The role of back-bonding in the determination of classical *vs*. non-classical bonding in EH_3^+ and EH_5^+ minimum structures for E = C, Si and Ge

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A rationalization of bonding in EH_3^+ and EH_5^+ classical and non-classical most stable minimum structures is proposed for E = C, Si and Ge by means of a back-bonding interaction which when present is clearly displayed by a configuration analysis and explains the lack of bridged hydrogens in the corresponding structure.

Very recently there has been a strong interest in the study of the species EH_3^+ and EH_5^+ for E = C, Si and Ge.[1–8] For CH_3^+ high level computations have rendered no side-on $HC^+\cdots H_2$ complex the classical D_{3h} symmetric structure being the most favored energetically. In contrast, for SiH_3^+ and GeH_3^+ two different minimum structures have been found: one of D_{3h} symmetry and the other, a non-classical side-on complex, of C_s symmetry.[1] On the other hand, for the EH_5^+ systems, the global minimum structures are non-classical C_s structures characterized by a three-center–two-electron bond having a five-coordinate central atom and bridged hydrogens. No classical five-coordinate minimum structure have been found for these EH_5^+ systems.[2–8] It has been argued that this is so because the energy required to break the H–H bond is not compensated by the two newly formed E–H bonds[7] in contrast with the classical EH_3^+ structures where the H_2 cleavage seems to be adequately compensated.

In this work we propose a rationalization of bonding in the title EH_3^+ and EH_5^+ systems by using the back-bonding concept which when present is clearly displayed by a configuration analysis.

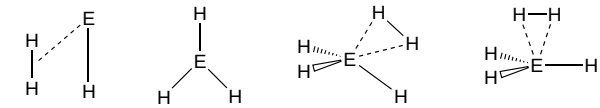
All structures were optimized at the Becke3LYP DTF level[9] with the standard 6-311++G(2d,2p) basis set using the Gaussian 94 program.[10] The nature of the stationary points was further characterized by frequency calculations which also gave the zero-point vibrational energy (ZPVE) correction. This theory level has previously proved to be adequate to study some of the title systems.[1] DFT wavefunctions were analyzed by means of a theoretical method developed by Fukui's group[11] using the ANACAL program.[12] This method is based on the expansion of the MOs of a complex system in terms of those of its fragments, and configuration analysis. This type of analysis has proved useful for understanding the chemical features of complex formation from chemically interacting systems.

Table 1 collects the Becke3LYP/6-311++G(2d,2p) total energies and ZPVE of the EH_3^+ and EH_5^+ (E = C, Si and Ge) minimum structures studied in this work: the classical D_{3h} minimum structures of CH_3^+, SiH_3^+ and GeH_3^+, the side-on C_s structures of SiH_3^+ and GeH_3^+, and the global minimum structures of C_s symmetry of CH_5^+, SiH_5^+ and GeH_5^+. For SiH_3^+ and GeH_3^+ the D_{3h} structures are the most stable ones by 28.4 and 11.1 kcal mol^{-1}, respectively (27.1 and 10.0 kcal mol^{-1} when ZPVE is included).

Table 2 presents the most important changes in the electronic population of the Kohn–Sham MOs of EH_3^+ and EH_5^+ minimum structures. Table 3 displays the coefficients of the most important electronic configurations of fragments in the minimum structures studied in this work.

We see from Table 2 that in the EH_3^+ structures of D_{3h} symmetry the HOMOs of both fragments and the NHOMO of the EH^+ fragment lose electronic population and the LUMO and the NLUMO of the EH^+ cationic fragment and the LUMO of H_2 become appreciably populated. Table 3 shows that this

Table 1 Becke3LYP/6-311++G(2d,2p) total energy (E_h) and ZPVE [kcal mol^{-1} (1 cal = 4.184 J)] of EH_3^+ and EH_5^+ minimum structures (E = C, Si, and Ge)



Species		Total energy	ZPVE
CH_3^+	D_{3h}	−39.49360	19.6
SiH_3^+	D_{3h}	−290.96382	13.9
	side-on, C_s	−290.91861	12.6
GeH_3^+	D_{3h}	−2078.46433	13.1
	side-on, C_s	−2078.44665	12.0
CH_5^+	C_s	−40.74944	31.9
SiH_5^+	C_s	−292.16795	23.8
GeH_5^+	C_s	−2079.66377	22.7

Table 2 Most important changes in the electronic population ($\Delta\nu$) of the Kohn–Sham MOs of EH_3^+ (A = EH^+; B = H_2) and EH_5^+ (A = EH_3^+; B = H_2) minimum structures (E = C, Si, Ge), net charge transfer (CT) from H_2 to the cation, and H–H distance (Å) where < 1 Å

		CH_3^+ D_{3h}	SiH_3^+ D_{3h}	SiH_3^+ side-on C_s	GeH_3^+ D_{3h}	GeH_3^+ side-on, C_s	CH_5^+ C_s	SiH_5^+ C_s	GeH_5 C_s
A	NLUMO	+0.09	+0.03	0.0	+0.75	+0.19	0.0	+0.03	+0.01
	LUMO	+1.05	+0.70	+0.22	+0.09	0.0	+0.83	+0.25	+0.22
	HOMO	−0.61	−0.70	−0.05	−0.61	−0.03	−0.24	−0.03	−0.02
	NHOMO	−0.14	−0.17	−0.01	−0.18	0.0	−0.03	0.0	0.0
B	LUMO	+0.72	+1.08	+0.04	+1.08	+0.03	+0.15	+0.02	+0.02
	HOMO	−1.33	−1.19	−0.25	−1.25	−0.22	−0.84	−0.29	−0.25
	CT	0.41	0.01	0.18	0.07	0.17	0.52	0.24	0.20
	d(H–H)			0.782		0.773	0.988	0.777	0.772

Table 3 Coefficients of the most important configurations of fragments in the EH_3^+ (A = EH^+; B = H_2) and EH_5^+ (A = EH_3^+; B = H_2) minimum structures (E = C, Si, Ge)

Configuration	CH_3^+ D_{3h}	SiH_3^+ D_{3h}	SiH_3^+ side-on, C_s	GeH_3^+ D_{3h}	GeH_3^+ side-on, C_s	CH_5^+ C_s	SiH_5^+ C_s	GeH_5^+ C_s
AB	0.0	0.0	+0.7620	0.0	+0.8017	+0.3152	+0.7480	+0.7793
A^-B^+(HO–LU)	0.0	0.0	+0.2515	0.0	−0.0247	+0.3691	+0.2626	+0.2513
A^-B^+(HO–NLU)	0.0	0.0	0.0	0.0	+0.2366	0.0	+0.0717	+0.0500
$A^{2-}B^{2+}$(HO–LU/HO–LU)	+0.1489	+0.0753	+0.0356	0.0	0.0	+0.1514	+0.0375	+0.0341
$A^{2-}B^{2+}$(HO–NLU/HO–NLU)	0.0	0.0	0.0	+0.0844	+0.0307	0.0	0.0	0.0
AB**(HO–LU/HO–LU)	+0.0844	+0.1291	0.0	+0.1415	0.0	0.0	0.0	0.0
A*B*(HO–LU/HO–LU)	+0.1638	+0.1808	0.0	0.0	0.0	0.0	0.0	0.0
A*B*(HO–NLU/HO–LU)	0.0	0.0	0.0	+0.1660	0.0	0.0	0.0	0.0
$A^{\pm}B^{\mp}$(HO–LU/HO–LU)	+0.1638	+0.1808	+0.0201	0.0	0.0	+0.0916	0.0	0.0
$A^{\pm}B^{\mp}$(HO–LU/HO–NLU)	0.0	0.0	0.0	+0.1660	0.0	0.0	0.0	0.0
A^-B^{+*}(HO–LU/HO–LU)	+0.1865	−0.1705	0.0	−0.0546	0.0	0.0	0.0	0.0
A^-B^{+*}(HO–NLU/HO–LU)	0.0	0.0	0.0	+0.1860	0.0	0.0	0.0	0.0
A^+B^{-*}(HO-LU/HO–LU)	+0.0741	−0.1368	0.0	−0.1262	0.0	0.0	0.0	0.0
$A^{*-}B^+$(HO–LU/HO–LU)	+0.1308	−0.0799	0.0	0.0	0.0	0.0	0.0	0.0

electronic rearrangement is caused by two different interactions between the fragments: a charge transfer from the HOMO of H_2 to the LUMO or NLUMO of the EH^+ moiety, and a back-donation from the HOMO of the cationic fragment to the LUMO of H_2. In the side-on structures of SiH_3^+ and GeH_3^+ the spatial disposition of the fragments is compatible only with an interaction of dihydrogen with the vacant orbitals of EH_3^+. In effect, Table 2 shows that the LUMO or NLUMO of the EH^+ cationic fragment gain electronic population whereas the HOMO of H_2 becomes less populated. We see in Table 3 that this redistribution of electrons is due to an HOMO(H_2)–LUMO (SiH^+) or HOMO(H_2)–NLUMO (GeH^+) interaction. These are then donor–acceptor complexes between the dihydrogen ligand (donor) and EH^+ as already reported.[1] The reason why there is no side-on structure in the case of CH_3^+ is that the LUMOs of CH^+ are more stable (−0.55 eV) than the HOMO of H_2 (−0.43 eV). As a consequence, in a hypothetical side-on structure of CH_3^+ a very strong charge transfer would take place from H_2 to CH^+ in a first phase. The depopulation of the HOMO of H_2 produced by this charge transfer would cause an important elongation of the H–H bond and a stabilization of the LUMO of dihydrogen which would allow the interaction of H_2 with the HOMO of CH^+ through back-bonding and the formation of the D_{3h} structure.

For the EH_5^+ systems the most stable structures have C_s symmetry with the H_2 unit bound sideways to the EH_3^+ fragment. However, there is a significant difference between CH_5^+ and SiH_5^+ and GeH_5^+. In SiH_5^+ and GeH_5^+ the H_2 unit preserves its entity only slightly perturbed by the interaction with the EH_3^+ fragment whereas in CH_5^+ the H_2 unit presents a considerably elongated bond (see Table 2). This difference can be understood in terms of the electronic configurations of the fragments (see Table 3). In effect, for SiH_5^+ and GeH_5^+ the wavefunction is a mixture mainly of the zero configuration and the monotransference from the HOMO of H_2 to the LUMO of EH_3^+ whereas for CH_5^+ the wavefunction includes in addition the ditransference from the HOMO of H_2 to the LUMO of EH_3^+ and a small contribution from the cross transference from the HOMO of H_2 to the LUMO of CH_3^+, and from the HOMO of CH_3^+ to the LUMO of H_2. Accordingly, we see in Table 2 that the LUMO of the EH_3^+ fragment is considerably more populated and its HOMO loses more electronic density, and the HOMO of H_2 loses more electronic population and its LUMO becomes more populated in the case of CH_5^+ than in the other two cases. This can be explained again as a consequence of the fact that the LUMO of CH_3^+ (−0.49 eV) is more stable than the HOMO of H_2. This determines a very strong charge transference from the H_2 fragment to CH_3^+ which causes the elongation of the H–H bond making possible even a back donation from the HOMO of CH_3^+ to the LUMO of H_2. As a consequence, while in SiH_5^+ and GeH_5^+ the H_2 fragment interacts only with the p_z orbital of the central atom whose three sp^2 hybrids form three E–H bonds, in CH_5^+ two of the sp^2 hybrids of the central atom form two C–H bonds and the NHOMO of the CH_5^+ is a linear combination of the third sp^2 hybrid, the 1s atomic orbital (AO) of the two H atoms of the H_2 moiety and the 1s AO of the remaining H atom. This difference is clearly appreciated in the geometry of the EH_5^+ systems. In the case of E = Si, Ge the H_2 fragment is symmetrically situated in front of the p_z AO of the central atom parallel to the sp^2 plane whereas in CH_5^+ the H_2 fragment is placed between one of the sp^2 hybrids and the p_z AO of C, the remaining H atom being displaced from the linear direction along the hybrid AO.

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