Nature of beryllium bonds in view of interacting quantum atoms and natural energy decomposition analysis

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ABSTRACT

In the light of interacting quantum atoms (IQA) and natural energy decomposition analysis (NEDA) the nature of different types of beryllium bonds is studied. IQA intra-atomic (self) energies indicate that, in most of the traditional beryllium bonds (in which the Lewis base is a lone pair donor), π-Be bonds (Lewis base is an unsaturated molecule) and also the Be–Ng (noble gases) interactions, the beryllium atom is stabilized upon complex formations. According to IQA inter-atomic energy components, the Be···Y bonds (Y is an atom in the Be-bond acceptor that is connected directly to the beryllium atom) have a dominant classical electrostatic character. However, in the IQA partitioning of total inter-molecular interactions, the contributions of non-classical (exchange–correlation) terms are non-negligible. Natural energy decomposition analysis of traditional and π-Be bonds indicate that the attractive interactions come from both the electrical and charge transfer terms. The electrical term in the Be–Ng bonds is negligibly small and the charge transfer is the most dominant contributor in the interaction energy.

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1. Introduction

The nature of beryllium bonds has been the subject of a number of recent theoretical and experimental investigations [1–13]. Indeed, a beryllium bond is a non-covalent interaction in which a beryllium atom acts as a strong Lewis acid and interacts with a base. Beryllium bonds share many common characteristics with hydrogen bonds, however, they are in general significantly stronger than conventional hydrogen bonds [1,2]. Similar to hydrogen, the beryllium atom is electropositive and when it is covalently bonded to a more electronegative, its low-lying empty orbitals turning it into a potent electron acceptor.

Yáñez and co-workers investigated the interactions between different Lewis bases and some beryllium derivatives, BeX_2, and showed that these interactions have a dominant electrostatic character in addition to some covalent character with a non-negligible charge transfer between interacting molecules [1]. On the other hand, Zhong et al. used SAPT-DFT [14] approach to explore the origin and nature of Be bonds [15]. Their results show that the electrostatic potential is the largest contributor to the binding, with induction and polarization playing important secondary roles. Yáñez et al. studied the so-called π-beryllium bonds between BeX_2 and unsaturated compounds (ethylene and acetylene) and

indicated that these complexes are stabilized by a significant charge transfer from π_u binding orbitals into the empty p orbitals of Be and σ^*_{BeH} antibonding orbitals [7]. Using localized molecular orbital energy decomposition analysis (LMOEDA) [16] they showed that in the π-beryllium bonds the largest stabilizing contribution comes from the electrostatic term, however, the polarization is also significant. In a different work, Franking and co-workers studied the interactions between noble gases (Ng) and beryllium compounds. They prepared $Ng - BeCO_3$ complexes and identified them via IR spectroscopy [8]. Their EDA of the $Ng - Be$ bonds indicates that the attractive interaction energy comes mainly from orbital interaction (charge transfer and polarization effects).

In our pervious work [2], we used quantum theory of atoms in molecules (QTAIM) [17,18] to investigate the nature of beryllium bonds, based on the properties of the electron density and its derivatives. It has been shown that these interactions are very similar to the very strong hydrogen bonds, however, some differences have been also observed. In the current study, to shed more light on the nature of different types of Be bonds, we will use again the real space QTAIM definitions, but our focus will be on the intra and inter-atomic energy terms within the framework of interacting quantum atoms (IQA) [19–21] energy partitioning. In addition, the natural energy decomposition analysis (NEDA) [22] will perform on the chosen beryllium bonded complexes. In this work, three different beryllium interactions are considered; traditional Be

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bonds (between Be and ammonia), π-Be bonds (between Be and unsaturated molecules, ethylene and acetylene) and Ng–Be bonds (between Be and noble gases, Ne and Ar).

2. Theory and computational details

The IQA scheme is a real space energy decomposition method which uses second order density matrix to partition the molecular energy into intra- and inter-atomic energy terms:

$$E = \sum_A E_{self}(A) + \sum_A \sum_{B \neq A} E_{int}(A, B) \tag{1}$$

in which, $E_{self}(A)$ is the intra-atomic (self) energy of the atom A and consists of all the monoatomic energy terms; kinetic energy, $T(A)$, nuclear–electron, $V_{ne}(A)$, and electron–electron interaction, $V_{ee}(A)$, inside the atomic basin:

$$E_{self}(A) = T(A) + V_{ne}(A) + V_{ee}(A) \tag{2}$$

$E_{int}(A, B)$ is the inter-atomic interaction energy and obtained by collecting all the two-center contributions:

$$E_{int}(A, B) = V_{nn}(A, B) + V_{en}(A, B) + V_{ee}(A, B) \tag{3}$$

here, $V_{nn}(A, B)$, $V_{en}(A, B)$ and $V_{ee}(A, B)$ are, respectively, nuclear–nuclear, electron nuclear and electron–electron interaction energies. In addition, V_{ee} can be splitted into Columbic, V_{ee}^C, and exchange–correlation, V_{ee}^{XC}, terms. Now, $E_{int}(A, B)$ can be written as:

$$E_{int}(A, B) = V_{cl}(A, B) + V_{XC}(A, B) \tag{4}$$

where $V_{cl}(A, B)$ consists of all the classical electrostatic interactions.

In the NEDA method the intermolecular interaction energy is portioned into a sum of electrical (EL), core repulsion (CORE) and charge transfer (CT) components:

$$\Delta E = EL + CORE + CT \tag{5}$$

Electrical component can be written as a sum of electrostatic (ES), polarization (POL) and self-energy (SE) contributions:

$$EL = ES + POL + SE \tag{6}$$

And finally, the core repulsion component is:

$$CORE = EX + DEF - SE \tag{7}$$

here, EX and DEF are, respectively, the exchange and deformation contributions.

The geometry of the molecules presented in this work were fully optimized with MP2/aug-cc-pvTZ level using GAMESS (US) quantum chemistry software [23]. IQA atomic energy terms were evaluated by AIMAll program [24]. This package has been also used to draw molecular graphs of the complexes. HF wavefunctions have used for IQA analyses. For NEDA calculations the NBO 5.0 program [25,26] implemented in the GAMESS was used.

3. Results and discussions

3.1. IQA analysis

All the Be bonded complexes studied in this work have been listed in Table 1. The first block indicates traditional Be bonded molecules ($CO_3Be \cdots NH_3$ and $X_2Be \cdots NH_3$; X = H, F, Cl and Br) while the second and third blocks correspond to Ng–Be ($Ne \cdots BeCO_3$ and $Ar \cdots BeCO_3$) and π-Be (H_2Be and F_2Be with ethylene and acetylene) complexes, respectively. The molecular graphs (MGs) of some of the complexes have been also presented in Fig. 1. Table 1 indicates the virial-based [17,27] atomic energies, ΔE_{VB}, and also IQA self energies, ΔE_{self}, of Be atom in these complexes relative to the corresponding values in their isolated optimized monomers.

Table 1

Changes in the virial-based atomic energies (ΔE_{VB}), IQA self-energy contributions and variation in the electronic population, ΔN, of beryllium atomic basin relative to relevant optimized monomers. The relative value for these properties have been defined as $\Delta P = P(complex) - P(isolated\ monomer)$. All energetic data are in kcal/mol.

Complex	ΔE_{VB}	ΔT	ΔV_{ee}	ΔV_{en}	ΔE_{self}	ΔN
$H_2Be \cdots NH_3$	32.49	−34.10	15.69	27.09	8.69	−0.005
$HFBe \cdots NH_3$	5.91	−6.40	12.38	−33.86	−27.88	0.022
$F_2Be \cdots NH_3$	34.76	−35.07	1.68	50.98	17.59	0.027
$HClBe \cdots NH_3$	3.66	−4.53	13.37	−35.29	−26.45	0.021
$Cl_2Be \cdots NH_3$	14.31	−14.75	2.57	9.22	−2.95	−0.002
$HBrBe \cdots NH_3$	2.05	−2.20	14.72	−38.97	−26.44	0.022
$Br_2Be \cdots NH_3$	−7.15	7.07	14.83	−50.33	−28.44	0.025
$CO_3Be \cdots NH_3$	−45.20	45.01	−6.94	−142.47	−104.40	0.053
$Ne \cdots BeCO_3$	−24.66	24.94	24.11	−79.86	−30.80	0.033
$Ar \cdots BeCO_3$	−24.78	29.23	37.32	−106.13	−39.58	0.046
$H_2Be \cdots C_2H_4$	13.61	−14.32	25.96	−28.24	−16.59	0.023
$F_2Be \cdots C_2H_4$	17.03	−17.11	0.44	9.47	−7.19	0.005
$H_2Be \cdots C_2H_2$	14.59	−14.97	28.15	−30.68	−17.51	0.023
$F_2Be \cdots C_2H_2$	19.99	−20.00	−2.71	16.88	−5.82	0.001

The relative values of all the contributions in the IQA self-energies have been also collected in the Table 1. All of the relative values have been defined as $\Delta P = P(complex) - P(isolated\ monomer)$, in which P refers to the atomic properties.

It has been previously shown that in the traditional Be-bonded complexes the absolute value of virial-based atomic energy of the beryllium atom decreases (i.e. $E_{VB}(Be)$ becomes less negative and $\Delta E_{VB}(Be)$ is positive) upon complex formation, comparable to the hydrogen atom in the hydrogen bonded complexes [2]. Similar results have been observed for most of the traditional Be bonds of this work (Table 1). $CO_3Be \cdots NH_3$ and $Br_2Be \cdots NH_3$ are the only exceptions in which $\Delta E_{VB}(Be)$ is negative and the beryllium atom is stabilized upon complex formation. In addition, in the π-Be bonded systems, similar to general trends in the traditional Be bonds, the Be atom is destabilized when the complex is formed. A different situation is found for Ng–Be complexes; the kinetic energy and hence the absolute value of virial-based energy of beryllium increases upon complex formation.

On the other hand, from the IQA self-energy point of view, there is distinction between beryllium bonds and hydrogen bonds; as indicated in Table 1, in most of the complexes the beryllium atom is stabilized upon complex formation, unlike to hydrogen atom in the hydrogen bonded complexes [20]. In the traditional Be bonds (with the exception of $H_2Be \cdots NH_3$ and $F_2Be \cdots NH_3$ complexes) the absolute values of beryllium self-energy increase ($\Delta E_{self}(Be)$ is negative) during complex formation. In these complexes, the formation of beryllium bond is accompanied by two stabilizing changes: a decrease in the Be kinetic energy and an increase in the absolute value of nuclear–electron attraction. The destabilizing effect arising from electron–electron repulsion is small and is overwhelmed by the other two contributions. In the $CO_3Be \cdots NH_3$ and $Br_2Be \cdots NH_3$ systems, in which $\Delta T(Be)$ is positive (destabilizing effect), $V_{ne}(Be)$ is the main stabilizing contributor, however, it is large enough to compensate for all destabilizing terms. In the $H_2Be \cdots NH_3$ and $F_2Be \cdots NH_3$ complexes $\Delta E_{self}(Be)$ is positive. Here, the negative values of $\Delta T(Be)$ are canceled out by two destabilizing effects: increase in the electron–electron repulsion and decrease in the absolute value of nuclear–electron attraction.

During formation of π-Be and Ng–Be complexes the beryllium atom experiences an increase in its absolute value of self-energy ($E_{self}(Be)$ becomes more negative). In the π-Be bonds of BeH_2, the beryllium atom suffers an increase in electron–electron repulsion (mirrored in the positive values of ΔV_{ee}) and absolute values of nuclear–electron attraction (ΔV_{ne} is negative) and a decrease in kinetic energy. The substitution of hydrogens of BeH_2 by fluorine