

STUDY OF POTENTIAL CURVES BY UHF TYPE METHODS. CH₄ MOLECULE AND ITS DISSOCIATION PRODUCTS

Viliam KLIMO and Jozef TIŇO

*Polymer Institute, Centre of Chemical Research,
Slovak Academy of Sciences, 842 36 Bratislava*

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Geometry and energy parameters of the individual dissociation intermediate steps of CH₄ molecule, parameters of the barrier to linearity and singlet-triplet separation of the CH₂ molecule have been calculated by means of the UMP2 method in the minimum basis set augmented with the bond functions. The results agree well with experimental data except for the geometry of CH₂(¹A₁) and relatively high energy values of CH(²Π) and CH₂(¹A₁) where the existence of two UHF solutions indicates a necessity of description of the electronic correlation by more exact methods of quantum chemistry.

Theoretical estimation of dissociation and atomization energies of polyatomic molecules belongs to the problems which have not yet been solved by quantum chemistry with satisfactory precision. This fact has two main reasons. First the problem involves the calculation of electronic correlation energy whose change is relatively large in the fragmentation processes mentioned. A quantitatively correct description of such changes necessitates application of highly exact methods which is, however, possible only with small molecules because of high computational demands. Besides that it is necessary to use a large and high-quality basis set which eliminates the problems of the basis set superposition error, involves the *f*-type functions, etc. A certain way out of this situation can be represented by the methodical approach in which the insufficient inclusion of the correlation energy is compensated by a selection of such a basis set which favours the region of chemical bonds in the molecule. Also of this type are our calculations which combine the UMP2 method¹ with the minimum basis set augmented with the bond functions of *s* and *p* types². Using this combinations we could obtain good geometry and energy parameters of splitting of chemical bonds between H atom and other light atoms (potential curves of diatomic hydrides², characteristic points of the hypersurfaces of H₃ system and H₂O molecule³, dissociation and inversion of NH₃ molecule⁴, dissociation and excitation energies of BH₂⁺ system⁵). Such mutual compensation of errors, however, seems insufficient for description of dissociation of homonuclear bonds between the second-row elements^{6,7} where it is necessary to adopt more efficient methods of description of the electronic correlation effects.

The first part of the present communication deals with the optimized geometry parameters of the CH, CH₂, CH₃, and CH₄ molecules in the ground state as well as of the CH₂ molecule in the excited singlet state and in collinear arrangement. The second part deals with estimation of the atomization energy of CH₄, dissociation energy of CH bond in the CH₄, CH₃, CH₂, and CH molecules, energy of singlet-

triplet splitting for CH₂ molecule, and barrier to linearity of CH₂ molecule in the ground state. The results are compared with available experimental values. The last part of this paper contains a discussion of details of the additionally decoupled UHF solution found for the CH(²Π) and CH₂(¹A₁) molecules.

Geometry Parameters

Table I gives the values found by optimization of independent geometry parameters at the UMP2 level for the given symmetry of the ground state of the CH₄, CH₃, CH₂, and CH molecules as well as of the CH₂ molecule in the excited state and in collinear configuration. A good agreement was reached with the experimental data of the equilibrium energy parameters. In analogy with the NH₃ molecule and its dissociation products⁴ and with the H₂O molecule³, here also the R_e values are slightly overestimated, especially so in the case of two- and three-atomic molecules. An exception from this trend is observed with the R_e and Θ_e values of CH₂(¹A₁). In this case distinct are overestimation of the H—C—H angle and underestimation of the equilibrium C—H distance, which is a consequence of decoupling of the free electron pair described below. A certain paradox can be seen in the fact that the energetically higher solution of RHF type gives the values $R_e = 1.128 \cdot 10^{-10}$ m and $\Theta_e = 102.8^\circ$ which agree better with the experiment. Since it is not easy to obtain the equilibrium geometry parameters of polyatomic molecules from experimental data (see *e.g.* discussions in refs^{8,9}), the data obtained in this way can serve as internally consistent source of geometry parameters for construction of analytical potential energy surfaces of reactions of methane and its dissociation products in the ground state.

TABLE I

Calculated and experimental values of equilibrium C—H distances (R_e) and equilibrium H—C—H angles (Θ_e)

Molecule	$R_e^{\text{calc.}}/10^{-10}$ m	$R_e^{\text{exp.}}/10^{-10}$ m	$\Theta_e^{\text{calc.}}/^\circ$	$\Theta_e^{\text{exp.}}/^\circ$
CH ₄ (¹ A ₁)	1.095	1.0862 ^a		
CH ₃ (² A ₂)	1.087	1.0767 ^c		
CH ₂ (³ B ₁)	1.086	1.0748 ^c	132.8	133.84 ^c
CH ₂ (¹ A ₁)	1.042	1.11 ^b	115.8	102.4 ^b
H—C—H linear (³ Σ _g ⁻)	1.074	1.060 ^c		
CH(² Π)	1.145	1.1199 ^d		

^a Ref.⁸, ^b R_0 and Θ_0 from ref.¹¹, ^c ref.¹⁰, ^d ref.¹², ^e ref.²⁵.

Energy Parameters

A reliable calculation of atomization energy of CH_4 molecule (endothermicity of the reaction $\text{CH}_4 \rightarrow \text{C} + 4 \text{H}$ at the absolute zero temperature) represents an exacting problem for the quantum chemistry methods. The considerable change in the so-called extramolecular correlation energy accompanying formation or splitting of C—H bonds in methane causes considerable difficulties for reaching a quantitative agreement with the experimental value. The experimental atomization energy determined from the ΔH_{f0}^0 values according to ref.¹³ and corrected with respect to the zero point energy according to the ω frequencies from ref.⁸ has the value of 1 760 kJ/mol, the value of 1 796 kJ/mol being obtained by the UMP2 method in our basis. This result can be considered to represent a relatively good agreement with experiment; so *e.g.* a much more exact approach¹⁴ (the UMP4 method connected with the 6-311G** basis) only gives the value of 1 685 kJ/mol.

In the next step we will focus our attention on comparison of the dissociation energy values (D_c) of the individual dissociation reactions.



As the atomization energy is the sum of the dissociation energies of (A)–(D), it will be interesting to examine the proportions in which the atomization energy error is distributed into the individual dissociation steps. The results in Table II show that

TABLE II

The dissociation energies (D_c) according to the reactions (A), (B), (C), (D) in kJ/mol

Molecule	$D_c^{\text{calc.}}$	$D_c^{\text{exp. } a,b}$
$\text{CH}_4(^1A_1)$	473.1	468.0
$\text{CH}_3(^2A_2')$	484.9	485.7
$\text{CH}_2(^3B_1)$	499.1	454.2
$\text{CH}(^2\Pi)$	338.8	351.2

^a Experimental values of ΔH_{f0}^0 are taken from refs^{13,15,16}; ^b experimental values of ω are taken from refs^{8-10,12}.

a good agreement with experiment was reached for the dissociations of CH_4 (A) and CH_3 (B). Much too high and low D_e values of the reactions (C) and (D), respectively, indicate that the electronic energy of CH molecule is too high as compared with that of the other molecules. Reasons of this defect will be discussed in the subsequent section.

With one of the methane dissociation products – methylene, there exist two energy parameters which were dealt with in a number of experiments. The first one concerns experimental estimation of the barrier corresponding to the potential energy difference between the equilibrium bent configuration $\text{CH}_2(^3B_1)$ and the respective optimum linear geometry arrangement H—C—H. On the basis of adjustment of the potential hypersurface for correct interpretation of 61 spectral data¹⁰ it was found that the height of the barrier to linearity was equal to 23.2 ± 1 kJ/mol. Our results give the value of 30.9 kJ/mol which agrees relatively well with the experimental value (see Table I for comparison of the optimum geometry of the linear configuration). The second experimentally examined parameter which has been given considerable attention recently is the singlet–triplet energy separation of methylene. For this energy gap between the lowest states 3B_1 and 1A_1 , two groups of values were originally measured, *viz.* about 38 kJ/mol and about 75 kJ/mol. With considerable contribution of the quantum chemical methods the two opinions were later unified (for a review see ref.¹⁷), the generally accepted value being now about 38 kJ/mol (refs^{17,18}). After correction with respect to the zero point energy¹⁷ the experimental value of the gap is 39.7 kJ/mol which can be compared with the value of 66.3 kJ/mol obtained by our approach. As this discrepancy is probably due to the relatively high singlet state energy, where there exists instability of the RHF solution¹⁹, a similar instability of the UHF solution being found with the CH radical, both the cases will be discussed in detail in the following section.

UHF Instabilities for CH and CH_2 Molecules

As it was mentioned in the previous section the relatively high electronic energies of $\text{CH}(^2\Pi)$ and $\text{CH}_2(^1A_1)$ molecules can be connected with the existence of another UHF solution which has a similar character with the two different systems. In both the cases the decoupling of lone electronic pair is typical for the new lower UHF solution. The new α - and β -spin orbitals with mutually considerably different directions of space parts cause not only a perturbation of the spin symmetry (see the $\langle \mathbf{S}^2 \rangle_{\text{UHF}}$ values in Table III), but they do not fulfil the requirements of the given space symmetry group either.

The following MO picture was obtained by the analysis for the CH radical. The unpaired electron occupies the molecular orbital of π type. Located below is the MO whose decoupling of the α - and β -space part represents a source of formation of a new UHF solution. The new MO has a σ character with an admixture of π -type

component, which causes a deviation of the α - and β -space parts from C—H axis to mutually opposite directions. The decoupling angle between space parts of these spin-orbitals is about 45° . The UHF energy value (Table III) decreases but little after the decoupling, the UMP2 energy being even slightly above the UHF energy of the I. solution. The equilibrium internuclear distance $R_e^{C-H} = 1.145 \cdot 10^{-10}$ m decreases to $1.142 \cdot 10^{-10}$ m after the decoupling. This internal instability^{20,21} of the UHF wave function can be denoted, according to the Fukutome classification^{19,22,23}, as the SDW solution. This is a type of solution which ascribes — to a certain extent — a triradical character to the CH molecule and which has not yet been described as far as we know (except for the general prediction²⁴). If this type of electronic structure is confirmed also by more exact methods of quantum chemistry, chemical reactions of a specific character can be expected with the CH radical (*e.g.* insertion into the chemical bond).

The decoupled solution of the $CH_2(^1A_1)$ molecule which imparts to it a character of singlet biradical was described by Yamaguchi¹⁹. As compared with the CH radical, this decoupling concerns the highest occupied MO, the space parts of the α - and β -spin orbitals being located in the plane perpendicular to the molecular plane and deviated from the C_2 symmetry axis (which lies in both the planes) by the same value in mutually opposite directions. The angle between the α - and β -space parts is about 73.9° . The decoupling has a greater effect on the UHF energy than in the case of the CH radical (Table III), and the UMP2 again acts in the direction of equalizing of the energy difference of the both solutions. The equilibrium angle $\theta_e = 102.8^\circ$ and $R_e = 1.128 \cdot 10^{-10}$ m obtained in the I. solution attain the values 115.8° and $1.042 \cdot 10^{-10}$ m, resp., in the II. solution.

In spite of the fact that the solutions with the lowest UMP2 energy were used in the study of the dissociation products in both the cases, the results indicate that in the presence of the mentioned type of instability the UMP2 method is insufficient for an acceptably correct description of electronic correlation effects. Under such conditions it is necessary to adopt more exact methods of description of the correlation energy.

TABLE III
Different UHF solutions for CH and CH_2 molecules

Molecule	I. solution			II. solution (decoupled)		
	$\langle S^2 \rangle_{UHF}$	E_{UHF}/E_H	E_{UMP2}/E_H	$\langle S^2 \rangle_{UHF}$	E_{UHF}/E_H	E_{UMP2}/E_H
$CH(^2\Pi)$	0.753	-38.2391	-38.2810	0.999	-38.2408	-38.2790
$CH_2(^1A_1)$	0.000	-38.8474	-38.9218	0.789	-38.8664	-38.9330

CONCLUSIONS

The results given (i) indicate that it is possible to expect a good description of geometry and energy parameters of C—H bond dissociation in hydrocarbons with electronic structure of various types when using the mentioned combination “UMP2 method – the minimum basis with bond functions” and (ii) prompt us to be increasingly careful, if special types of instability of the RHF or UHF wave function are indicated.

As this paper represents the last communication of the series²⁻⁷, it will be useful to outline the region in which good results can be expected from the described UMP2 method in the minimum basis set augmented with the bond functions. This methodical combination gives the energy differences comparable with experimental results in the case of chemical reactions involving formation or splitting of chemical bonds between H atom and atoms of the 1st row of periodic table of the elements (recently this was extended also for H—Br). When using the bond functions we can encounter certain problems concerning their location in the case of isomerization reactions. Nevertheless, the methodical combination described usually gives better results than some of other much more time-consuming methods and basis sets even in the cases which do not belong to the application region recommended, and, therefore, it can be recommended for general interpretation purposes.

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