Vol 17 No 6, June 2008
1674-1056/2008/17(06)/2023-04

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Ground state for CH_2 and symmetry for methane decomposition*

Zhang Li(张 莉), Luo Wen-Lang(罗文浪), Ruan Wen(阮 文),
Jiang Gang(蒋 刚), and Zhu Zheng-He(朱正和)†

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, *China*

(Received 6 June 2007; revised manuscript received 28 September 2007)

Using the different level of methods B3P86, BLYP、B3PW91, HF, QCISD、CASSCF (4,4) and MP2 with the various basis functions 6-311G**, D95, cc–pVTZ and DGDZVP, the calculations of this paper confirm that the ground state is $\tilde{X}^3B_1$ with C_{2v} group for CH_2. Furthermore, the three kinds of theoretical methods, i.e. B3P86、CCSD(T, MP4) and G2 with the same basis set cc-pVTZ only are used to recalculate the zero-point energy revision which are modified by scaling factor 0.989 for the high level based on the virial theorem, and also with the correction for basis set superposition error. These results are also contrary to $\tilde{X}^3\Sigma_g^-$ for the ground state of CH_2 in reference. Based on the atomic and molecular reaction statics, this paper proves that the decomposition type (1) i.e. $CH_4 \rightarrow CH_2+H_2$, is forbidden and the decomposition type (2) i.e. $CH_4 \rightarrow CH_3+H$ is allowed for CH_4. This is similar to the decomposition of SiH_4.

Keywords: symmetry, free radical CH_2, decomposition of CH_4
PACC: 3000, 3310C, 3520B

1. Introduction

Just as mathematician and philosopher A. N. Whitehead (1861–1947) said early, 'It is no paradox that in our most theoretical moods we may be nearest to our most practical applications'. Symmetry is one of them. The dissociation of SiH_4 itself has been most widely studied .The question of whether the decomposition proceeds by a reaction of type (1) or type (2) remains controversial,[1] i.e.

$$SiH_4 \rightarrow SiH_2 + H_2 \quad (1)$$

$$SiH_4 \rightarrow SiH_3 + H. \quad (2)$$

Furthermore, the dissociation of SiH_4 is closely related with the decomposition of disilane and dimethylsiloxane, which would be rather important for practical applications[1−3] and extend much progress in this field.[4−6]

Based on the atomic and molecular reaction statics[7] and group theory, we have proved that the decomposition type (1) of CH_4 is forbidden by symmetry, however, the decomposition type (2) of CH_4 is allowed .

The question is that does the decomposition of CH_4 have the same symmetry as SiH_4? It is worth notice because both of them have the same group T_d .The procedure in consideration of dissociation for CH_4 leads to an interesting discovery that one of decomposition constituent CH_2 is not $^3\Sigma_g^-$ of $D_{\infty h}$ group but the C_{2v} group with state $^3B_1$.This is why we have to confirm what is the ground state of CH_2 first of all.

2. Theoretical method

2.1. What are the possible electronic states of CH_2 by atomic and molecular reaction statics

Suppose the molecule CH_2 is linear, i.e.$D_{\infty h}$ group. Using the resolution and direct product of group representations, we have the following possible electronic states[8] of CH_2 if H_2 is ground state and C is in ground state ^3P_g or excited state ^1D_g:

$$\begin{array}{cccc} & C & + \ H_2 & \rightarrow CH_2(D_{\infty h}) \\ 1 & ^3P_g & ^1\Sigma_g^+ & ^3\Sigma_g^-, {}^3\Pi_g \\ 2 & ^1D_g & ^1\Sigma_g^+ & ^1\Sigma_g^+, {}^1\Pi_g, {}^1\Delta_g \end{array}$$

On the other hand, if molecule CH_2 is C_{2v} symmetry. Using the resolution and direct product of group

*Project supported by the Joint Funds of the National Natural Science Foundation of China (Grant No 10576029).
†Corresponding author. E-mail: zhuxm@scu.edu.cn

representations, we have the following possible electronic states of CH_2 if H_2 is ground state and C is in ground state ^3P_g or excited state ^1D_g:

$$\begin{array}{cccc} C & + & H_2 & \rightarrow CH_2(D_{2v}) \\ 1\ ^3P_g & & ^1\Sigma_g^+ & ^3A_2, ^3B_1, ^3B_2 \\ 2\ ^1D_g & & ^1\Sigma_g^+ & 2^1A_1, ^1A_2, ^1B_1, ^1B_2 \end{array}$$

So, the most possible electronic states of CH_2 are $^3A_2$, $^3B_1$, $^3B_2$. The ground state $^3B_1$ of CH_2, which will be confirmed by the following calculation, is one of them.[9]

2.2. The quantum mechanical calculations of the electronic states of CH_2

Using Gaussian 03,[10] we have applied the different level of methods B3P86, BLYP, B3PW91, HF, QCISD, CASSCF (4,4) and MP2 with the various basis functions 6-311G**, D95, cc–pVTZ and DGDZVP to optimize the geometry of CH_2 for the symmetry $D_{\infty h}$ and C_{2v}. The calculated results are listed in Table 1.

Table 1. The energy of the states $^3\Sigma_g^-$, $^3B_1$ and $^1A_1$ for CH_2.

Method	Basis function	Energy (E/arb. units)		
		Symmetry		
		C_{2v}		$D_{\infty h}$
		Electronic State		
		$^3B_1$	$^1A_1$	$^3\Sigma_g^-$
B3P86	6-311G**	–39.3056	–39.2800	–39.2979
	D95	–39.2930	–39.2582	–39.2861
	cc–pVTZ	–39.3094	–39.2852	–39.3018
	DGDZVP	–39.2970	–39.2730	–39.2886
BLYP	6-311G**	–39.1387	–39.1206	–39.1317
	D95	–39.1251	–39.0978	–39.1192
	cc–pVTZ	–39.1432	–39.1265	–39.1363
	DGDZVP	–39.1320	–39.1147	–39.1246
B3PW91	6-311G**	–39.1500	–39.1222	–39.1423
	D95	–39.1378	–39.1006	–39.1308
	cc–pVTZ	–39.1540	–39.1274	–39.1463
	DGDZVP	–39.1417	–39.1155	–39.1333
HF	6-311G**	–38.9341	–38.8875	–38.9220
	D95	–38.9180	–38.8620	–38.9078
	cc–pVTZ	–38.9379	–38.8925	–38.9259
	DGDZVP	–38.9189	–38.8754	–38.9058
QCISD	6-311G**	–38.9339	–38.8871	–38.9219
	D95	–38.9173	–38.8608	–38.9072
	cc–pVTZ	–38.9377	–38.8923	–38.9258
	DGDZVP	–38.9184	–38.8747	–38.9055
CASSCF(4,4)	6-311G**	–38.9351	–38.9177	–38.9187
	D95	–38.9196	–38.8875	–38.9053
	cc–pVTZ	–38.9388	–38.9248	–38.9227
	DGDZVP	–38.9200	–38.9045	–38.9028
MP2	6-311G**	–38.9340	–38.8873	–38.9220
	D95	–38.9177	–38.8614	–38.9076
	cc–pVTZ	–38.9378	–38.8924	–38.9259
	DGDZVP	–38.9186	–38.8751	–38.9057

In order to have precise results, we would prefer to recalculate the radical CH_2 and confirm that its ground electronic state is $\tilde{X}^3B_1$ with C_{2v} group, but not the $\tilde{X}^3\Sigma_g^-$. Therefore, the three kinds of theoretical methods, i.e. B3P86, CCSD (T, MP4) and G2, are used with the same basis set cc-pVTZ to consider

the zero-point energy (ZPE) revision which are modified by scaling factor 0.989 for the high level based on the virial theorem, and also with the correction for basis set superposition error (BSSE).[11] So, the total energy E_{tol}=E_e+E_{zpe}×0.989 + E_{BSSE}. All are listed in the Table 2. In comparison with these results, it is deeply believed that the ground electronic state of CH_2 is $\tilde{X}^3B_1$ indeed.

Table 2. The Energy corrected.

method and basis function	Energy	$^3B_1$	$^1A_1$	$^3\Sigma_g^-$
B3P86/cc–pVTZ	E_e/arb. units	–39.3094	–39.2852	–39.3018
	E_{zpe}/arb. units	0.0172500	0.016599	0.0154260
	E_{BSSE}/arb. units	0.000243818	0.000402556	0.000256100
	E_{tol}/arb. units	–39.2921	–39.2684	–39.2863
CCSD(T,MP4)/cc–pVTZ	E_e	–39.0779	–39.0614	–39.0684
	E_{zpe}/arb. units	0.0173420	0.0166460	0.0153630
	E_{BSSE}/arb. units	0.00166766	0.00316860	0.00159383
	E_{tol}/arb. units	–39.0590	–39.0418	–39.0517
G2/cc–pVTZ	E_e	–39.0855	–39.0744	–39.0764
	E_{zpe}/arb. units	0.0164530	0.0160340	0.0142910
	E_{BSSE}/arb. units	0.00327217	0.00976972	0.00305947
	E_{tol}/arb. units	–39.0659	–39.0488	–39.0592

From Table 1 and Table 2, it is obvious to see that for the all methods with the basis functions used here, the lowest energy is the state $^3B_1$, therefore, it would be the ground state, which is quite contrary to Ref.[12] which shows the linear molecule with ground state $\tilde{X}^3\Sigma_g^-$ for CH_2 .

2.3. The symmetry for CH_4 decomposition

In the following we shall prove the symmetry of decomposition type (1) and (2) of CH_4 based on the atomic and molecular reaction statics and group theory.

At first, we prove whether the symmetry of the decomposition type (2) of CH_4 is allowed.

$$\mathrm{CH_4}(T_d, {}^1A_1)\underset{c}{\overset{b}{\rightleftarrows}}\mathrm{CH_4}(C_{3v}, {}^1A_1) \underset{d}{\overset{e}{\rightleftarrows}}\mathrm{CH_3}(D_{3h}, {}^2A_2'') + \mathrm{H}({}^2S_g).$$

Because the group C_{3v} is the subgroup of T_d, the decomposition from CH_4[13,14] (T_d, $^1A_1$) to CH_4 (C_{3v}, $^1A_1$) is possible, i.e. the irreducible representation $^1A_1$ of T_d can be resolved into the irreducible representation $^1A_1$ of C_{3v}. Therefore, the process b is possible. According to the principle of microscopic reversibility, the process c is also possible. Moreover, because C_{3v} is the subgroup of D_{3h} and O (3) too, the process d is possible. Then, the process e is also possible. Therefore, the decomposition type (2) of CH_4 is symmetrically allowed.

Then, we will prove the symmetry problem of the decomposition type (1) of CH_4. The possible process is as follows:

$$\mathrm{CH_4}(T_d, {}^1A_1)\underset{c}{\overset{b}{\rightleftarrows}}\mathrm{CH_4}(C_{3v}, {}^1A_1)\underset{d}{\overset{e}{\rightleftarrows}}\mathrm{CH_2}(C_{2v}, \tilde{X}^3B_1, {}^1A_1;$$

or

$$D_{\infty h}, \tilde{X}^3\Sigma_g^-;$$

or

$$D_{\infty h}, {}^1\Sigma_g^+, {}^1\Delta_g, [{}^3\Sigma_g^-]) + \mathrm{H_2}(D_{\infty h}, {}^1\Sigma_g^+, {}^3\Sigma_u^+).$$

On a similar way above, processes b and c are possible. Although C_{2v} is a subgroup of $D_{\infty h}$, however, both C_{3v} and C_{2v} are not subgroup each other, so the processes d and e are forbidden, the decomposition type(1)of CH_4 is not allowed on the symmetry.

3. Conclusions

(1) The present work explores that the ground electronic state is $\tilde{X}^3B_1$ with C_{2v} group for CH_2, which is contrary to $\tilde{X}^3\Sigma_g^-$ in reference.

(2) We prove that the decomposition type (1) is forbidden and the decomposition type (2) is allowed based on the theory of atomic and molecular reaction statics for CH_4 .This is similar to the decomposition of SiH_4.

(3) We believe that the decomposition of CH_4 would be firstly to form CH_3 not the CH_2 as an intermediate. By some possibility, the two free radical CH_3 will be formed to ethane C_2H_6, and dehydrogenate to form ethylene C_2H_4 or acetylene C_2H_2. It is hopeful that the present work would be beneficial to evaluate the mechanism of CH_4 decomposition.

References

[1] Thomas N B, Kathryn A P and Peter G P 1984 *J. Phys. Chem* **88** 116

[2] Huang W, Fu Y B and Wang C Y 2001 *Journal of Radiation Research and Radiation Processing* **19** 99 (in Chinese)

[3] Noorbatcha L M, Raff D L and Donald L 1986 *J. Chem. Phys.* **84** 4341

[4] Pauline H, Michael E C and Binkley J S 1985 *J. Phys. Chem.* **89** 4647

[5] Huang W and Fu Y B 2002 *Atomic Energy Science and Technology* **36** 503 (in Chinese)

[6] Huang W and Fu Y B 2002 *Radiation Physics and Chemistry* **64** 229 (in Chinese)

[7] Zhu Z H 1996 *Atomic and Molecular Reaction Statics* (Beijing: Science Press) p30

[8] Ludwig W and Falter C 1999 *Symmetries in Physics Group Theory Applied to Physical Problems* (Beijing: Springer) p4

[9] Wolfram Koch and Max C Holthausen 2001 *A Chemist's Guide to Density Functional Theory (Second Edition)* (New York: Wiley-VCH Verlag) p14

[10] Frisch M J, Trucks G W and Schlegel H B 2003 *Gaussian 03 Revision* B 04 (Pittsburgh: Gaussian Inc.) p10

[11] Boys S F and Bemardi F 1970 *Mols. Phys.* **19** 553

[12] Gerhard Herzberg 1966 *Molecular Spectra and Molecular Structure III Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Princeton, NJ: D Van Nostrand) p584

[13] Xu G L, Zhu Z H and Ma M Z 2005 *Acta Phys. Sin.* **54** 3087

[14] Ma M Z, Zhu Z H, Chen X J, Xu G L, Zhang Y B, Mao H P and Shen X H 2005 *Chin. Phys.* **14** 1101