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Quantum chemical studies of non-covalent interactions between the ethyl cation and rare gases



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ABSTRACT

By taking into consideration the facts that rare gases (Ar, He, Kr, and Ne) are practically inert and that the structure of the ethyl cation ($C_2H_5^+$) is stabilized through the hyperconjugation effect, a theoretical study at the B3LYP/6-311++G(d,p) level of calculation was carried out here in order to investigate the formation of the $C_2H_5^+ \cdots Ar$, $C_2H_5^+ \cdots He$, $C_2H_5^+ \cdots Kr$, and $C_2H_5^+ \cdots Ne$ complexes. The charge transfers among H and Ar, He, Kr or Ne prove that the loss of electronic density on the rare gases are clearly noticeable. Additionally, the synergism between the structural changes and the vibration shifts have been demonstrated and justified on the basis of the Bent rule and QTAIM calculations. In complement, the interaction strength in $H^+ \cdots Ar$, $H^+ \cdots He$, $H^+ \cdots Kr$, and $H^+ \cdots Ne$ was examined, although the covalent character is completely null because these contacts are very weak.

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1. Introduction

Nowadays, the studies of interatomic interactions have attained a level of complexity never seen before [1–5]. Besides dihydrogen bonds [6–10], halogen bonds [11–14], dihydride–halogen bonds [15–17], beryllium bonds [18], and pnictogen bonds [19,20], in general the electron flux on these interactions occur from high-electron-density centers, such as proton acceptors, towards the electron-depleted ones, which are represented by hydrogen donors [21–24]. Clearly, this electronic gearing controls the formation of these non-covalent links [25–27]. Anyhow, the research of new forms of intermolecular contacts is focused on the analysis of the high electron-density entity, because it is from the hyperconjugative interaction (charge transfer) [28] between the frontier molecular orbitals occurs. Otherwise, in some circumstances, hybridization (*ab initio* wave function) can manifest itself and outweigh hyperconjugation [29,30]. Actually, depending on the strength of the interaction, these two interpretative lines

rationalize the state-of-the-art to evaluate whether an intermolecular system is a stronger or a weaker bound.

Regarding proton donating in hydrogen bonding, it is known that they must not necessarily be neutral acids, and indeed, they can originate from ionic species. In agreement with this, it was established a very long time ago that some carbonium ions have the capability to acquire extra stability [31], but in this case, the occurrence of inconstant electronic fluxes plays a great role in the formation of electron-depleted molecular sites. If it happens, the carbocation may function as a proton donor, such as the ethyl cation ($C_2H_5^+$) does, for instance. Beyond being a typical representative of carbocations [32], $C_2H_5^+$ has been already examined and validated as a proton donor in the formation of hydrogen complexes with similar neutral molecules, such as acetylene, ethylene, as well as cyclopropane [33], wherein $\pi \cdots H$ hydrogen bonds appear. Moreover, $C_2H_5^+$ is also able to form dihydrogen bonds when it binds to magnesium hydride or beryllium hydride to form binary ($C_2H_5^+ \cdots MgH_2$ and $C_2H_5^+ \cdots BeH_2$) and ternary ($C_2H_5^+ \cdots 2MgH_2$ and $C_2H_5^+ \cdots 2BeH_2$) complexes [34,35].

Concerning the proton's acceptor nature, it is well known that molecules with lone pairs of electrons [36,37],

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unsaturated bonds [22,38] or even those with hydride groups [16,17] are able to receive acid protons. Otherwise, there is also another possibility of unusual proton receptors, for instance, the rare gases. In line with this, Cappelletti et al. [39] have stated the “birth of the hydrogen bond” between water and some rare gases, Barreto et al. [40] described van der Waals forces in complexes of water and peroxides with rare gases, whereas Jamshidi et al. [41] have asserted that metals and rare gases bind to each other in a stable form. Although the existence of protonated rare gas clusters is known [42], the main goal of the current work is focused on a quantum chemical study of intermolecular interactions between rare gases, such as argon, helium, krypton, or neon, and the ethyl cation ($C_2H_5^+$), whose $H\cdots Ar$, $H\cdots He$, $H\cdots Kr$, and $H\cdots Ne$ contacts will be examined by means of structural investigation, determination of electronic parameters, infrared spectroscopy analysis, topological integrations of charge densities, and molecular orbital calculations.

From a spectroscopic standpoint, the researches related to hydrogen bonds or any other similar interaction are currently performed on the basis of the s -(H) and p -(X) orbitals in the $H-X$ proton donor system (wherein X is more electronegative than hydrogen) [43], whose contributions as well as variations accord well with the Bent rule [44]. Being aware of this statement, the analysis of these orbitals should be one of the objectives to be fulfilled here because the Bent rule corroborates the hybridization theory and justifies the frequency shifts of the proton donors. As such, the shortening in the bond length of the proton donor is followed by a decrease in its polarity, by which an increase in the s -character of the orbital of X (within the $H-X$ molecule) is evidenced. If this occurs, displacements in the coordinates of H and X are expected, and surely this can be justified through the computation of their atomic radii by means of the Quantum Theory of Atoms in Molecules (QTAIM) [45]. Specifically, if the distance between these atoms is reduced, the relationship $\Delta r_H > \Delta r_X$ is valid. This inequality is related to the shortening of the bond length and with a blue shift in the stretch frequency [43]. On the other hand, if $\Delta r_H < \Delta r_X$, it means that a weakness in the proton donor bond is testified, which leads to an increase in the bond length, which, in turn, causes the appearance of a red shift in the $H-X$ oscillator [43].

On a purely theoretical viewpoint, these atomic radii are computed in the light of the QTAIM approach, with localization of Bond Critical Points (BCP) along each internuclear axis [46]. In addition, other topological properties are also determined, namely: electronic density (ρ), Laplacian ($\nabla^2\rho$), kinetic (G) and potential (U) electronic density energies. It is through the low and high values of ρ , the positive and negative ones of $\nabla^2\rho$, and finally if G outweighs U or vice-versa, that all $H\cdots RG$ (with $RG = Ar, He, Kr, \text{ and } Ne$) interactions and π bond of $C_2H_5^+$ are modeled. In practice, it is expected that the interaction strength profile of the $C_2H_5^+\cdots RG$ systems may be in good agreement with these kinds of analysis presented above, although it is widely known that the charge transfer mechanism still governs the formation of some intermolecular interactions [28,47–50], even if partially. Due to

this, the algorithms of the Charges from Electrostatic Potentials using a grid-based method (ChelpG) [51], Natural Bond Orbitals (NBO) [52], the traditional Mulliken population analysis [53], and naturally the QTAIM integrations [54] were applied during routine calculations. By these codes, the loss of atomic charge on the rare gases being transferred towards H, the phenomenon of shift in the frequency of the proton donor ($C_2H_5^+$), and of course the formation of the $H\cdots RG$ interaction can be certainly evidenced.

2. Computational procedure

The optimized geometries of the $C_2H_5^+\cdots RG$ complexes (with $RG = Ar, He, Kr, \text{ and } Ne$) were modeled at the B3LYP/6-311++G(d,p) level of theory. All calculations were carried out by the GAUSSIAN 98 W quantum software [55], by which the calculations of the ChelpG, NBO, and Mulliken atomic charges were also obtained. Moreover, the Boys and Bernardi function counterpoise method [56] implemented to eliminate the Basis Sets Superposition Error (BSSE) [57] and the Zero-Point vibrational Energy (ZPE) [58] were also included to correct the interaction energies. Regarding the QTAIM calculations, they were performed by AIMAll 11.05.16 software [59] after generation of the “*wfn*” archive by GAUSSIAN 98W.

3. Results and discussions

3.1. Structure and spectrum

Through the calculations performed at the B3LYP/6-311++G(d,p) level of theory, Fig. 1 illustrates the optimized geometries of the $C_2H_5^+\cdots Ar$ (I), $C_2H_5^+\cdots He$ (II), $C_2H_5^+\cdots Kr$ (III), and $C_2H_5^+\cdots Ne$ (IV) complexes. The distance values of 2.5822 (I), 2.4116 (II), 2.6126 (III), and 2.3956 Å (IV) for the $H\cdots RG$ interactions are shorter than the corresponding sum of the van der Waals radii [60–62], whose amounts are 2.97 ($H = 1.09 + Ar = 1.88$), 2.490 ($H = 1.09 + He = 1.40$), 3.11 ($H = 1.09 + Kr = 2.02$), and 2.63 Å ($H = 1.09 + Ne = 1.54$). In conformity with these assertions, but in view of the applicability in investigations of chemical bonds and interatomic distances [63,64], the interaction distance at the B3LYP/6-311++G(d,p) of I is shorter than the values reported by Goswami and Arunan [65] regarding the $H_2O\cdots 2Ar$ and $H_2S\cdots 2Ar$ complexes at the MP2(full)/aug-cc-pVTZ level of theory. Absolutely, this is not enough to discriminate the efficiency between these levels of theory, but otherwise it also serves to show that ternary structures have not necessarily shorter intermolecular distances and higher interaction energies compared with binary ones [21,27,66,67].

In addition to $H\cdots RG$, the values of the bond lengths of both $C\cdots H$ and π are also depicted in Fig. 1. Unlike many other intermolecular systems [68–70], the shorter interactions of II and IV are not responsible for the most intense molecular changes, in particular on the ethyl cation. Note that IV is a much shorter bound than III, although the corresponding values of Δr_π are -0.0006 and -0.0037 Å. Because the hyperconjugation controls the stabilization of

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