upon the formation of linear dihydrogen bonds, and further, Grabowski *et al.* [13] have also documented evi-

dences that BeH₂ also yields stable hydride bonds with cations derived from alkaline metals, such as Li⁺, Na⁺ and Mg⁺². In an emphatic conclusion, hydrides bonds are not covalent interactions, and besides, no significant similarity in comparison with classical hydrogen bonds is known [16]. Based in this context, we present a theoretical study of hydride complexes formed by BeH₂ and cations derived from the alkaline earth elements, such as potassium (K⁺) and calcium (Ca⁺²), and thereby the BeH₂⋯K⁺ and BeH₂⋯Ca⁺² binary hydride complexes, as well as the BeH₂⋯K⁺⋯BeH₂ and BeH₂⋯Ca⁺²⋯BeH₂ ternary ones are the systems to be investigated here. In a direct qualitative comparison with other systems [17,18], we expect that our study becomes a guide of forward arguments in order to discuss more carefully the formation of the hydride bonds.

2. Criteria for Choice of the Theoretical Level

In general, one of the main objectives of the theoretical studies of intermolecular systems is devoted to a maximum reproducibility regarding the available experimental data [19,20], where bond lengths and the infrared stretch frequencies are often the most examined parameters [21]. However, the great clog is the accounting of the London's dispersion forces, but in association with the Hartree-Fock architecture, a lot of schematic works were elaborated with the purpose to quantify the dispersion in order to obtain accurate structures of intermolecular complexes [22,23]. On the other hand, it is widely established the efficiency of some computational approaches in studies of bound complexes, either MP2 or any other Post-Hartree-Fock method [24], or even by applying the hybrid functionals derived from the Density Functional Theory (DFT) [25]. In this scenery, the B3LYP functional is one of the most popular codes with large applications in several studies of hydrogen bonded-complexes [26-31], and due to this, we elect it to be used in this current work.

Moreover, it is not only through the classical quantum calculations that the molecular parameters of the n(BeH₂)⋯X (with n = 1 or 2 and X = K⁺ or Ca⁺²) hydride complexes will be determined. In fact, the Quantum Theory of Atoms in Molecules (QTAIM) [32-34] disposes of a great capability for investigating the nature of the hydride bonds Be^{+δ}-H^{-δ}⋯K^{+δ} and Be^{+δ}-H^{-δ}⋯Ca^{+δ}. This our affirmation is based on the QTAIM faculty to locate Bond Critical Points (BCP) along the Bond Path (BP) between each nuclear pairing interactions, wherein the computation of the electronic density amounts is developed, and thus, it can be discussed the hydride bond strength. Nevertheless, it is also granted to QTAIM the

co-valent assignments of the hydride bonds, as well as the remaining ones, Be-H. This reasoning is developed at light of QTAIM topological parameters, such as the Laplacian ∇²ρ(r) of the electronic density ρ(r) [35,36], and other components of the local density: local kinetic energy density G(r) and local potential energy density U(r) [37,38]. In QTAIM, the Laplacian content provides a link between the form of the electronic density and the quantum mechanical formalism, whose result is the interpretation of ∇²ρ(r) in conformity with the local equation of the virial theorem:

$$\frac{\hbar^2}{4m} \nabla^2 \rho(r) = 2G(r) + U(r) \quad (1)$$

or

$$H(r) = G(r) + U(r) \quad (2)$$

One direct comparison between these equations was suggested by Cremer and Kraka [39,40], where G(r) and U(r) represent the kinetic and potential energy densities, respectively. Once U(r) is always negative whereas G(r) in turn is positive, H(r) and ∇²ρ(r) determine which of these terms (kinetic or potential) are dominant on the virial theorem, *i.e.*, ∇²ρ(r) < 0 denotes that ρ(r) is locally concentrated with great contribution of U(r), as observed in covalent bonds or even π sites [41]. On the other hand, ∇²ρ(r) > 0 is obtained when electronic density vacuities are modeled, and in these cases, the intermolecular interactions can be efficiently analyzed. In QTAIM, there is a slight and fundamental difference in the conception of U(r) with regard to U(Ω). Well, U(r) is the pure potential energy of the electronic density at any r point of the molecular surface, whose statement is also valid to G(r). However, when the virial theorem for all forces act on the surfaces of an atom in a molecule, it is yielded U(Ω). This is a suitable spatial condition for molecular modeling not only to electronic density, but also applied to the atomic charges computation:

$$q_i = Z_i - \int_{\Omega} \rho(r) dr \quad (3)$$

As can be seen, q_i is an atomic charge partition with no dependence of the theoretical level, but closely related to the electronic density [42]. In studies of intermolecular systems, surely the quantification of the atomic charges and thereby the measurement of the charge transfer is very useful, and in practice, it can be used to justify a lot of molecular parameters, such as polarizability or even vibrational chemical shifts. In these insights presented hitherto about the QTAIM, our goal in this work is concentrated in the molecular topology of the n(BeH₂)⋯X hydride complexes, but also motivated by the covalent

interpretation of the Be-H bonds and mainly, but specially difficult, in the hydride bonds $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}^{+\delta}$.

3. Computacional Details

The optimized geometries of the $n(\text{BeH}_2)\cdots\text{X}$ (with $n = 1$ or 2 and $\text{X} = \text{K}^+$ or Ca^{+2}) hydride complexes were determined by the GAUSSIAN 98 W [43] quantum packages in which all calculations were carried out at the B3LYP/6-311++G(d,p) level of theory. The QTAIM calculations were also performed by the GAUSSIAN 98 W [44], although some additional computations were developed by the AIMAll 11.05.16 suite of codes [45], more properly by its implementations named as AIMStudio and AIMQB subparts. After completing all calculations, the values of the hydride bond energies (ΔE) were obtained in conformity with the supermolecule approach [46], by which is stated that $\Delta E = E_{\text{complex}} - E_{\text{isolated molecules}}$. Furthermore, these ΔE values were refined with mandatory corrections, where the Boys and Bernardi's counterpoise based on the Basis Sets Superposition Error (BSSE) [47], as well as the contribution of the Zero Point Vibrational Energies (ZPE) [48] also were included. In the end, the corrected hydride bond energy (ΔE^{C}) is obtained as follows: $\Delta E^{\text{C}} = \Delta E + \text{BSSE} + \Delta\text{ZPE}$.

4. Results and Discussion

4.1. Structural Parameters

The optimized geometries of the hydride-bonded complexes, $\text{BeH}_2\cdots\text{K}^+$ (**I**) and $\text{BeH}_2\cdots\text{Ca}^{+2}$ (**II**) binaries, as well as the $\text{BeH}_2\cdots\text{K}^+\cdots\text{BeH}_2$ (**III**) and $\text{BeH}_2\cdots\text{Ca}^{+2}\cdots\text{BeH}_2$ (**IV**) ternaries, all of them are illustrated in **Figure 1**. As cationic acceptor, the structure of the BeH_2 molecule is modified after the complexation. Note that, by taking into account $\text{Be}^{+\delta}\text{-H}^{-\delta}$ bond length value of 1.3267 \AA , an enhancement tendency is verified, whose values are 1.3485 , 1.3656 , 1.3464 and 1.3560 \AA to (**I**), (**II**), (**III**) and (**IV**), respectively. Well, these enhanced values are those directly affected by the hydride bonds $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{K}^+$ and $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{Ca}^{+2}$, whereas the H-Be opposite bonds are slightly reduced.

It can be seen that elongation of the H-Be bonds is the more intense complexation effect, and at this point, the distance of the hydride bonds $\text{H}^{-\delta}\cdots\text{X}$ also should be included in this statement. The decrease and increase of the $\text{H}^{-\delta}\cdots\text{X}$ lengths reflect on the BeH_2 structure. Are then contrary effects, because whereas the shortest distances of $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}$ promotes the increasing of $\text{Be}^{+\delta}\text{-H}^{-\delta}$, and H-Be $^{+\delta}$ in turn reduces. Due to this, Grabowski *et al.* [13] have declared that $\text{Be}^{+\delta}\text{-H}^{-\delta}$ acts as Lewis base after the complexation with cationic species. On the other view-

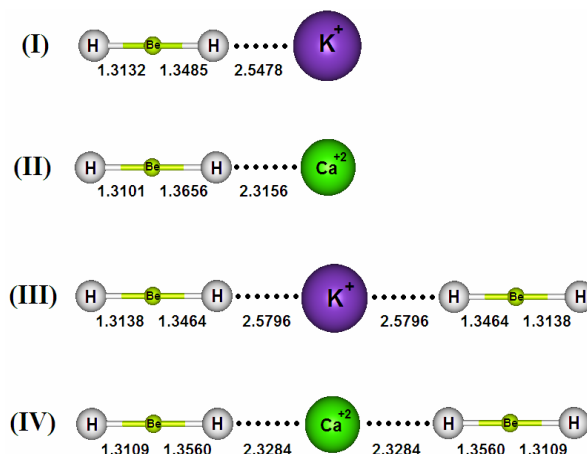


Figure 1. Optimized geometries of the hydride-bonded complexes, $\text{BeH}_2\cdots\text{K}^+$ (**I**) and $\text{BeH}_2\cdots\text{Ca}^{+2}$ (**II**) binaries, as well as the $\text{BeH}_2\cdots\text{K}^+\cdots\text{BeH}_2$ (**III**) and $\text{BeH}_2\cdots\text{Ca}^{+2}\cdots\text{BeH}_2$ (**IV**) ternaries. All these geometries were obtained at the B3LYP/6-311++G(d,p) level of theory.

point, $\text{H-Be}^{+\delta}$ is enlarged at long bonding distances. In other words, at prior the bonding distances determine the interaction strength as follows: (**II**) > (**IV**) > (**I**) > (**III**). Therefore, it can be concluded initially that calcium produces the strongly bound hydride complexes.

In an additional brief comment about the hydride distances, we would like to use a fundamental criterion widely used in chemical bonds and interactions studies: the van der Waals [49] covalent radii, as well as the ionic radii estimated by Goldschmidt [50] and Pauling [51]. By definition, covalent radius is the dimensional measure of an uncharged atom that composes a covalent bond, whereas ionic radius is the measure of atom size as ion within a crystal structure. However, the values of the hydride distances in this current work computed at the B3LYP/6-311++G(d,p) level are not exempt of criticism. In structural viewpoint, only the complexes formed by potassium can be considered bonded because the distance values of 2.5478 \AA (**I**) and both 2.5796 \AA (**III**) are shortest than the sums of the covalent ($\text{H} = 1.2000 \text{ \AA}$) and ionic ($\text{K}^+ = 1.3800 \text{ \AA}$) tabulated radii. Complexes (**II**) and (**IV**), formed by calcium, are not geometrically bonded because their hydride distances of 2.3156 \AA and both 2.3284 \AA are longest than 2.2000 \AA ($\text{H} = 1.2000 \text{ \AA}$ and $\text{Ca}^{+2} = 1.000 \text{ \AA}$). At prior, this can reveal interesting features on the electronic structure of the hydride complexes, precisely, meaning an accumulation of charge density within the intersystem region. However, this is a question to be answered hereafter.

4.2. Infrared Stretching Frequencies and Absorption Intensities

The interpretation of the vibrational modes of intermo-

lecular systems is seen as routine procedure. This is a secure way to affirm that a minimum of potential energy surface was found due to the absence of imaginary frequencies [52-54]. About this, our systems studied in this work were characterized with no imaginary frequency. The values of the harmonic stretching frequencies (ν) and absorption intensities (A) of the hydride-bonded complexes (I), (II), (III), and (IV) are organized in **Table 1**. In the binary complexes (I) and (II), their red-shifts of -9 cm^{-1} and -59 cm^{-1} accompanied by the absorption intensities of $197.9\text{ km}\cdot\text{mol}^{-1}$ and $632.9\text{ km}\cdot\text{mol}^{-1}$ related to the $\text{Be}^{+\delta}\text{-H}^{-\delta}$ oscillator are the most important spectroscopic events [55].

Note that, the non-polarity of BeH_2 makes it inactive in the infrared region, but the absorption intensities above presented emerge due to the formation of the hydride complexes. Contrary to this, the inactivity of the $\text{Be}^{+\delta}\text{-H}^{-\delta}$ is not altered by the formation of the (III) and (IV) systems, although the variation of -5.1 cm^{-1} and -17.2 cm^{-1} in the stretch frequencies indicate the formation of the red-shifting hydride bonds, as already documented by Yáñez *et al.* [14]. Furthermore, the stretch frequencies of the $\text{Be}^{+\delta}\text{-H}^{-\delta}$ displaced to downward values corroborates with the reduction of their bond length, as discussed in structural analysis. At this step of examination, it can be assumed that structural alterations on BeH_2 cause vibrational displacements on its stretch frequencies, and as far as the structure is deformed, in spectroscopy analysis is more detectable, *i.e.*, the red-shift effects are quite clear and distinguishable.

About the new vibrational modes, the stretch frequencies of 178.4 cm^{-1} and 216.4 cm^{-1} of (I) and (II) are active in infrared spectrum due to their absorption intensities of $7.2\text{ km}\cdot\text{mol}^{-1}$ and $13.6\text{ km}\cdot\text{mol}^{-1}$. In comparison with (III) and (IV), the affirmation that inactive absorptions are caused by the intermolecular (hydride bonds) distances is not cautious, *i.e.*, this event seems not to be caused by the interaction strength. Meaningfully, the

Table 1. Values of the red-shift effects, absorption intensity ratios, new vibrational frequencies and absorption intensities at the B3LYP/6-311++G(d,p) level of theory.

Parameters	Hydride-bonded complexes			
	(I)	(II)	(III)	(IV)
$\Delta\nu(\text{Be}^{+\delta}-\text{H}^{-\delta})$	-9	-59.6	-5.1	-17.2
$\frac{A(\text{Be}^{+\delta}-\text{H}^{-\delta}),C}{A(\text{Be}^{+\delta}-\text{H}^{-\delta}),m}$	197.9	632.9	0.0	0.0
$\nu(\text{Be}^{+\delta}-\text{H}^{-\delta}\dots\text{H}^{+\delta})$	178.4	216.4	149.0	179.9
$A(\text{Be}^{+\delta}-\text{H}^{-\delta}\dots\text{H}^{+\delta})$	7.2	13.6	0.0	0.0

*Values of ν and A are given in cm^{-1} and $\text{km}\cdot\text{mol}^{-1}$, respectively.

relative weakest new vibrational modes were observed in (III) and (IV), what also lead us to consider the vibrational activity of these systems in our discussion. So, as is well-known that the absorption intensity ratios is the mainstream to characterize the formation of bound systems, here our criteria are the detection of the red-shift stretch effects on the BeH_2 molecule when (III) and (IV) are formed.

4.3. Bonding Energies and Polarizability

The stability and bond strength of an intermolecular system is well analyzed at light of the bond energies computed through the B3LYP/6-311++G(d,p) approach. In **Table 2** are gathered all ΔE^C values calculated for the (I), (II), (III) and (IV) systems, and besides, the BSSE and ZPE corrections for these energies are also listed in this same computational level. Firstly, one interesting point are the negative values of the hydride bond energies, which are in range between the $-29.11\text{ kJ}\cdot\text{mol}^{-1}$ (III) and $-47.06\text{ kJ}\cdot\text{mol}^{-1}$ (II), what indicate high stability related to the binary complexes. However, the ternary complexes are not weakly bound, for instance (IV) is stabilized by means of a high bonding energy of $-42.66\text{ kJ}\cdot\text{mol}^{-1}$. It should be mentioned that these bonding energies were corrected by the BSSE and ZPE contributions, and in this context, it is noteworthy to comment that small BSSE values contributed to the correction of ΔE [56,57]. In a careful analysis, as is well-known that density functional calculations yields much smaller BSSE amounts, it become required the application of complete basis sets.

Moreover, it can be seen that negative BSSE values were computed, what is not usual. This must occur because the energy of the cations (K^+ and Ca^{+2}) are much more negatives, whereas the beryllium hydride is less negative in the presence of the wave function of the cations above cited. Moreover, the long hydride distances should affect the counterpoise calculation on the overlap wave functions, what can lead to uncommon results similar in nature to those found in this current work. In **Table 2** are also listed the values of dipole moment enhancements ($\Delta\mu$). With similar procedures to those performed for the hydride bonding energies, the $\Delta\mu$ values are determined by subtracting the complex dipole (μ_{complex}) minus its monomers ($\mu_{\text{isolated molecules}}$) [58,59]. Nevertheless, the specialized literature informs "...how much stronger bonded the intermolecular system more enhanced its dipole moment...", of course motivated by great structural perturbations on the molecular electronic distribution. Here, to our knowledge, this conclusion is not applied because the isolated molecules (BeH_2 , K^+ and Ca^{+2}) are non polar. In other words, the computed $\Delta\mu$

Table 2. Values of the uncorrected (ΔE) and corrected (ΔE^C) hydride energies, BSSE and ZPE corrections, dipole moment enhancements calculated by the B3LYP/6-311++G(d,p) level of theory.

Parameters	Hydride-bonded complexes			
	(I)	(II)	(III)	(IV)
ΔE	-33.29	-49.35	-31.73	-45.96
ΔE^C	-30.14	-47.06	-29.11	-42.66
BSSE	-0.3	-1.00	-0.78	0.00
ZPE	3.45	3.29	3.40	3.30
$\Delta\mu$	3.17	0.86	0.00	0.00

*Values of ΔE , ΔE^C , BSSE, and ZPE are given in $\text{kJ}\cdot\text{mol}^{-1}$; *Values of $\Delta\mu$ are given in Debye.

results are features of the own polarizabilities of (I), (II), (III) and (IV). In this context, we should take into account the traditional chemical bond insights to comprehend these phenomena. It is well defined that polar bonds arise due to the electronegative difference between two atoms, meaning that the charge is much more concentrated on nuclei and less located along the chemical bond. Well, this is also verified in our hydride complexes studied here, in which it can be observed that (I) is the weaker binary bound. Due to this, its hydride bond is longer as well as its structure with $\Delta\mu$ value of 3.17 Debye is more polarized in comparison with (II), whose $\Delta\mu$ value is 0.86 Debye. However, we would like to say that a topological exam based on the QTAIM concepts can be more secure to express some affirmation about that, whose results are listed in next section.

4.4. QTAIM Topology: Charge Transfer, Electronic Density, Laplacian Shapes, and Virial Theorem

First of all, we would like to introduce some comments about hydride bonds and its analysis on the QTAIM viewpoint. As widely known, the Bader's QTAIM has been useful in many research types [60], and of course, those with focus in hydrogen bonding are the most studied [61]. Very recently, a group of experts in hydrogen bonds reunited in order to discuss and plan the scientific future of this interaction [12]. Through the QTAIM analysis, it was accorded whether any noncovalent interaction is formed at the BCP (3, -1), it should be considered as typical hydrogen bond [62-64]. Only for mention, the number 3 represents the number of eigenvalues of the Laplacian at the zero-flux surface, whereas -1 is the sum of these eigenvalues. Note that, in **Figure 2**, the hydride bond of the complex $\text{BeH}_2\cdots\text{Ca}^{+2}$ presents a BCP with coordinate (3, -1). This could be a conflict, but this is justly an interpretative problem because hydrogen bond

is treated as protic donating whereas hydride bonds as hydric donating. In this point, we are not wishing to debate this question here.

In **Table 3** are listed the topological results derived from the Bader's QTAIM approach for the hydride-bonded complexes examined here. At this point, our discussion continuous related to the analysis previously initiated about the dipole moment enhancements. By taking into account the traditional works of intermolecular systems with great goal dedicated to the atomic charge measurement and sequentially the charge transference quantities, it can be expected a suitable justification to the dipole moment enhancements. As noted, integrating the electronic density is physically much more reliable than any others atomic charge partitions [65], of which neither of them are considered observable parameters. Once again, taken the hydrogen bond portfolio as reference, the charge transfer shows itself efficient if the proton donor acquires any electronic charge amount or if the proton acceptor loses it. This is a classical observation of the charge transfer flux (from HOMO to LUMO), which occur between the Frontier Molecular Orbitals (FMO) LUMO and HOMO related to the donor and acceptor of protons [66], respectively.

In fact, the slight values of charge transfer ($\Delta Q = \sum q_{\text{complex}} - \sum q_{\text{isolated molecules}}$) of -0.030 a.u. and -0.036 a.u. were determined in (I) and (II). These positive amounts were computed on the beryllium hydride, what means a loss of charge over it. On the other hand, this lost charge was transferred, and thereby is so-called as charge transfer, then to the K^+ and Ca^{+2} cations. This can be noted through the charge values of 0.968 a.u. and 0.964 a.u. computed after complexation in comparison with 1.000 a.u. for the potassium and calcium isolated. In summary, it can be stated that K^+ and Ca^{+2} received -0.030 a.u. and

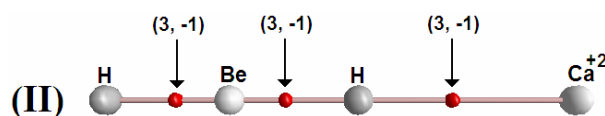


Figure 2. BCP and BP of the $\text{BeH}_2\cdots\text{Ca}^{+2}$ hydride complex.

Table 3. Values of the QTAIM topological parameters.

Parameters	Hydride-bonded complexes			
	(I)	(II)	(III)	(IV)
ΔQ	-0.03	-0.036	0.000	0.000
$\rho_{(r)}(\text{Be}^{\delta+}\text{-H}^{\delta-})$	0.088	0.082	0.089	0.085
$\nabla^2\rho_{(r)}(\text{Be}^{\delta+}\text{-H}^{\delta-})$	0.154	0.154	0.035	0.158
$\rho_{(r)}(\text{Be}^{\delta+}\text{-H}^{\delta-}\cdots\text{H}^{\delta+})$	0.012	0.019	0.011	0.018
$\nabla^2\rho_{(r)}(\text{Be}^{\delta+}\text{-H}^{\delta-}\cdots\text{H}^{\delta+})$	0.038	0.058	0.035	0.056
$G_{(r)}(\text{Be}^{\delta+}\text{-H}^{\delta-}\cdots\text{H}^{\delta+})$	0.008	0.013	0.007	0.012
$U_{(r)}(\text{Be}^{\delta+}\text{-H}^{\delta-}\cdots\text{H}^{\delta+})$	-0.012	-0.012	-0.006	-0.011

*All values are given in atomic units (a.u.).

-0.036 a.u. of atomic charge, indicating that these species behaves as Lewis acid, whereas beryllium hydride as base. Unfortunately, the quantification of ΔQ has not supplied consistent values to evaluate the dipole moment enhancement. Surely, the ΔQ values of -0.030 a.u. and -0.036 a.u. agrees with the hydride bond strength $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}$ in structural and electronic terms, but it seems to be not useful to explain $\Delta\mu$. It is incoherent that higher charge transfer (-0.036 a.u.) and stronger bonding energies ($-47.06 \text{ kJ}\cdot\text{mol}^{-1}$) present small dipole moment enhancement (0.86 Debye). In this conjecture, we believe that a more detailed analysis should be made in future, but ideally we believe that the dipole moment enhancements are not synchronized with the charge transfers and hydride bond energies. As aforesaid, this is not a question to be debated at this time.

The measure of the electronic density is one of the QTAIM ways to evaluate the chemical bond strength. In Table 3 are listed all values of electronic densities of the $\text{Be}^{+\delta}\text{-H}^{-\delta}$ bonds and $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}$ hydride contacts. In comparison with the BeH_2 monomer, the electronic densities on the $\text{Be}^{+\delta}\text{-H}^{-\delta}$ bonds is reduced, indicating a weakness of this bond upon the formation of the hydride-bonded complexes (I), (II), (III) and (IV). As recently documented, it was shown a direct relationship between the variations of the electronic density and vibrational shifts, in this current case, the red ones. Comparing the values of $\Delta\nu(\text{Be}^{+\delta}\text{-H}^{-\delta})$ and $\rho_{(r)}(\text{Be}^{+\delta}\text{-H}^{-\delta})$ listed respectively in Tables 1 and 3, it is clearly perceived that larger shifts are explained by larger variations of $\rho_{(r)}$, what corroborates with our arguments used to discuss the polarizability of (I) and (II). So, we have affirmed that the high polarizability of (I) is caused by a relative high charge density concentration over potassium, as also demonstrated by the charge transfer. So, the slight variation of -0.011 a.u. of $\rho_{(r)}$ in $\text{Be}^{+\delta}\text{-H}^{-\delta}$ of (I) associated with the smaller electronic density of 0.012 a.u.

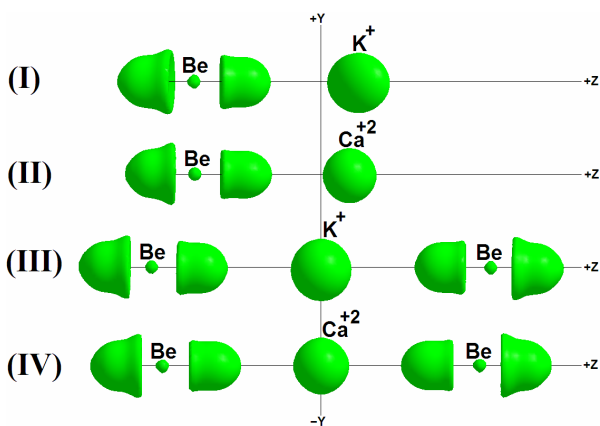


Figure 3. Laplacians of the hydride-bonded complexes, $\text{BeH}_2\cdots\text{K}^+$ (I) and $\text{BeH}_2\cdots\text{Ca}^{+2}$ (II) binaries, as well as the $\text{BeH}_2\cdots\text{K}^+\cdots\text{BeH}_2$ (III) and $\text{BeH}_2\cdots\text{Ca}^{+2}\cdots\text{BeH}_2$ (IV) ternaries.

of the hydride bond $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}$ reinforce our statement. Well, high polarizability occurs when the intermolecular electronic charge is limited towards to a minimum along the BP. Moreover, a closed-shell profile is supported by the positive Laplacian fields (see Figure 3) [67], which are increased from 0.114 a.u. to an average value of 0.154 a.u. in (I), (II) and (III), and exceptionally 0.158 a.u. in (IV). Revisiting the QTAIM literature, positive Laplacian values are characteristic of Lewis' acid, not base [68]. Thereby, BeH_2 should be treated as acid.

Nevertheless, as expected the positive Laplacian values in range of 0.035 - 0.158 a.u. certifies the theoretical characterization of the $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}$ hydride interaction at the light of the QTAIM formalism. Moreover, smallest values of electronic density were computed indicating that $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}$ is a weak hydride bond more than others similar interactions, such as some dihydrogen bonds for instance [69]. However, the most highlighted impact of the electronic density amount in intermolecular systems is the possibility to measure the interaction strength [70], whose content is a close relationship between $\rho_{(r)}$ and ΔE^C .

In Table 3 are also gathered the parameters of the electronic energy densities computed in according with the formalism of the local virial theorem (see Equation (1)), by which the values of the kinetic electronic density, $G_{(r)}$, accompanied by the potential electronic density, $U_{(r)}$, are used to discuss the real covalent character of the chemical bonds and intermolecular interactions. As aforesaid, the positive Laplacians reveal that $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}$ hydride bonds are interactions of closed-shell type, although this same profile is also verified in the $\text{Be}^{+\delta}\text{-H}^{-\delta}$ bond. Through the Equation (1), the values of $G_{(r)}$ and $U_{(r)}$ are summed whose result is the electronic energy density $H_{(r)}$ at intermolecular BCP. It can be seen that all values of $H_{(r)}$ are positive, leading us to admit that all systems studied here are not formed by covalent interaction. However, this is not an unique tendency, e.g., $\text{H-Be-H}\cdots\text{Mg}^{+2}$ is a particular case with its geometry obtained at sophisticated *ab initio* calculations at the MP2/aug-cc-pVTZ level of theory, presenting a negative value of $H_{(r)}$ towards zero [13].

5. Conclusions

The capability of the beryllium hydride to form intermolecular complexes with cations derived from potassium and calcium was theoretically demonstrated in this work. In a first step of our analysis, we observe that the lengths of the hydride interactions $\text{Be}^{+\delta}\text{-H}^{-\delta}\cdots\text{X}$ are very long, what in structural point of view, their formations should be not allowed. On the other hand, the bonding energies are very stable, in particular on the binary systems, what

justifies their formations and stabilities, although it must be highlighted that a symmetric charge distribution was observed on the ternary. Either in binary or in ternary, the cation Ca^{+2} yields more stable complexes, although the dipole moment variation does not justify this statement. Because the ternary complexes are non-polar, their polarizabilities are nulls, but in binary not. Our expectation was motivated to obtain stronger bound systems formed by high polarizability. However, it is not occurred. Independent of this, the computation of the charge transferences also reinforce our ideas that the high polarizability of $\text{BeH}_2 \cdots \text{K}^+$ is derived from the electronic charge accumulated on the nuclei (H^δ and K^+) with residues of charge density distributed along the hydride interaction. In regards to the infrared stretch frequencies and absorption intensities, besides the red-shifts on the Be-H bonds but, the fact by which their oscillators are inactive in regards to the ternary complexes deserves great attention once these are the most important criteria used in the characterization of intermolecular systems. Due to this spectroscopic event, our analysis was concentrated in the interpretation of the new vibrational modes of the hydride bonds $\text{Be}^{+\delta}-\text{H}^{-\delta} \cdots \text{X}$. By taking into the account the topological QTAIM analysis, it was verified that only closed-shell interactions compose the structure of the $n(\text{BeH}_2) \cdots \text{X}$ hydride complexes. Beyond that, the local virial theorem aided us to conclude that covalent features were not observed in both $\text{Be}^{+\delta}-\text{H}^{-\delta} \cdots \text{X}$ hydride bonds or even in the Be-H ones. In a general conclusion, the hydride complexes studied here can be considered closed-shell clusters as a whole.

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7. References

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