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Ab initio Calculations of Small Hydrides Including Electron Correlation

XII. The Ions CH_5^+ and CH_5^-

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Five different structures of CH_5^+ and one structure of CH_5^- are calculated using a gaussian basis both in the SCF approximation and with the inclusion of electron correlation in the independent electron pair approximation (IEPA). While on SCF level the C_s structure of CH_5^+ has to lowest energy, the energy difference between the C_s and C_{2v} structures becomes negligible if correlation is included. In contrast to this the approach of a proton to CH_4 at large and intermediate distances is most favorable towards a corner of the CH_4 tetrahedron which means a structure. The decomposition of CH_5^+ into CH_3^+ and H_2 requires ~20 kcal/mol on SCF level and ~40 kcal/mol if correlation is included.

Key words: Correlation energy – Independent electron pair approximation – Electrophilic substitution on saturated center

1. Introduction

In a previous paper of the present authors together with Staemmler [1] the results of SCF-calculations for different geometrical configurations of the CH_5^+-ion were reported.[1] These results were recently confirmed [2]. We have meanwhile extended the calculations by inclusion of electron correlation within the "independent electron pair approximation" IEPA. Some improvement of the SCF results with respect to Ref. [1] was also obtained as a result of a more careful "relaxation" of the internal coordinates. Finally we have complemented our study by an investigation of the "reaction path" for the approach of a proton to a CH_4 molecule. For CH_5^- a few SCF-calculations are known [3, 4, 9]. As far as the inclusion of correlation is concerned neither calculations on CH_5^+ nor on CH_5^- have so far been published. An unpublished CI – calculation of CH_5^- by Veillard *et al.* [6] came to the authors' knowledge after completion of this work.

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[1] In the abstract of Ref. [1] it was stated erroneously that the C_{4v} structure corresponds to a local minimum, it is only a saddle point. Further on Fig. 1 config. IV "D_{2h}" should be replaced by "C_{2v}".

2. The Gaussian Basis

In Ref. [1] three basis sets, designated as *A*, *B*, *C*, were used. Basis *C* which was described in detail [1] consists of 10 *s*-lobes [in the contraction (5, 1, 1, 1, 2)] and 5 *p*-groups [in the contraction (3, 2)] for carbon, 5 *s*-lobes [contraction (4, 1)] for hydrogen and one group, consisting of two lobes in each CH bond [1], the orbital exponents and the contraction coefficients being determined from calculations on CH_3^+. The SCF results of the present paper have mainly been obtained with basis *D* which differs from basis *C* by addition of a full set of *d*-type groups (with $\eta = 0.32144$) on carbon and in a different contraction of the 5 *s*-lobes of hydrogen (3, 1, 1) rather than (4, 1). This choice of the basis set is a compromise between what one ought to use and what is tolerable from the point of view of computation time. The shifts of the *s*-lobes on hydrogen [1] and the use of lobes in the bonds is more or less equivalent to the inclusion of *d*-AO's on carbon and $p\sigma$-AO's on hydrogen [2], or to be more specific, to the inclusion of *d*-AO's with an η-value of about 0.8 [2], which was found in independent calculations [2, 5, 7, 8, 16] to be the optimum value if *no* lobes in the bonds are used. In fact this equivalence is confirmed by the closeness (see Table 1) of the SCF energies obtained with basis *C* [1] and those of Hariharan *et al.* [2] who included *d*-AO's on carbon and *p*-AO's on hydrogen. The *d*-functions with $\eta \approx 0.3$ influence the SCF energies only slightly, but differently for structures of different symmetries. Structures of low symmetry are lowered more. The *d*-functions contribute somewhat more to the correlation energy.

For the calculation of the pair correlation energies the basis was augmented by additional basis functions on the hydrogen atoms, namely by one (decoupled) $p\sigma$- and two $p\pi$-groups in either direction with $\eta = 0.6$. For the interpair contributions *p*-functions (both σ and π) centered in the bonds and one

Table 1. SCF-energies (negative)

		CH_5^+				CH_4	CH_3^+	CH_5^-
		I	II	III	IV			
	Basis	D_{3h}	C_{4v}	C_s	C_{2v}	T_d	D_{3h}	D_{3h}
Ref. [1]	*A*	40.3643	40.3710	40.3909	40.3801	40.1950	39.2340	
	B	40.3739	40.3819	40.3933	40.3838	40.2003	39.2343	
	C	40.3806	40.3916	40.4039	40.3944	40.2036	39.2400	
This work	*D*	40.3837	40.3957	40.4101	40.4012	40.2052	39.2428	40.5819[a]
HF-limit (estimated)		40.399	40.412	40.426	40.417	40.220	39.257	
Ref. [4]		40.2842	40.2892	40.2896				40.4659
Ref. [9]								40.5883
Ref. [2]								
Without polarisation functions		40.3565		40.3682			39.2162	
		40.3802		40.4057			39.2363	
With valence shell correlation, this work		40.6044	40.6115	40.6216	40.6213	40.4169	39.3889	40.8341
Estimated total energy		40.703	40.710	40.720	40.720	40.514	39.476	40.956

[a] Basis *E* for CH_5^+

s-lobe on the line bisecting the HCH angle were included as well. The negative ions H^- and CH_5^- required a further *s*-lobe with a small exponent [7] of $\eta = 0.03$ and $p\sigma$-groups on the "negative" hydrogens with $\eta = 0.32$. Also in CH_5^- the $p\sigma$-groups with smallest η-values were decoupled. This defines basis *E*.

The extension of basis *D* to basis *E* did not change the results for CH_4, but it led to an improvement of the SCF energy of CH_5^- from -40.565 to -40.582 a.u. The correlation energy of CH_5^- was computed with basis *D* like the other molecules.

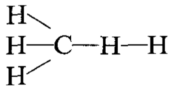
With the experience that we gained meanwhile we would now choose the basis in a more systematic way (see [7, 8]).

3. The Hartree-Fock Results

For CH_5^+ the same possible structures (Fig. 1) as in Ref. [1] were considered, and in addition also a structure with C_{3v} geometry, for CH_5^- only the D_{3h} arrangement. For CH_5^- only the CH-distance of the axial bonds was optimized, the equatorial bonds were given the same values as the corresponding ones of the D_{3h} structure of CH_5^+. As far as CH_5^- is concerned van der Lugt and Ros [4] have shown that the D_{3h} structure has by far a lower energy than the C_{4v} or C_s geometries. Nevertheless the D_{3h} configuration is not a minimum but rather a saddle point of the energy hypersurface. The real minimum, investigated by Dedieu and Veillard [9] is a loose complex between CH_4 and H^- (see also [3]). The D_{3h} geometry is regarded as the transition state for a S_N2 reaction.

For comparison also CH_4 and CH_3^+ in their equilibrium geometry calculated with the same basis are included. The results are collected in Table 1. The lowering of the energy on going from the calculations with basis *C* to those with basis *D* is partly due to an additional optimization of the geometry. In the calculation of the C_s structure with basis *C* the three CH-bonds not involved in the three-center bond were supposed to have local C_{3v}-symmetry, this restriction and the analogous restriction in the C_{2v} structure were relaxed in the calculation with basis *D*.

Structure $I(D_{3h})$ can be regarded as being obtained from CH_4 by adding a proton to the face of the CH_4-tetrahedron which would yield a C_{3v} geometry – and rearrangement of the CH-bonds of the original methane. Similarly structures III and IV come from the addition of the proton to the edge of a CH_4-tetrahedron, for structure IV in the center of the edge, for structure III off-center. Structure II is not obtained from CH_4 and a proton in a simple way.

In the structures considered so far the addition of the proton to the corner of the CH_4 tetrahedron, i.e. directly to an hydrogen atom of CH_4 keeping C_{3v} symmetry, was not included. We calculated the optimum arrangement for this structure *V* of the form  $H{-}\underset{H}{\overset{H}{C}}{-}H{-}H$ as well (though with a slightly smaller basis). It is not documented in Table 1, because it is by no means competitive. The SCF energy (for not fully optimized geometry) is 40.3426 a.u., it is 0.08 a.u. ≈ 50 kcal/mol above the C_s-structure (calculated with the same basis).

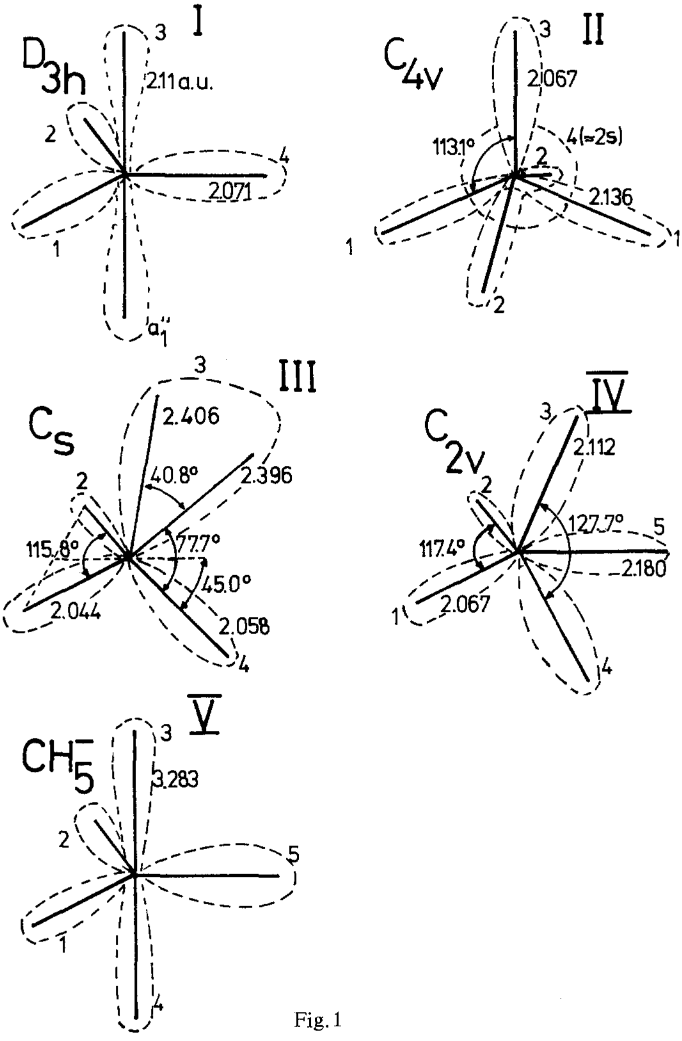


Fig. 1

The CH-distances of the CH-bonds and the angles were taken as those of methane, whereas the distances in the C—H—H-bond were optimized to yield $r_{CH} = 2.156\, a_0$, $r_{HH} = 1.296\, a_0$.

The order of stability of the different geometries from the SCF calculation is

$$III(C_s) < IV(C_{2v}) < II(C_{4v}) < I(D_{3h}) < V(C_{3v}).$$

The optimized geometries are indicated on Fig. 1. We have varied the geometries only on SCF level and calculated the correlation contributions for the optimized geometries.

For the C_s geometry there are two alternative structures, called IIIa and IIIb in Ref. [1], which are energetically so close (almost free rotation of the CH_3-group), that we have studied in detail only one of them, namely IIIa.

4. The Correlation Energy

The correlation energy of the molecules in various geometries (except *V*) was calculated with the IEPA–PNO-Method used in the papers of this series. As usual the Hartree-Fock orbitals were first transformed to localized ones according to the Boys criterion. The localization leads to the classical equivalent CH-orbitals in CH_4 and CH_3^+. In the C_s-configuration of CH_5^+ three of the localized orbitals correspond to CH-bonds, the fourth one to a three-center H—C—H bond. In the D_{3h}-configuration the a_1-MO was taken as such, i.e. as a three-center orbital and the Boys procedure was applied to the remaining three orbitals for which it yielded three equivalent CH-bond-MO's. For CH_5^+ in the C_{4v} and C_{2v} configurations localization is less straightforward since there are genuine many-center many-electron bonds, so localization to two-electron-bonds is somewhat artificial. Consequently there is a non-negligible differential overlap of the "localized" orbitals for either geometry. In CH_5^- the localization is straightforward again. The results for the different pair correlation contributions of the valence shell are given in Table 2. Their sums are compared with the estimated "experimental" valence shell correlation energies (i.e. experimental energies corrected for zero-point vibration minus relativistic corrections minus estimated

Table 2

Molecule	Intrapair	Number	Type	Interp. sing.	Interp. tripl.	Number	Type	E_{corr} Calculated (estimated)
CH_3^+	0.03205	3		0.00759	0.00906	3		0.1461
								(0.160)
CH_4	0.02989	4		0.00586	0.00950	6		0.2117
								(0.232)
CH_5^+ D_{3h} (I)	0.02758	3	1	0.00650	0.00749	3	1–2	
								0.2207
	0.3023	1	3	0.00885	0.1309	3	1–4	(0.242)
C_{4v} (II)	0.02726	2	1	0.00647	0.01859	1	1–2	
	0.02915	1	3	0.00706	0.01142	2	1–4	0.2158
				0.00323	0.00460	1	3–4	
	0.01269	1	4	0.01639	0.00842	2	1–3	(0.236)
C_s (III)	0.03286	1	3	0.00602	0.00928	1	1–2	
				0.00561	0.00989	2	1–4	
	0.02876	1	4					0.2115
				0.00513	0.00857	2	1–3	(0.232)
	0.02928	2	1	0.00722	0.01044	1	3–4	
C_{2v} (IV)				0.00612	0.01024	4	1–4	
	0.02882	2	1					0.2201
				0.00618	0.00858	1	1–2	(0.241)
				0.01444	0.01140	1	3–4	
	0.02824	2	3					
CH_5^- D_{3h}				0.00496	0.00860	3	1–2	
	0.03237	3	1					0.2690
				0.00421	0.00673	6	1–3	(0.295)
	0.03022	2	3	0.00227	0.00279	1	3–4	

Hartree-Fock limit minus estimated correlation energy involving the *K* shell) as far as they are known, i.e. for CH_3^+ and CH_4. Since the computed values are about 90% of the estimated ones in CH_3^+ and CH_4 we can estimate "correct" valence shell correlation energies for the different configurations of CH_5^+ and for CH_5^-.

If we add these extrapolated correlation energies to the estimated Hartree-Fock limits for the different configurations we get the total energies that are given in Table 1. Since the correlation energy is somewhat larger for the C_{2v} than for the C_s structure, the total energies of these two structures come very close to each other.

We do not think that the calculated correlation energies are so accurate that one can rely on energy differences of less than say 5 kcal/mol. The reason for this lack of accuracy lies mainly in the independent electron pair approximation, i.e. the neglect of the interaction between the different pairs (see e.g. [10]). We do not want to comment on a possible variation of these interaction terms with a variation of geometry, but rather plan to investigate this problem by explicitly computing those correction terms, either for this of for related systems [11, 12].

In spite of the effort necessary to calculate the pair correlation energies there is not much information concerning the relative stabilities of the different structures, obtained in addition to that available from SCF calculations, since the presence of an extra proton changes the correlation energy of the 8 valence electrons of CH_4 only to a very slight extent, namely by less than 0.01 a.u. = 6 kcal/mol if we consider all possible CH_5^+ structures and by virtually nothing if we refer to the C_s-geometry for CH_5^+. Anyway the almost-constancy of the correlation energy with respect to protonation is worth mentioning.

In CH_5^- the valence shell correlation energy (0.2690 a.u.) differs definitely more from the sum of the respective correlation energies of CH_4 and H^- calculated with the same basis (−0.2447 a.u.), namely by 0.027 a.u. = 17 kcal/mol. In a recent unpublished study Veillard *et al.* found that the D_{3h} structure of CH_5^- lies 59.3 kcal/mol above $CH_4 + H^-$ in the SCF approximation and that this "barrier height" is reduced by 4 kcal/mol to 55.2 kcal/mol if correlation is allowed for in a CI-scheme. Our calculated value for this barrier is 70 kcal/mol on SCF level and 55 kcal/mol if correlation is included. The discrepancy in the SCF values indicates that the problem of having balanced basis sets is not yet settled for negative ions. Our SCF energy is somewhat better for $CH_4 + H^-$ (−40.6927 compared to −40.6842 a.u.) whereas we are somewhat poorer for CH_5^- (−40.5819 compared to −40.5883).

5. Approach of a Proton to a CH_4 Molecule

CH_5^+ is the transition state of the prototype of a SE_2 reaction on a saturated center, so it seemed to us worthwhile to limit our study not just to be transition state itself, i.e. to the CH_5^+ configuration of lowest energy, but to investigate how a proton approaches a methane molecule coming from infinity. The calculations were performed in three different levels of approximation:

1) without an AO-basis on the approaching proton,

Table 3. SCF-potential curves for the approach of a proton to methane

R a.u.	Without GF's	With GF's	Opt. geom.
	a) Approach towards an edge (C_{2v})		
	−40.204165	−40.204165	−40.204165
12	−40.204453	−40.204455	—
10	−40.204751	−40.204763	—
8	−40.205591	−40.205966	—
6	−40.208628	−40.215080	−40.216625
4	−40.221654	−40.273592	−40.279518
3.5	−40.227754	−40.305722	—
3	−40.233155	−40.343358	−40.351055
2.5	−40.231404	−40.377247	—
2.11	−40.218418	−40.383759	−40.396976 (CH_5^+; C_{2v}; IV)
	b) Approach towards a corner (C_{3v})		
	−40.204165	−40.204165	−40.204165
12	−40.204371	−40.204385	—
10	−40.204633	−40.204812	—
8	−40.205501	−40.206687	—
6	−40.209738	−40.224597	−40.230291
4	−40.231752	−40.318395	−40.333897
3.8	−40.232654	−40.330233	—
3.5	−40.230070	−40.339116	−40.342611
3.3	−40.202628	−40.330511	(C_{3v}; V)
	c) Approach towards a plane (C_{3v})		
	−40.204165	−40.204165	−40.204165
12	−40.204454	−40.204460	—
10	−40.204766	−40.204771	—
8	−40.205571	−40.205590	—
6	−40.208325	−40.212049	−40.212691
4	−40.221480	−40.255871	−40.260919
3.5	−40.230076	−40.281964	—
3	−40.242457	−40.314910	−40.324700
2.5	−40.255543	−40.347552	—
2.112	—	−40.356718	−40.380270
2.0	—	−40.357390	(CH_5^+; D_{3h}; I)

2) with an AO-basis on the approaching proton, but without relaxing the equilibrium geometry of CH_4,

3) like 2) but with readjusting the CH_4 geometry.

The results can be seen from Table 3.

With approximation 1) one gets mainly the electrostatic interaction (charge of the proton with the octopole-moment of methane) and the induction (charge with induced dipole). Both effects are asymptotically proportional to $1/R^4$. The angular dependence of the first contribution should be proportional to the cubic harmonic xyz/r^3 and vanish in the angular average whereas the second contribution should be isotropic. In fact with approximation 1) there is for distances larger than 6 a_0 practically no difference whether the proton approaches a corner, an edge, or a face of the CH_4 tetrahedron.

In approximation 2) charge transfer and the formation of an (electron deficient) chemical bond is allowed for as well. On this level the anisotropy of the interaction potential between CH_4 and H^+ ist more pronounced. In the region between about 6 and 3.5 a_0 the energetically most favourable approach is that towards a corner, i.e. that in which the proton approaches directly one H-atom of methane. This result is somewhat surprising, since from the competitive equilibrium structure of CH_5^+ in C_s and C_{2v} geometry one would have expected that the approach towards an edge, i.e. towards the line connecting two H-atoms should be favoured. This approach becomes the most favourable one only in the region of distance $R \approx 2$ to 3 a_0 (between approaching proton and C-atom). The potential curve for the approach towards a corner has its minimum for $R = 3.3$ a.u. (corresponding to an H—H distance of 1.30 a_0, which is shorter than that in H_2) and is repulsive for shorter distances, whereas for the two other approaches the minimum occurs for $R = 2.1$ a.u.

Although the minimum corresponding to the "corner-approach" is (see Section 3) by no means competitive with the other structures considered, for *large* and intermediate distances the proton wants to approach the CH_4 towards a corner. The proton probably approaches the CH_4 where its electron density is highest, i.e. near the hydrogens.

The Decomposition of CH_5^+ *into* CH_3^+ *and* H_2

Olah *et al.* [13] have postulated that the addition of a proton to CH_4 to yield CH_5^+ is followed by a decomposition of the CH_5^+ ion into CH_3^+ and H_2. The reaction path for this decomposition therefore deserves some interest. We have calculated the SCF-energy along a plausible reaction path from CH_5^+ to $CH_3^+ + H_2$. The increase in energy was monotonous and no indication of a possible barrier was found.

The decomposition is endothermic, it requires 22 kcal/mol in SCF approximation and 43 kcal/mol if correlation is included. While for the reaction $CH_4 + H^+ \rightarrow CH_5^+$ correlation had rather little effect the energy of the reaction $CH_3^+ + H_2 \rightarrow CH_5^+$ is substantially changed by correlation.

In view of the strong endothermicity of the decomposition of CH_5^+ into CH_3^+ and H_2 it is hard to understand why CH_5^+ should decompose in this way. One whould rather expect that CH_3^+ adds H_2 to form CH_5^+. The abstraction of H_2 from CH_5^+ can only occur if some other process involves CH_3^+ in a sufficiently exothermic reaction. It is hard to see which process this can be.

6. Conclusions

The geometries I to IV considered for CH_5^+ are rather close in energy. Whereas the C_s structure is the most stable one in the Hartree-Fock approximation, inclusion of correlation energy leads to a negligible difference between the C_s and the C_{2v} geometries. Since the isomerisation between two equivalent C_s-structures goes via the C_{2v} structure and since we can be sure that the barrier for this isomerisation is very small and since in the C_s-structure there is practically free rotation of the three-center bond with respect to the other three hydrogens one can conclude that at room temperature all the protons are dynamically equivalent.

For the approach of a proton to methane at large and intermediate distances approach to a corner is energetically most favourable, for small distances aproach to an edge.

The energy of the reaction $CH_4 + H^+ \rightarrow CH_5^+$ is practically not changed by the inclusion of electron correlation, the energy of the CH_5^- in the D_{3h}-structure refered to $CH_4 + H^-$ is reduced somewhat by the electron correlation, whereas the energy necessary to decompose CH_5^+, into $CH_3^+ + H_2$ is changed from ~20 kcal/mol on SCF level to ~40 kcal/mol if correlation effects are included.

One may wonder whether the effort spent on the CH_5^+ calculations is worthwhile or whether one could get the same results in a cheaper way. It may even seem that CNDO-calculations [14, 15] were able to give all the relevant informations about CH_5^+. The inadequacy of the CNDO-approach even in a version improved for the present purpose becomes abvious if one looks more closely on energy differences. Kollmar and Smith [15] find e.g. a proton affinity of ~170 kcal/mol, the correct value being ~120 kcal/mol. *Ab-initio* calculations with moderate Gaussian basis sets [4] *without* polarization functions (*d* on C and *p* on H) lead (almost by chance) to the right relative order of the C_s, D_{3h}, and C_{4v} configurations of CH_5^+, but gave much too small energy differences between these structures. (C_{4v} 0.3 kcal/mol above C_s, D_{3h} 3.5 kcal/mol above C_s, the corresponding correct being ~6 and ~20 kcal/mol, respectively.)

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