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# A Systematic Multireference Perturbation-Theory Study of the Low-Lying States of SiC<sub>3</sub>

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# A Systematic Multireference Perturbation-Theory Study of the Low-Lying States of SiC<sub>3</sub>

## Abstract

The three known lowest-energy isomers of SiC<sub>3</sub>, two cyclic singlets (2s and 3s) and a linear triplet (1t), have been reinvestigated using multireference second-order perturbation theory (MRPT2). The dependence of the relative energies of the isomers upon the quality of the basis sets and the sizes of the reference active spaces is explored. When using a complete-active-space self-consistent-field reference wave function with 12 electrons in 11 orbitals [CASSCF (12, 11)] together with basis sets that increase in size up to the correlation-consistent polarized core-valence quadruple zeta basis set (cc-pCVQZ), the MRPT2 method consistently predicts the linear triplet to be the most stable isomer. A new parallel direct determinant MRPT2 code has been used to systematically explore reference spaces that vary in size from CASSCF (8,8) to full optimized reaction space [FORS or CASSCF (16,16)] with the cc-pCVQZ basis. It is found that the relative energies of the isomers change substantially as the active space is increased. At the best level of theory, MRPT2 with a full valence FORS reference, the 2s isomer is predicted to be more stable than 3s and 1t by 4.7 and 2.2 kcal/mol, respectively.

## Keywords

Wave functions, Basis sets, Perturbation theory, Band gap, Excitation energies

## Disciplines

Chemistry

## Comments

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# A systematic multireference perturbation-theory study of the low-lying states of SiC<sub>3</sub>

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The three known lowest-energy isomers of SiC<sub>3</sub>, two cyclic singlets (**2s** and **3s**) and a linear triplet (**1t**), have been reinvestigated using multireference second-order perturbation theory (MRPT2). The dependence of the relative energies of the isomers upon the quality of the basis sets and the sizes of the reference active spaces is explored. When using a complete-active-space self-consistent-field reference wave function with 12 electrons in 11 orbitals [CASSCF (12, 11)] together with basis sets that increase in size up to the correlation-consistent polarized core-valence quadruple zeta basis set (cc-pCVQZ), the MRPT2 method consistently predicts the linear triplet to be the most stable isomer. A new parallel direct determinant MRPT2 code has been used to systematically explore reference spaces that vary in size from CASSCF (8,8) to full optimized reaction space [FORS or CASSCF (16,16)] with the cc-pCVQZ basis. It is found that the relative energies of the isomers change substantially as the active space is increased. At the best level of theory, MRPT2 with a full valence FORS reference, the **2s** isomer is predicted to be more stable than **3s** and **1t** by 4.7 and 2.2 kcal/mol, respectively. © 2006 American Institute of Physics. [DOI: 10.1063/1.2140687]

## I. INTRODUCTION

The study of silicon-carbon clusters is appealing from a fundamental point of view in that silicon and carbon have substantially different chemical properties even though they are in the same group in the periodic table. Especially different are the geometries and properties of the elemental C<sub>n</sub> and Si<sub>n</sub> clusters. Mixed Si<sub>n</sub>C<sub>m</sub> clusters have long been a focus of interest in the fields of materials science and astrophysics, the latter due to the observation of small silicon-carbide clusters in interstellar space.<sup>1–6</sup> Therefore, several experimental studies have been performed on silicon-carbide clusters in an effort to discover their geometries and electronic structures. Recently, these experimental techniques include photoelectron spectroscopy<sup>7,8</sup> and Fourier transform microwave spectroscopy.<sup>9–12</sup> SiC<sub>3</sub> is of particular interest as there is experimental evidence for the presence of three isomers, two singlet cyclic rings with either two (**2s**) or three (**3s**) Si–C bonds,<sup>9,11</sup> and a linear triplet (**1t**).<sup>8</sup> These structures are illustrated in Fig. 1.

Well before the experiments mentioned above were reported, high level theoretical calculations on SiC<sub>3</sub> by Alberts *et al.*<sup>13</sup> indicated that the three isomers in Fig. 1 were close in energy. Their best prediction at the time was that **2s** was the global minimum with isomers **1t** and **3s** lying higher in energy by 4.1 and 4.3 kcal/mol, respectively. Since then there have been many theoretical studies on SiC<sub>3</sub><sup>14–19</sup> and a sum-

mary of the methods together with their results is given in Table I. Note that **2s** is consistently predicted to be the global minimum, except by Rintelman and Gordon<sup>17</sup> who calculated **1t** to be lower than **2s** by 4.4 kcal/mol. In their study they used the multireference second-order Møller-Plesset method (MRMP2) of Hirao<sup>20</sup> and Nakano,<sup>21</sup> with a complete-active-space self-consistent-field<sup>22</sup> (CASSCF) reference space containing 12 electrons in 11 orbitals [CASSCF (12,11)] and the augmented correlation-consistent polarized valence double zeta basis set (aug-cc-pVDZ).<sup>23–25</sup> In a subsequent study, Sattelmeyer *et al.*<sup>18</sup> used the coupled-cluster singles and doubles with perturbative triples correction [CCSD(T)] method with the correlation-consistent polarized

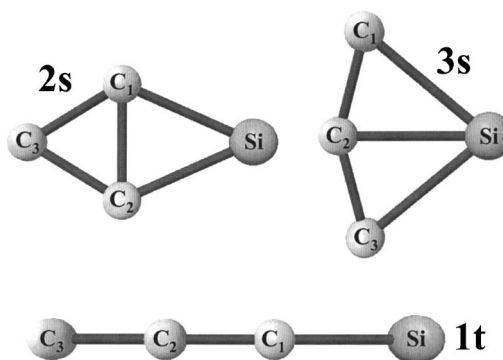


FIG. 1. Illustrations of the three low-lying isomers of SiC<sub>3</sub> studied in this work. Isomers **2s** and **3s** are singlets and have C<sub>2v</sub> symmetry. Isomer **1t** is a triplet and is linear.

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TABLE I. Compilation of previous theoretical predictions of relative energies, in Kcal/mol, of the three low-lying isomers of SiC<sub>3</sub>.

Method	Basis set	2s	3s	1t	Ref.
SCF	TZ2P	0	4.3	3.0	13
CISD <sup>a</sup>	TZ2P	0	5.3	5.0	13
CISD+Q <sup>a</sup>	TZ2P	0	4.3	4.1	13
DFT/LSD	Plane wave	0	1.8	0.2	14
MP2	6-31G( <i>d</i> )	0	12.5	12.0	15
MP4 <sup>b</sup>	6-31G( <i>d</i> )	0	8.5	7.8	15
MRMP2(12,11) <sup>c</sup>	aug-cc-pVDZ	0	3.4	-4.4	17
CCSD <sup>b</sup>	cc-pCVQZ	0	7.0	8.5	16 and 18
CCSD(T)	cc-pCVQZ	0	6.2	7.5	16 and 18
GMC-PT(SA) <sup>d</sup>	aug-cc-pVQZ	0	5.3	0.9	19
GMC-PT(SD) <sup>d</sup>	aug-cc-pVQZ	0	5.3	6.7	19

<sup>a</sup>Energies at SCF/TZ2P optimized geometries.

<sup>b</sup>Energies at MP2/6-31G<sup>\*</sup> optimized geometries.

<sup>c</sup>Energies at CASSCF[12,10(11 for 1t)]/6-31G(*d*) optimized geometries.

<sup>d</sup>Energies at CCSD(T)/cc-pCVQZ optimized geometries.

core-valence quadruple zeta basis set<sup>26,27</sup> (cc-pCVQZ) and found **2s** to be lower than **1t** by 7.5 kcal/mol. They also suggested that the relative energies predicted by Rintelman and Gordon differed due to a lack of basis set convergence.

Kurashige *et al.*<sup>19</sup> suggested that the sizes of the active spaces used by Rintelman and Gordon were not large enough, and further argued that the use of spin-averaged (SA) orbital energies in their MRMP2 calculations underestimated the relative energy of **1t**. In their study Kurashige *et al.*<sup>19</sup> used reference spaces that attempted to approximate full optimized reaction space<sup>28-30</sup> (FORS) wave functions, that is, a full valence space CASSCF (16,16). Their reference space consisted of the SCF determinant plus configurations formed from singles and doubles excitations (CISD) from the eight occupied SCF valence orbitals into the eight unoccupied valence orbitals. The configuration-interaction (CI) coefficients and the orbital coefficients were then simultaneously optimized to yield multiconfigurational self-consistent-field (MCSCF) wave functions labeled MC (16,16). Application of multireference perturbation theory to these general MCSCF references (GMC-PT) (Ref. 31) with SA orbitals and the aug-cc-pVQZ basis set<sup>23-25</sup> predicted that **2s** is the global minimum. However, at this level of theory **1t** is only 0.9 kcal/mol higher in energy. Kurashige *et al.* then used spin-dependent (SD) orbitals,<sup>32</sup> intended to compensate for the underestimation of the energies of high spin states. These calculations predict **1t** to be 6.7 kcal/mol higher than **2s**, in apparent better agreement with the CCSD(T)/cc-pCVQZ result.<sup>18</sup> It is important to note, however, that the SD orbitals are in fact not *spin* dependent, but *M<sub>s</sub>* dependent. For instance, if the **1t** calculation was executed using a configurational basis with *M<sub>s</sub>*=0, the energy would not be the same as that reported,<sup>19</sup> which used a configurational basis with *M<sub>s</sub>*=1.

The present study aims to explore the dependence of the relative energies of SiC<sub>3</sub> isomers upon the basis set and active space size in CASSCF and multireference second-order perturbation-theory (MRPT2) calculations.

TABLE II. Relative energies, in kcal/mol, of isomers of SiC<sub>3</sub> at the MRPT2 level of theory using various basis sets. All calculations used CASSCF (12, 11) references. (See Ref. 17 for further details regarding the active spaces.)

Basis set	2s	3s	1t
6-31G( <i>d</i> )	0.6	5.6	0
aug-cc-pVDZ	4.4	7.8	0
cc-pCVQZ	1.1	5.1	0

## II. COMPUTATIONAL DETAILS

Three basis sets were used in this study: the 6-31G(*d*) set<sup>33,34</sup> and the aug-cc-pVDZ (Refs. 23-25) and cc-pCVQZ (Refs. 26 and 27) sets. First (Sec. III) CASSCF reference wave functions were obtained using a determinant-based full configuration-interaction<sup>35</sup> (FCI) code together with an approximate second-order orbital optimization program.<sup>36</sup> Final MRPT2 energies were obtained using the Hirao-Nakano MRMP2 method.<sup>20,21</sup> All calculations kept the 1s orbitals doubly occupied. Second (Sec. IV), CASSCF wave functions were determined using parallelized versions<sup>37</sup> of the determinant FCI code<sup>35</sup> and the second-order orbital optimization program of Dupuis.<sup>38</sup> Final MRPT2 energies for these CASSCF reference wave functions were then obtained using a parallel direct determinant implementation<sup>39</sup> of the method by Hirao.<sup>20</sup> Note that the Hirao method is identical to the Kozłowski-Davidson MROPT1 method<sup>40</sup> if in the latter method, the barycentric definition of the zeroth-order energy (*E*<sub>0</sub>) is used and their effective Hamiltonian (*H*<sub>eff</sub>) is not diagonalized. Excitations from the 1s core orbitals were included in some of the second set of calculations to determine their influence upon the relative energies of the SiC<sub>3</sub> isomers. All calculations were executed using the GAMESS package.<sup>41</sup>

## III. BASIS SET DEPENDENCE

In this section we gauge the dependence of the relative energies of the three isomers shown in Fig. 1 on the basis set. MRPT2 energies for all species were determined using a CASSCF (12,11) reference space. Geometries and active space character were taken from Ref. 17. Table II shows the calculated relative energies of the isomers when using the 6-31G(*d*), aug-cc-pVDZ, and cc-pCVQZ basis sets. Isomer **1t** is consistently predicted to be the global minimum, in disagreement with all other results listed in Table I. However, isomer **2s** is predicted to lie higher by only 0.6 and 1.1 kcal/mol when using the 6-31G(*d*) and cc-pCVQZ basis sets, respectively. The 6-31G(*d*) and cc-pCVQZ basis sets also give similar predictions of 5.6 and 5.1 kcal/mol, respectively, for the relative energy of isomer **3s**. It appears that the aug-cc-pVDZ basis set overestimates the stability of the **1t** isomer, as compared with the larger cc-pCVQZ basis, with respect to both the **2s** and **3s** isomers. Nonetheless, it appears that the prediction of **1t** as the lowest-energy SiC<sub>3</sub> isomer is not a result of the basis sets used. The possibility that this prediction is due to the choice of the MRPT2 active space is explored further in the next section.



TABLE III. Comparison of structures of SiC<sub>3</sub> isomers determined from theory (All methods used the cc-pCVQZ basis set (361 contracted functions) and all electrons were correlated. The MRPT2 method used a CASSCF(8,8) reference space for isomers **2s** and **3s**, and a CASSCF (8,9) reference space for isomer **1t**) and empirical fitting. Interatomic distances are given in Angstroms.

	Isomer <b>2s</b>			Isomer <b>3s</b>			Isomer <b>1t</b>	
	MRPT2 <sup>a</sup>	CCSD(T) <sup>b</sup>	Emp. <sup>b,c</sup>	MRPT2 <sup>a</sup>	CCSD(T) <sup>b</sup>	Emp. <sup>b,c</sup>	MRPT2 <sup>a</sup>	CCSD(T) <sup>d</sup>
$r[\text{Si}-\text{C}_1]$	1.825	1.829	1.828	2.018	2.021	2.019	1.722	1.725
$r[\text{Si}-\text{C}_2]$				1.887	1.886	1.886		
$r[\text{C}_1-\text{C}_2]$	1.432	1.434	1.433	1.342	1.343	1.343	1.290	1.290
$r[\text{C}_2-\text{C}_3]$							1.307	1.306
$r[\text{C}_1-\text{C}_3]$	1.487	1.483	1.483					

<sup>a</sup>This work.

<sup>b</sup>Reference 16.

<sup>c</sup>Least-squares fit to data derived from microwave spectroscopy and calculated harmonic and cubic force fields at the CCSD(T)/cc-pVTZ level of theory.

<sup>d</sup>Reference 18.

#### IV. ACTIVE SPACE DEPENDENCE

Preliminary calculations on all three isomers were performed at the geometries given in Ref. 17. FORS [CASSCF (16,16)] wave functions were optimized using a parallelized MCSCF program.<sup>37</sup> In these calculations, initial guess correlating orbitals were obtained by generation of modified virtual orbitals (MVOs).<sup>42</sup> For each isomer, natural orbitals (NOs) were determined and these were arranged in order of decreasing occupation. Smaller active spaces were derived directly from these NO sets by first eliminating highly occupied orbitals (closest to occupation number of 2.0) in order of decreasing FORS NO occupation and then eliminating correlating orbitals in order of increasing FORS NO occupation (closest to occupation number of 0.0) until the desired numbers of electrons and orbitals were obtained. The cc-pCVQZ basis set was used for all calculations described below.

##### A. Geometry optimizations

Geometries were optimized at the MRPT2 level of theory using a CASSCF (8,8) reference space for isomers **2s** and **3s** and a CASSCF (8,9) reference space for isomer **1t**. All electrons, including those in 1s core orbitals, were correlated and gradients were computed numerically. Table III reports the geometries optimized in this work together with those optimized at the CCSD(T) level<sup>16,18</sup> and determined empirically.<sup>16</sup> Atom labels are given in Fig. 1. The MRPT2 and CCSD(T) optimized geometries are in excellent agreement for all isomers, with the largest deviation being only 0.004 Å for the  $r(\text{C}_1-\text{C}_3)$  distance in isomer **2s**. The empirical parameters were determined by least-squares fits to data derived from microwave spectroscopy and calculated force fields at the CCSD(T)/cc-pVTZ level of theory.<sup>16</sup> Even though the empirical parameters are somewhat dependent on the CCSD(T)/cc-pVTZ theoretical data, the MRPT2 and empirically determined geometries are nearly identical for isomer **3s** and only slightly different for isomer **2s**. It would seem that the MRPT2 optimized geometries for all three isomers are of a very high quality, so these structures are used for subsequent calculations.

##### B. CASSCF results

FORS wave functions were calculated at the MRPT2 optimized geometries and smaller active spaces were designed using the method described above. Energies were determined at the CASSCF level of theory using active spaces that ranged in size from (8,8) to (16,16) for isomers **2s** and **3s**, and (8,9) to (16,16) for isomer **1t**. Absolute energies are of little interest here so only the relative energies of the isomers, with respect to active space size, are given in Table IV. Isomer **1t** is predicted to be the global minimum for all active spaces except the largest FORS (16,16) active space. Isomer **3s** is predicted to be the highest in energy of the three isomers for all active spaces except (12,12) for which it switches order with isomer **2s**. It is clear that as the active space sizes are increased, presumably providing improved accuracy, there are no trends occurring in the relative energies. In other words, it is almost impossible to predict what will happen from one active space to the next. The most likely reason for this is that the relative levels of improvement in the wave functions of the isomers are different as the active space sizes are increased. We expect the results at the full valence FORS level to be the most reliable of all the CASSCF calculations described here for two reasons: (1) it has the largest active space, and (2) by definition its active space contains *all* valence orbitals and hence it is the most *balanced*. At the full valence FORS level of theory, isomer **2s** is calculated to be the global minimum and isomers **3s** and **1t** lie higher by 6.8 and 2.3 kcal/mol, respectively. These energy separations are the most similar of any dis-

TABLE IV. Relative energies of SiC<sub>3</sub> isomers, in kcal/mol, calculated at the CASSCF level of theory with varying active space sizes. (Calculations used the cc-pCVQZ basis set.) See text for further details.

Active space size	<b>2s</b>	<b>3s</b>	<b>1t</b>
(8,8[9])	0	11.3	-12.5
(10,10)	0	1.7	-4.4
(12,12)	0	-1.5	-7.9
(14,14)	0	4.9	-4.3
FORS (16,16)	0	6.8	2.3

TABLE V. Relative energies of SiC<sub>3</sub> isomers, in kcal/mol, calculated at the MRPT2 level of theory with varying active space sizes. (Calculations used the cc-pCVQZ basis set.) See text for further details.

Active space size	Isomer <b>2s</b>		Isomer <b>3s</b>		Isomer <b>1t</b>	
	1s core <sup>a</sup>	No core <sup>b</sup>	1s core <sup>a</sup>	No core <sup>b</sup>	1s core <sup>a</sup>	No core <sup>b</sup>
(8,8[9])	0	0	3.4	3.6	-0.9	-1.3
(10,10)	0	0	7.7	7.9	-2.3	-2.7
(12,12)	0	0	5.7	5.8	2.3	1.8
(14,14)	0	0	0.8	1.0	2.9	2.5
FORS (16,16)	0	0	4.5	4.7 <sup>c</sup>	2.6	2.2 <sup>c</sup>

<sup>a</sup>The four 1s core orbitals were kept doubly occupied.

<sup>b</sup>Excitations from all orbitals, including the four 1s core, were included.

<sup>c</sup>Effect of excitations from 1s core orbitals upon relative energies estimated using results from MRPT2 (14,14) calculations.

cussed in this work so far to the CCSD(T) (Refs. 16 and 18) and GMC-PT (Ref. 19) results reported earlier and given in Table I.

### C. MRPT2 results

All of the CASSCF wave functions described in Sec. IV B were used as references for MRPT2 calculations. In order to gauge the influence of correlation from the four 1s core orbitals upon the relative energies of the isomers, two calculations have been performed for each active space, except FORS (16,16). The first of these calculations omits, and the second includes, excitations from these orbitals. For the FORS (16,16) reference, the four 1s orbitals were kept doubly occupied. Relative energies of the isomers for the different active spaces are given in Table V. First, note that the variations in the relative energies, as the active spaces are changed, are not as large as was seen for the CASSCF calculations. However, the relative energies do change with no noticeable trends. This is not unexpected considering the CASSCF reference results described above. For active spaces smaller than (12,12) isomer **1t** is predicted to be the global minimum and isomer **3s** is the highest in energy of the three species. In contrast to the CASSCF results, isomer **2s** becomes the most stable species when using active spaces (12,12) and larger and isomers **3s** and **1t** switch positions when the active space is increased from (12,12) to (14,14) and then revert at FORS (16,16). Inclusion of excitations from core 1s orbitals consistently stabilizes isomer **1t**, relative to **2s**, by 0.4–0.5 kcal/mol whereas isomer **3s** is consistently destabilized, relative to **2s**, by 0.1–0.2 kcal/mol. These core effects are not large but play a non-negligible role in such a sensitive system.

At the best level of theory, MRPT2 with a full FORS (16,16) reference (MRPT2 [FORS (16,16)]) and 1s orbitals doubly occupied, isomer **2s** is the most stable species and isomers **3s** and **1t** lie higher in energy by 4.5 and 2.6 kcal/mol, respectively. If we take differences in relative energies due to core excitations at the MRPT2 (14,14) level, and add these into the MRPT2 (FORS) results, we obtain best all electron estimates of the relative energies for isomers **2s**, **3s**, and **1t** of 0, 4.7, and 2.2 kcal/mol, respectively. These results agree with the previously reported CCSD(T) (Refs. 16 and 18) and GMC-PT (Ref. 19) calculations in the pre-

dictions that isomer **2s** is the global minimum and that isomer **3s** is less stable by over 4 kcal/mol. However, the present results disagree with the CCSD(T) (Refs. 16 and 18) and GMC-PT(SD) (Ref. 19) results that indicate isomer **1t** is less stable than isomer **3s**. In fact, it is predicted here that isomer **1t** lies only 2.2 kcal/mol higher in energy than the lowest-energy isomer **2s** and 2.5 kcal/mol lower in energy than isomer **3s**.

### V. CONCLUSIONS

The present work has, to some degree, analyzed the influence of the basis set upon the relative energies of three low-lying SiC<sub>3</sub> isomers. With a CASSCF (12,11) reference space and the 6-31G(*d*), aug-cc-pVDZ, and cc-pCVQZ basis sets, MRPT2 calculations predict the ordering to be **1t** < **2s** < **3s**. It appears that the aug-cc-pVDZ basis set overestimates the stability of isomer **1t** over isomers **2s** and **3s**, by approximately 3 kcal/mol, when compared with the larger cc-pCVQZ basis set. In addition, the influence of the active spaces upon the relative energies of the SiC<sub>3</sub> isomers has been systematically, and, it is felt, conclusively studied at the CASSCF and MRPT2 levels of theory. Great variations in the calculated energy separations at the CASSCF level of theory are seen as the active spaces are increased. With the largest, full valence active space, FORS (16,16), isomer **2s** is predicted to be the global minimum with isomers **3s** and **1t** lying higher by 6.8 and 2.3 kcal/mol, respectively.

Calculated relative energies at the MRPT2 level of theory also change as the active spaces are increased, although these variations are smaller than seen for CASSCF calculations. When using FORS (16,16) references, and including an estimate of core correlation effects, the MRPT2 level of theory predicts that isomer **2s** is the lowest-energy species with isomers **3s** and **1t** lying higher by 4.7 and 2.2 kcal/mol, respectively. The FORS (16,16) and MRPT2 (FORS) results are almost equivalent in that they predict the same ordering for the energies of the three isomers and agree to within a tenth of a kcal/mol in the **2s-1t** separation. The only real contrast between the FORS (16,16) and MRPT2 (FORS) results are predictions of the **2s-3s** energy gap, which differ by 2.3 kcal/mol. The MRPT2 (FORS) results

are expected to be more reliable than the FORS (16,16) relative energies, but the semiquantitative agreement between both methods is satisfying.

The work reported here agrees with previously reported results that isomer **2s** is predicted to be the global minimum. However, the present MRPT2 (FORS) calculations disagree with the CCSD(T) (Refs. 16 and 18) and GMC-PT(SD) (Ref. 19) calculations on the magnitude of the **2s-1t** energy gap. The reasons for these are not immediately obvious, unless one accepts the argument by Kurashige *et al.* that the use of their SD orbitals leads to greater accuracy in estimations of singlet-triplet energy gaps.<sup>32</sup> However, this is not universally the case (see, for example, O<sub>2</sub> and *o*-benzynes in Ref. 32), and use of SD orbitals has not been tested for energy gaps between structural isomers having different spins. The CCSD(T) method is sometimes referred to as the “gold standard”<sup>43</sup> for single reference calculations, but it is well known that this method can lose accuracy for multireference problems (see, for example, N<sub>2</sub>O<sub>2</sub> in Ref. 44). Remaining possible sources of error include further improvements in the level of theory (e.g., higher orders of multireference perturbation theory, the use of multireference configuration interaction, or higher orders of coupled cluster theory), even larger basis sets, and improved geometries at the highest levels of theory. So, obtaining accurate relative energies for the low-lying electronic states of SiC<sub>3</sub> is indeed a challenge.

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