

## Comparative study of density functional theory and conventional *ab initio* methods: Electronic structure of Si<sub>2</sub>C cluster

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**Abstract.** Theoretical calculations have been performed on Si<sub>2</sub>C using density functional theories (DFT) and conventional *ab initio* method employing 6–311G\* basis set. Present calculations indicate that some of the DFT methods (B3LYP, B3P86, BHandH, BHandHLYP) employed in this study cannot predict the observed bent structure in the case of Si<sub>2</sub>C cluster whereas, MP2, SVWN5 and B3PW91 calculations predict the bent structure, as observed by experiment.

**Keywords:** Density functional theory; *ab initio* calculations; Si<sub>2</sub>C cluster.

### 1. Introduction

Silicon clusters have been the subject of numerous theoretical and experimental investigations in recent years<sup>1–16</sup>. Mass spectral experiments have shown that the predominant species in silicon carbide vapours in gas phase are Si, SiC<sub>2</sub> and Si<sub>2</sub>C<sup>1,17</sup>. It has been reported that Si<sub>2</sub>C has a linear geometry (<sup>1</sup>Σ<sub>g</sub><sup>+</sup> state, D<sub>∞h</sub>) at the RHF level and with the inclusion of electron correlation, a bent structure (<sup>1</sup>A<sub>1</sub> state, C<sub>2v</sub>) is predicted whose geometrical parameters are close to the experimental values<sup>4</sup>. It has also been reported that, inclusion of polarized and diffuse basis set would also increase the quality of prediction<sup>18</sup>. In the experimental study of Si<sub>2</sub>C, Presilla–Marquez and Graham have reported vibrational frequency relating to symmetric stretching of Si–C bond in Si<sub>2</sub>C at 839.5 cm<sup>-1</sup><sup>19</sup>. Schaefer and coworkers have made extensive investigations on the vibrational spectra of Si<sub>2</sub>C using CISD and CCSD(T) methods and have predicted the presence of this vibrational feature at 839 cm<sup>-1</sup><sup>20</sup>. They have also analysed the importance of contribution from correlation and polarization functions in the calculation within the framework of coupled cluster methods. The geometries and energies of Si<sub>n</sub>C and Si<sub>n</sub>C<sup>-</sup> clusters have been calculated using MP2 and CI methods<sup>21</sup>.

The inclusion of electron correlation can be achieved using several models of DFT much less expensively than the traditional correlation methods. In DFT calculations, electron correlation is included from the general functionals of electron density. The electron–electron interaction has been accounted in the DFT methods, based on several exchange and correlation components. Several hybrid schemes have become possible by combining Hartree–Fock exchange with DFT exchange–correlation functionals to get better prediction. In fact, HF method is a special case of DFT method.

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Since electron correlation and type of basis set determine the predicted geometry and other electronic properties, the nature of correlation provided by the various DFT calculations have been probed in this study. In this investigation, the calculations have been carried out on Si<sub>2</sub>C using the following density functional approaches.

- Slater's exchange functional with Vosko, Wilk and Nusair correlation functional (SVWN5) <sup>22,23</sup>.
- The more recent B3LYP hybrid method which employs Becke's three parameter method with Lee, Yang, Parr correlational functional (B3LYP) <sup>24,25</sup>.
- The B3P86 method which uses Becke's three parameter exchange functional and Perdew86 correlational functional <sup>26</sup>.
- The B3PW91 method used the same exchange functional as B3LYP method but employs more recent correlation functional <sup>27</sup>.
- The BH and H, BH and HLYP methods which employ Becke's three parameter exchange functional <sup>28</sup>.

The results obtained from DFT calculations are also compared with the MP2 and HF calculations.

## 2. Theoretical approach

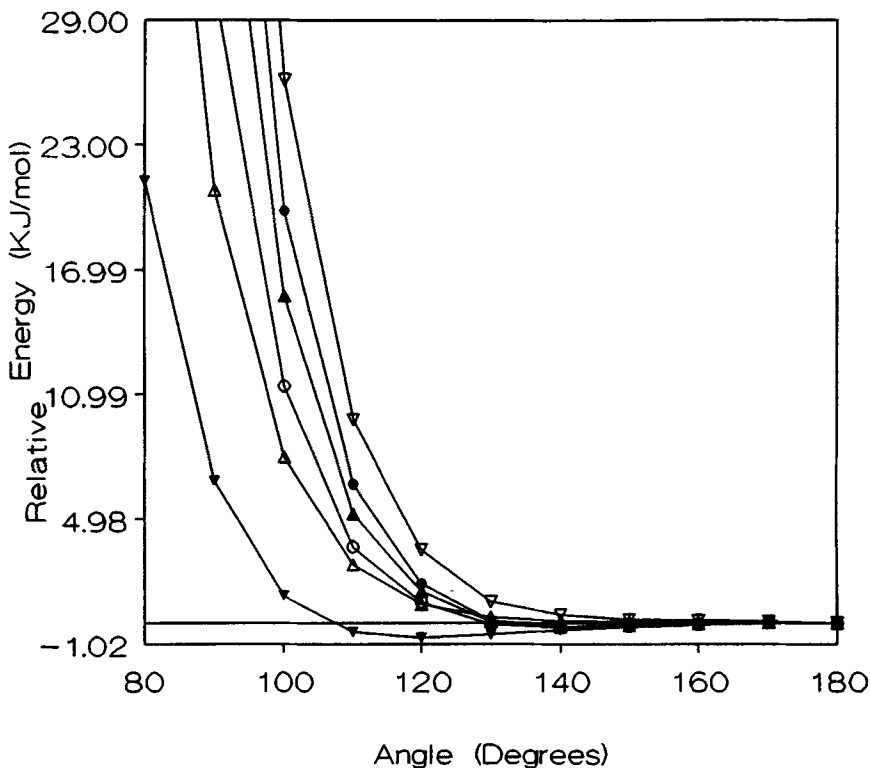
In this communication, RHF, MP2 and DFT methods as implemented in the Gaussian 94W <sup>29</sup> package have been used to compute the geometry of Si<sub>2</sub>C. All calculations have been carried out using the 6-311G\* basis set. Complete optimization on the Si<sub>2</sub>C geometry were done using the Berny method.

## 3. Results and discussion

The total energy, optimized bond length and bond angle for Si<sub>2</sub>C calculated using various methods have been presented in table 1. The total energy of Si<sub>2</sub>C as a function of bond angle (Si-C-Si) for a fixed Si-C bond length of 1.7072 Å have been calculated. The relative energy (difference in total energies between bent and linear structures) as a function of Si-C-Si bond angle for fixed bond length is shown in figure 1. We find that the RHF and B3LYP, BHandH, BHandHLYP calculations predict a linear <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state (D<sub>∞h</sub>) for Si<sub>2</sub>C whereas, the treatment of electron correlation using MP2, SVWN5 and B3PW91 methods turn the structure into a bent <sup>1</sup>A<sub>1</sub>(C<sub>2v</sub>) ground state.

**Table 1.** Total energy, bond length angle calculated for Si<sub>2</sub>C using RHF, MP2 and DFT methods with 6-311G\* basis set.

Method	Energy (au)	Bond length (Å)	Bond angle (Degree)
RHF	-615.6327205	1.6699	180.0
MP2	-615.9172854	1.7072	120.0
B3LYP	-617.0346181	1.6949	180.0
SVWN5	-614.3560132	1.6970	133.0
B3P86	-617.6373902	1.6910	180.0
B3PW91	-616.9058096	1.6944	140.0
BHandH	-615.0385837	1.6705	180.0
BHandHLYP	-616.9663736	1.6766	180.0



**Figure 1.** Potential energy curves for  $\text{Si}_2\text{C}$  as a function of Si-C-Si bond angle  
 ▼-MP2 method ▽-BH and HLYP method ▲-B3P86 method △-B3LYP  
 method ●-B3PW91 method ○-SVWN5 method

As discussed in the literature, the prediction of equilibrium geometry of  $\text{Si}_2\text{C}$  needs a somewhat delicate balance between basis set and the degree to which the electron correlation is included. Calculated Si-C bond length and Si-C-Si bond angle by the MP2 method are in reasonable agreement with the values ( $1.71 \text{ \AA}$  and  $119.5^\circ$ ) calculated by Rittby<sup>30</sup> with second-order many-body perturbation theory and with the geometry obtained from experimental asymmetric stretching vibrational frequency  $\nu_3(b_2)$  of  $\text{Si}_2\text{C}$ <sup>2</sup>. In accordance with the previous findings, electron correlation tend to lengthen the Si-C bond with a substantial diminishing of Si-C-Si bond angle. It can be observed from the table 1 and figure 1 that the SVWN5 and B3PW91 methods predict bent structure, but the deviation of equilibrium bond length and bond angle from the experimental value is very high. Though, the DFT methods are known to handle electron correlation effectively, they are unable to predict the experimental geometry for  $\text{Si}_2\text{C}$ . B3LYP method's failure is surprising, since it is widely used in the electronic structure calculations. It is relevant to point out that in the most recent study on linear and cyclic clusters of hydrogen cyanide and cyanoacetylene, the inability of B3LYP method to predict intermolecular energy surfaces has been reported<sup>31</sup>. The requirement of methods to take account of electron correlation, preferably beyond MP2 level, has been stressed. In yet another recent *ab initio* and DFT calculations on thiophene and furan, it is concluded that when optimized geometry is of interest, MP2 method is more reliable and scaled B3LYP force fields are preferred for vibrational analysis<sup>32</sup>.

**Table 2.** Theoretical vibrational frequencies (in  $\text{cm}^{-1}$ ) for bent  $\text{Si}_2\text{C}$ 

Method	$\gamma_1(a_1)$	$\gamma_2(a_2)$	$\gamma_3(b_2)$
MP2	812.78	97.79	1235.22
SVWN5	743.54	80.48	1292.38
B3PW91	718.69	56.92	1343.43
MBPT2/6-311G(2d) <sup>a</sup>	808	131	1223
TZ + 2P CCSD(T) <sup>b</sup>	818	147	1203
TZ + 2P + fCISD <sup>b</sup>	883	151	1300
EXPT. <sup>c</sup>	839.5	–	1188

<sup>a</sup>From <sup>30</sup><sup>b</sup>From <sup>20</sup><sup>c</sup>From <sup>19</sup>**Table 3.** Theoretical vibrational frequency (in  $\text{cm}^{-1}$ ) for linear  $\text{Si}_2\text{C}$ 

Method	$\gamma_1(\sigma_g)$	$\gamma_2(\pi_n)$	$\gamma_3(\sigma_n)$
B3LYP	60.42	582.18	1399.66
B3P86	39.42	589.03	1414.41
B3PW91	37.05	586.32	1407.99
BHandHLYP	65.15	616.67	1473.27
MBPT2/6-311G(2d) <sup>a</sup>	559	99i	1368

<sup>a</sup>From <sup>30</sup>

The nature of minimum energy structure is analysed by calculating frequencies. Calculated frequencies have been compared in tables 2 and 3 with experimental values and those values obtained in the earlier investigations. Since, the scaling factor is not optimized for some of the DFT methods employed in this study, the unscaled frequencies have been used to understand the predictive power of the methods employed in this work. The frequencies calculated for the minimum energy structure obtained from DFT and MP2 methods are all positive, confirming the minimum energy nature of the geometry. The experimental vibrational frequencies ( $839.5\text{ cm}^{-1}$  and  $1188.4\text{ cm}^{-1}$ ), which were the  $\gamma_1(a_1)$  symmetric stretching mode and the  $\gamma_3(b_2)$  anti-symmetric stretching mode were in close agreement with the unscaled MP2 values. Since B3LYP, B3P86, BHandH and BHandHLYP methods could not reproduce the experimental geometry; their vibrational frequencies cannot be compared with the experimental values. MP2, SVWN5 and B3PW91 methods estimate lower values for  $\gamma_1(a_1)$  mode when compared with the experimental value. Proper scaling of the MP2, SVWN5 and B3PW91 values may improve the  $\gamma_3(b_2)$  mode. The decreasing Si–C–Si angle at the correlated level of theory can be attributed to bonding interactions between terminal silicon atoms. Dispersion forces arising due to electron correlation can also cause decrease in the bond angle.

#### 4. Conclusion

The structure and energy of  $\text{Si}_2\text{C}$  have been probed using conventional *ab initio* and various DFT methods. Our results reveal that B3LYP, B3P86, BHandHLYP, BHandH methods are not able to predict the experimental bent structure for  $\text{Si}_2\text{C}$  but inclusion of

electron correlation at MP2 level reliably predicts the bent structure for the molecule. Though SVWN5 and B3PW91 methods predict bent ground state for Si<sub>2</sub>C, the equilibrium bond angle and bond length are not in good agreement with the experimental values. These results consequently reveal that the electron correlation provided by the DFT methods is inadequate to arrive at the structure for Si<sub>2</sub>C and stress the importance of including electron correlation atleast at the MP2 level and beyond.

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### References

1. Verhaeger G, Stafford F E and Drowart J Jr 1964 *J. Chem. Phys.* **40** 1622
2. Kafafi Z H, Hauge R H, Fredin L and Margrave J L 1983 *J. Chem. Phys.* **87** 797
3. Michalopoulos D L, Geusic M E, Langeridge-Smith P R R and Smalley R E 1984 *J. Chem. Phys.* **80** 3356
4. Diercksen G H F, Gruner N E, Oddershede J and Sabin J R 1985 *Chem. Phys. Lett.* **29** 117
5. Fitzgerald G, Cole S J and Bartlett R J 1986 *J. Chem. Phys.* **85** 1701
6. Raghavachari K 1986 *J. Chem. Phys.* **84** 5672
7. Sabin J R, Oddershede R J, Diercksen G H F and Gruner N E 1986 *J. Chem. Phys.* **84** 354
8. Brown W L, Freeman R R, Raghavachari K and Schluter M 1987 *Science* **235** 860
9. Cheshnovsky O, Yang S H, Pettiette C L, Craycraft M J, Liu Y and Smalley R E 1987 *Chem. Phys. Lett.* **138** 119
10. Jarrold M F 1991 *Science* **252** 1085
11. Jarrold M F and Honea E C 1991 *J. Phys. Chem.* **95** 9181
12. Raghavachari K and Rohlfling C M 1991 *J. Chem. Phys.* **94** 3670
13. Rohlfling C M and Raghavachari K 1992 *J. Chem. Phys.* **96** 2114
14. Honea E C, Ogura A, Murray C A, Raghavachari A, Sprenger W O, Jarrold M F and Brown W L 1993 *Nature (London)* **336** 42
15. Kitsopoulos T N, Chick C J, Weaver A and Neumark D M 1993 *J. Chem. Phys.* **99** 7809
16. Von Niessen W and Zakrzewski G 1993 *J. Chem. Phys.* **98** 1271
17. Behrens R G and Rinehart G H 1979 *Natl. Bur. Stand. (US) Spl. Publ. No.* 561-1, 125
18. Grev R S and Schaefer H F III 1985 *J. Chem. Phys.* **82** 4126
19. Presilla-Marquez J D and Graham W R M 1991 *J. Chem. Phys.* **95** 5612
20. Bolton E E, Deleevw B J, Fowler J E, Grev R S and Schaefer H F III 1992 *J. Chem. Phys.* **97** 5586
21. Kishi R, Gomei M, Nakajima A, Iwata A S and Koya K J 1996 *J. Chem. Phys.* **104** 8593
22. Slater J C 1974 *Quantum theory of molecules and solids The self-consistent field for molecules and solids* (New York: Tata McGraw-Hill) vol. 4
23. Vosko S H, Wilk L and Nusair M 1980 *Can. J. Phys.* **58** 1200
24. Lee C, Yang W and Parr R G 1988 *Phys. Rev.* **B37** 785
25. Becke A D 1993 *J. Chem. Phys.* **98** 5648
26. Perdew J P 1986 *Phys. Rev.* **B33** 8822
27. Perdew J P and Wang Y 1992 *Phys. Rev.* **B45** 1324
28. Foresman J B and Frisch A E 1993 *Exploring chemistry with electronic structure methods* (Gaussian Inc. Pittsburg, USA)
29. Frisch M J, Trucks G W, Schlegel H B, Gill P M W, Johnson B G, Robb M A, Cheesemen J R, Keith T, Petersson G A, Montgomery J A, Raghavachari K, Al-Laham M A, Zakrzewski V G, Ortiz J V, Foresman J B, Cioslowski J, Stefanov B B, Nanayakkara A, Challacombe M, Peng C Y, Ayala P Y, Chen W, Wong M W, Andres J L, Replogle E S, Gomperts R, Martin R L, Fox D J, Binkley J S, Defrees D J, Baker J, Stewart J P, Head-Gordon M, Gonzalez C and Pople J A 1995 *Gaussian 94W (Revision D.3)* (Gaussian Inc., Pittsburg, USA)

30. Rittby C M L 1991 *Chem. Phys.* **95** 5609
31. Karpfen A J 1996 *J. Phys. Chem.* **100** 13474
32. El-Azhary A and Suter H U 1996 *J. Phys. Chem.* **100** 15056