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Ab Initio Calculations of the Structures and Energies of $Ge(CH_3)_2$ from Tetramethylgermane in CVD

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ABSTRACT

Ab initio calculations, at several levels of theory including density functional calculations, have been performed with a high level basis set for the two lowest energy states of $Ge(CH_3)_2$*. The ground-state singlet configuration, at the B3PW91/"6-311G*" level of theory, is one in which the methyl hydrogen atoms are eclipsed. Similar calculations at the same level of theory, but using an effective core potential (ECP), do not predict the same geometry, indicating that the use of ECP basis sets should be avoided in organogermanium molecules. This is the first reported calculation of the configurations and energies of* $Ge(CH_3)_2$ *and is expected to be useful in the spectroscopic monitoring of CVD processes involving tetramethylgermane, a common precursor. Comparison is made to calculations for* GeH_2 *performed at the same levels of theory.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:195–200, 1998

INTRODUCTION

Semiconductor materials containing silicon or germanium are typically produced by chemical vapor deposition (CVD) from hydrides or tetralkylmetals [1]. Germanium containing radicals are postulated as intermediates in the CVD process [2]. Recently, the first experimental information [3–5] for GeH_2 appeared in the literature, and a number of ab initio calculations, at varying levels of theory, have been reported for this radical [6–8]. However, there is no spectroscopic or kinetic information for other germanium hydrides, nor has any data been reported for dialkylgermanium radicals. In the absence of experimental information, ab initio calculations are useful in the development of spectroscopic methods of monitoring CVD and plasma deposition processes. Moreover, the availability of computational results provides a road map in the experimental search for the relevant intermediates in these processes.

In addition to the practical concerns noted above, the calculation of singlet–triplet-splitting energy gaps represents a major challenge in computational chemistry and is a rigorous testing ground for the suitability of a given level of theory to the problem at hand. In the work reported here, in addition to testing the relevance of several theoretical models in optimizing the geometry, we test the viability of single-point calculations at high levels of theory using optimized geometries from Hartree–Fock calculations. Finally, we explore the reliability of effective core potential (ECP) basis sets for germanium containing radicals and compare the use of the computationally less expensive density functional methods with costly MRCI techniques. The focus of this effort is $Ge(CH_3)_2$, a radical expected to be observed in thin-film production processes involving

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Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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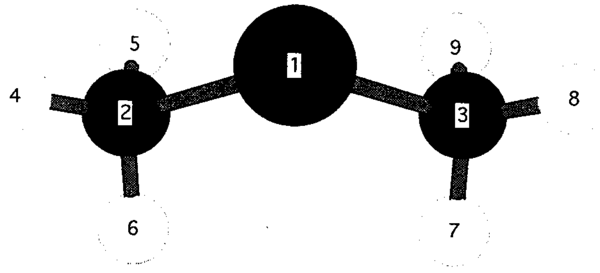
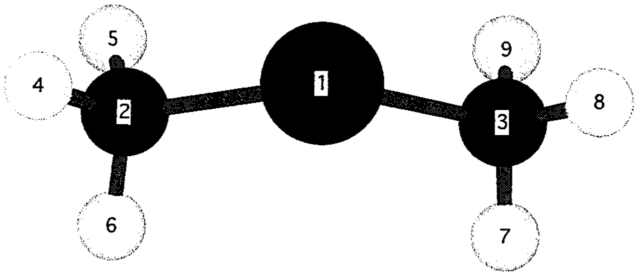


(I) Ground State (singlet)



(II) Lowest Triplet State

FIGURE 1 Optimized structures at the B3PW91/6-311G* level of theory for $Ge(CH_3)_2$ structures. See Tables 1 and 4 for parameters.

tetramethylgermane, a common CVD precursor. Calculations at identical levels of theory using GeH_2 are also reported, since the available experimental evidence and wealth of computational results allows for a stringent comparison of the various techniques applied to the target radicals. This is the first theoretical examination of the $Ge(CH_3)_2$ molecule in an isolated system and provides high-level calculations of the structure and energetics of the two lowest energy states, as well as predicted vibrational frequencies for these levels.

COMPUTATIONAL METHODS

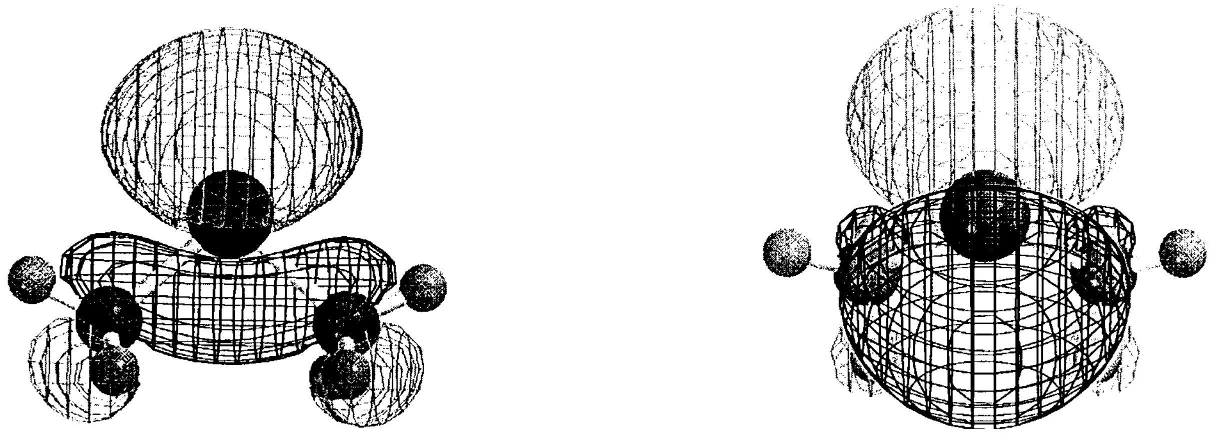
Calculations were carried out using the GAUSSIAN 94 system of programs [9]. Split valence basis sets such as 6-31G* and 6-311G* are not defined for third-row elements. However, recently, basis sets that approximate 6-311G* quality have been reported [10] for third-row elements, and we shall refer to these basis sets as 6-311G or 6-311G* in this report.

Initial geometry optimizations were performed to locate the lowest-energy singlet and triplet structures at the HF/6-311G* level without any symmetry constraints. These minimized structures were further optimized, again in the absence of symmetry constraints, using density functional theory (DFT) with hybrid correlation functionals [11–13], B3PW91/6-311G*. Harmonic vibrational frequencies were calculated at the HF/6-311G* level for both structures to characterize the stationary points as minima and to allow zero-point vibrational energy (ZPVE) corrections to the relative energies.

Our earlier calculations of the structures of the ethylene sulfide radical cations, as well as those involving neutral molecules from other researchers, have indicated that some of the computational costs may be reduced by employing high-level single-point energy calculations with electron correlation to HF optimized geometries [14,15]. Single-point energy calculations at the MP2 (frozen core), QCISD(T), B3LYP, and B3PW91 levels of theory were carried out using the HF/6-311G* optimized geometries and the 6-311G* basis set. Singlet–triplet energy gaps were computed from both the optimized structure energies and the single-point calculations. Calculations at identical levels of theory using an effective core potential and the 6-311G basis sets were also performed for comparison purposes to test the suitability of these basis sets for relative accuracy. Since the spectrum of $Ge(CH_3)_2$ has not yet been reported, analogous calculations were undertaken for GeH_2, which has been reported and has been studied using high-level ab initio methods. Comparison of our ab initio results for GeH_2 with the available experimental and theoretical data was used as an indication of the suitability of a particular theoretical model to $Ge(CH_3)_2$.

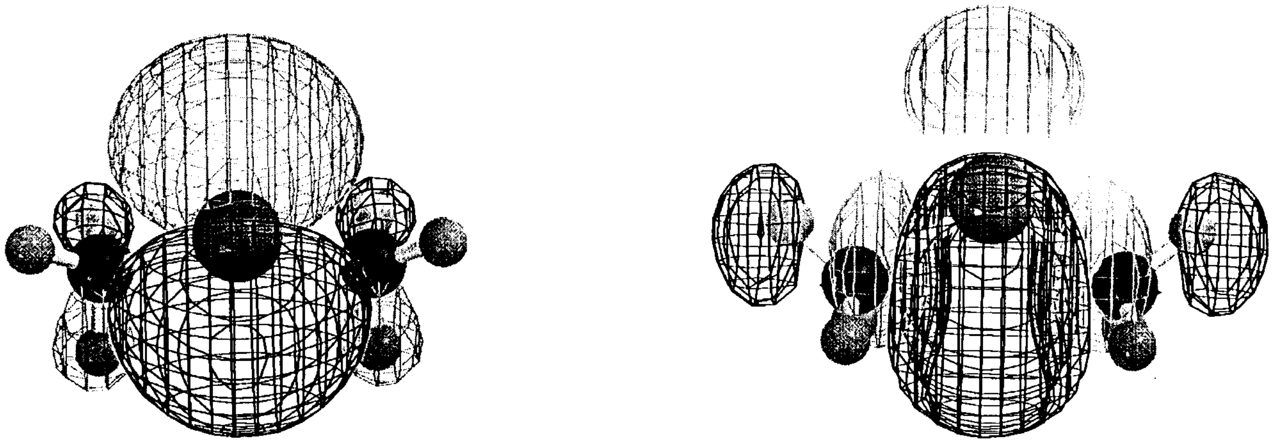
RESULTS AND DISCUSSION

Figure 1 shows the $Ge(CH_3)_2$ geometries for the B3PW91/6-311G* optimization in the absence of any restrictions. The figure indicates that there are subtle structural differences between the ground-state singlet of C_{2v} symmetry (**I**) and the lowest triplet level, also of C_{2v} symmetry, (**II**). These differences are consistent with the difference in molecular orbitals determined at the optimized geometries. Figure 2 presents density maps of the highest occupied and lowest vacant orbitals for the two states of this radical. The HOMO for the ground state may be described as bonding between the Ge atom and both carbons but also as having bonding character between the carbons. In the case of the triplet state, there is a pair of degenerate orbitals, which are primarily Ge nonbonding. As a result of these difference, we see that the C–Ge–C bond angle for the ground state is smaller and that the Ge–C bond length is slightly longer. Table 1 provides the geometry parameters for



Ground State HOMO

Ground State LUMO



Triplet State HOMO

Triplet State LUMO

FIGURE 2 HOMOs and LUMOs at the HF/6-311G* level of theory for the ground and lowest triplet state of Ge(CH$_3$)$_2$.

TABLE 1 Optimized Geometries[a] for Ge(CH$_3$)$_2$

		I (*singlet*)			***II*** (*triplet*)	
	HF/6-311G	*HF/6-311G**	*B3PW91/6-311G**	*HF/6-311G*	*HF/6-311G**	*B3PW91/6-311G**
Ge–C$_2$	1.996	2.002	2.005	1.979	1.982	1.989
C$_2$–H$_4$	1.081	1.084	1.092	1.083	1.083	1.090
C$_2$–H$_5$	1.087	1.089	1.097	1.079	1.084	1.093
C$_2$–H$_6$	1.087	1.089	1.097	1.079	1.084	1.093
$<$C$_2$–Ge–C$_3$	100.6	96.6	95.4	118.5	118.4	119.2
$<$Ge–C$_2$–H$_4$	114.3	112.7	112.9	108.5	109.8	109.4
$<$Ge–C$_2$–H$_5$	109.6	110.4	110.2	111.3	110.5	110.0
$<$Ge–C$_2$–H$_6$	109.6	110.4	110.2	111.3	110.5	110.0

[a] Bond lengths in Å, angles in degrees.

TABLE 2 Scaled HF/6-311G* Harmonic Frequencies for $Ge(CH_3)_2$

I (*singlet*)	**II** (*triplet*)
35.4	90.4
94.8	93.2
202.9	149.9
501.4	503.0
507.4	549.0
554.7	709.8
621.3	742.5
697.1	785.7
824.2	832.0
1237.7	1236.7
1248.9	1254.2
1402.6	1422.0
1415.7	1423.4
1416.6	1427.5
1432.8	1427.8
2802.8	2838.8
2806.5	2840.2
2851.4	2906.2
2858.6	2907.1
2896.9	2917.3 (2)

structural optimization at three different levels of theory. Scaled HF/6-311G* vibrational frequencies for the two stationary states are contained in Table 2. Both the absolute energies and the singlet–triplet energy gaps are contained in Table 3.

Comparison of the HF calculations in Table 1 indicates that the polarization functions do not play as large a role in the optimization of the triplet state as they do in the geometry of the ground state. In the singlet, the C–Ge–C bond angle decreases by ~4%, and the remaining bond angles are also modified, but to a lesser degree. The effect on the bond lengths is much less pronounced but not insignificant. While the C–Ge–C bond angle is not affected by the added *d*-functions in the basis set, the other angles in the triplet do change significantly. For comparison purposes, the optimized geometries of the ground-state singlet (**III**) and the lowest triplet (**IV**) for GeH_2 are presented in Table 4. A pronounced effect of polarization functions is also seen for that radical. In the case of GeH_2, the major influence is on the bond lengths that increase significantly with the addition of the *d*-functions. Geometry optimization for $Ge(CH_3)_2$ using DFT, B3PW91/6-311G*, results in slight bond lengthening but has minimal effect on the bond angles. However, in the case of GeH_2, this bond lengthening is significant. Experimental data are available for the ground state of GeH_2, and Table 4 indicates that the DFT calculation provides a geometry that is within the uncertainty of the experimentally derived structural parameters. Other calculations for GeH_2, using computationally more expensive models such as CASSCF and MRCI, result in predicted geometries that are nearly identical to that reported here, indicating that the DFT model used with the 6-311G* basis set is an excellent choice for Ge-containing molecules at a very reasonable computational cost.

Calculated energies are provided in Table 3 [$Ge(CH_3)_2$] and 5 (GeH_2). Although the geometry differences were minimal, the absolute energies, as well as the singlet–triplet energy gap, are strongly dependent on the model employed to optimize the geometry. HF/6-311G* optimization results in ground-state energies that are higher, relative to the triplet, than those obtained using DFT optimization, resulting in a smaller energy gap for HF models. This observation is valid whether one considers the dihydride or the dimethyl radical. Focusing first on the hydride, HF methods produce an energy gap that is less than half that predicted by more sophisticated models [6–8]. The B3LYP/6-311G* model, on the other hand, appears to overestimate the energy gap, in comparison to the available data. This has been reported in another third-row computational study that also suggests the use of the Perdew functional for these elements [5]. Looking at the single-point calculations in Table 5, one observes that the predicted energy gaps are essentially identical to those resulting from full optimization. That is, the B3PW91/6-311G*//HF/6-311G* energy gap is identical to that for the full B3PW91/6-311G* optimization. Now turning to the $Ge(CH_3)_2$ results, we can employ the information we derived from the GeH_2 analysis to this system for which experimental data are lacking. We note that once again, the HF energy gap is approximately half of that predicted by the B3PW91/6-311G* optimization. Also, once more, the single-point calculations using the HF geometry reproduce the energy gap result from the full DFT optimization. Our best calculations predict a singlet–triplet energy gap of 27.6 kcal $mole^{-1}$. This is consistent with the experimental GeH_2 results. Further comparison must await experimental results, which should be available shortly, since $Ge(CH_3)_4$ is a common CVD precursor, and the predictions presented here should be useful in searching for the experimental emission due to the $Ge(CH_3)_2$ radical.

Not included in the tables are calculations using the same models, but with the LANL1DZ basis set. The optimized geometries for these calculations are significantly different from those reported above. The C_{2v} structure has one imaginary frequency, indicating that at the HF/LANL1DZ level, that struc-

TABLE 3 Singlet and Triplet Absolute Energies[a] and Energy Gaps[b] for $Ge(CH_3)_2$

Theoretical Method	*Absolute Energy* (**I**) *Singlet*	 (**III**) *Triplet*	*Singlet–Triplet Energy Gap*[c]
HF/6-311G*	−2154.49235	−2154.50664	14.6
B3PW91/6-311G*	−2156.76134	−2156.71834	28.0
MP2/6-311G*//HF/6-311G*	−2155.03739	−2154.99890	25.1
QCISD(T)/6-311G*//HF/6-311G*	−2155.08690	−2155.04471	27.5
B3LYP/6-311G*//HF/6-311G*	−2156.82200	−2156.77294	31.8
B3PW91/6-311G*//HF/6-311G*	−2156.75940	−2156.71634	28.0

[a] Energies in Hartree.
[b] Energies in kcal mole^{-1}.
[c] ZPVE correction of 1.0 kcal mole^{-1} has been applied.

TABLE 4 Optimized Geometries[a] for GeH_2

	III (*singlet*)				**IV** (*triplet*)		
	Exp[b]	*HF/6-311G*	*HF/6-311G**	*B3PW91/6-311G**	HF/6-311G	HF/6-311G*	B3PW91/6-311G*
Ge–H	1.591(7)	1.575	1.586	1.600	1.519	1.532	1.546
<Ge–H	91.2(8)	93.4	92.9	90.6	119.3	118.5	119.4

[a] Bond lengths in Å, angles in degrees.
[b] Reference [8] (singlet).

TABLE 5 Singlet and Triplet Absolute Energies[a] and Energy Gaps[b] for GeH_2

Theoretical Method	*Absolute Energy* (**III**) *Singlet*	 (**IV**) *Triplet*	*Singlet–Triplet Energy Gap*[c]
HF/6-311G*	−2076.41084	−2076.50664	10.0
B3LYP/6-311G*	−2087.12344	−2078.08674	27.6
B3PW91/6-311G*	−2078.15690	−2078.11348	23.3
MP2/6-311G*//HF/6-311G*	−2076.65126	−2076.62277	18.2
B3LYP/6-311G*//HF/6-311G*	−2078.15503	−2078.11179	27.4
B3PW91/6-311G*//HF/6-311G*	−2078.12160	−2078.08515	23.2

[a] Energies in Hartree.
[b] Energies in kcal mole^{-1}.
[c] ZPVE correction of 0.3 kcal mole^{-1} has been applied.

ture is a transition state. The lowest energy state has C_1 symmetry and has the methyl hydrogen atoms on the two carbons offset by 7.2°. In addition, as is expected from the results in Table 3, the singlet–triplet energy gap is less than half of the B3PW91/6-311G* value. We conclude that this model is not sufficient to predict the geometry or energy ladder for this molecule.

SUMMARY

These results indicate that single-point calculations at the B3PW91/6-311G*//HF/6-311G8 level of theory are sufficient to reproduce the singlet–triplet energy gap calculated using full optimization with more sophisticated electron-correlation techniques. The single-point DFT calculations offer a substantial, 3–4 orders of magnitude, savings in CPU time as compared to optimization using full MRCI or CASSCF methods. The computational savings over full optimization using DFT techniques is much less, approximately a factor of 5, but accurate geometries require full optimization using the DFT methods. Comparison of various calculations indicated that polarization functions on Ge and C are essential to accurate calculations and that the LANL1DZ basis set is not suitable for geometry optimizations for these third-row atoms.

ACKNOWLEDGMENTS

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REFERENCES

[1] See, for example, W. Du, L. A. Keeling, C. M. Greenlief, *J. Vac. Sci. Technol. A, 12,* 1994, 2281.
[2] A. Matsuda, M. Koyama, N. Ikuchi, Y. Imanishi, K. Tanaka, *Japan. J. Appl. Phys., 25,* 1986, L54.
[3] K. Saito, K. Obi, *Chem. Phys. Lett., 215,* 1993, 193.
[4] K. Saito, K. Obi, *Chem. Phys., 187,* 1994, 381.
[5] R. Becerra, S. E. Boganov, M. P. Egorov, O. M. Nefedov, R. Walsh, *Chem. Phys. Lett., 260,* 1996, 433.
[6] C. J. Cramer, F. J. Dulles, J. W. Storer, S. E. Worthington, *Chem. Phys. Lett., 218,* 1994, 387.
[7] T. Mineva, N. Russo, E. Sicilia, M. Toscano, *Int. J. Quantum Chem., 56,* 1995, 669.
[8] J. Karolczak, W. W. Harper, R. S. Grev, D. J. Clouthier, *J. Chem. Phys., 103,* 1995, 2829.
[9] Gaussian 94, Revision D.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.
[10] L. A. Curtiss, M. P. McGrath, J. P. Blaudeau, N. E. Davis, R. C. Binning, L. Random, *J. Chem. Phys., 103,* 1995, 6104.
[11] A. D. Becke, *J. Chem. Phys., 98,* 1993, 1372.
[12] A. D. Becke, *J. Chem. Phys., 98,* 1993, 5643.
[13] J. P. Perdew, Y. Wang, *Phys. Rev. B. 45,* 1992, 13244.
[14] J. J. BelBruno, *Chem. Phys. Lett., 254,* 1996, 321.
[15] J. J. BelBruno, *Chem. Phys. Lett., 263,* 1996, 84.