A Systematic Multireference Perturbation-Theory Study of the Low-Lying States of SiC3

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Abstract
The three known lowest-energy isomers of SiC3, 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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The three known lowest-energy isomers of SiC₃, 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 Cₙ and Siₙ clusters. Mixed SiₙCₙ 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.¹–⁶ 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 spectroscopy⁷,⁸ and Fourier transform microwave spectroscopy.⁹–¹² SiC₃ 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,⁹,¹¹ and a linear triplet (1t).⁸ These structures are illustrated in Fig. 1.

Well before the experiments mentioned above were reported, high level theoretical calculations on SiC₃ by Alberts et al.¹³ 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 SiC₃¹⁴–¹⁹ and a summary 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 Gordon¹⁷ 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 Hirao²⁰ and Nakano,²¹ with a complete-active-space self-consistent-field (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).²³–²⁵ In a subsequent study, Sattelmeyer et al.²⁶ used the coupled-cluster singles and doubles with perturbative triples correction [CCSD(T)] method with the correlation-consistent polarized

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FIG. 1. Illustrations of the three low-lying isomers of SiC₃ studied in this work. Isomers 2s and 3s are singlets and have C₂ᵥ symmetry. Isomer 1t is a triplet and is linear.
TABLE I. Compilation of previous theoretical predictions of relative energies, in Kcal/mol, of the three low-lying isomers of SiC_3.

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

1Energies at SCF/TZ2P optimized geometries.
2Energies at MP2/6-31G* optimized geometries.
3Energies at CASSCF[12,10(11 for 1t)]/6-31G(d) optimized geometries.
4Energies at CCSD(T)/cc-pVQZ optimized geometries.

The present study aims to explore the dependence of the relative energies of SiC_3 isomers upon the basis set and active space size in CASSCF and multireference second-order perturbation-theory (MRPT2) calculations.

II. COMPUTATIONAL DETAILS

Three basis sets were used in this study: the 6-31G(d) set,33,34 and the aug-cc-pVQZ (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 (FCI) code together with an approximate second-order orbital optimization program.36 Final MRPT2 energies were obtained using the Hirao-Nakano MRMP2 method.20,21 All calculations kept the 1s orbitals doubly occupied. Second (Sec. IV), CASSCF wave functions were determined using parallelized versions37 of the determinant FCI code35 and the second-order orbital optimization program of Dupuis.38 Final MRPT2 energies for these CASSCF reference wave functions were then obtained using a parallel direct determinant implementation39 of the method by Hirao.20 Note that the Hirao method is identical to the Kozlowski-Davidson MROPT1 method40 if in the latter method, the barycentric definition of the zeroth-order energy (\(E_0\)) is used and their effective Hamiltonian (\(H_{\text{eff}}\)) 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_3 isomers. All calculations were executed using the GAMESS package.41

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_3 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$_3$ 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 isomer 2s and 3s, and a CASSCF (8,9) reference space for isomer 1t) and empirical fitting. Interatomic distances are given in Angstroms.

<table>
<thead>
<tr>
<th>Isomer 2s</th>
<th>Isomer 3s</th>
<th>Isomer 1t</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MRPT2$^a$</td>
<td>CCSD(T)$^b$</td>
</tr>
<tr>
<td></td>
<td>2s</td>
<td>3s</td>
</tr>
<tr>
<td>$r[\text{Si}–C_1]$</td>
<td>1.825</td>
<td>2.018</td>
</tr>
<tr>
<td>$r[\text{Si}–C_2]$</td>
<td>1.829</td>
<td>2.021</td>
</tr>
<tr>
<td>$r[C_1–C_2]$</td>
<td>1.432</td>
<td>1.342</td>
</tr>
<tr>
<td>$r[C_1–C_3]$</td>
<td>1.434</td>
<td>1.343</td>
</tr>
<tr>
<td></td>
<td>1.433</td>
<td>1.343</td>
</tr>
<tr>
<td></td>
<td>1.487</td>
<td>1.483</td>
</tr>
</tbody>
</table>

$^a$This work.
$^b$Reference 16.
$^c$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.
$^d$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. In these calculations, initial guess correlating orbitals were obtained by generation of modified virtual orbitals (MVOs). 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$^{16,18}$ and determined empirically.$^{16}$ 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 $r(C_1–C_3)$ 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.$^{16}$ 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$_3$ 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.

<table>
<thead>
<tr>
<th>Active space size</th>
<th>2s</th>
<th>3s</th>
<th>1t</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8,8)[9]</td>
<td>0</td>
<td>11.3</td>
<td>−12.5</td>
</tr>
<tr>
<td>(10,10)</td>
<td>0</td>
<td>1.7</td>
<td>−4.4</td>
</tr>
<tr>
<td>(12,12)</td>
<td>0</td>
<td>−1.5</td>
<td>−7.9</td>
</tr>
<tr>
<td>(14,14)</td>
<td>0</td>
<td>4.9</td>
<td>−4.3</td>
</tr>
<tr>
<td>FORS (16,16)</td>
<td>0</td>
<td>6.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>
 TABLE V. Relative energies of SiC₃ 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.

<table>
<thead>
<tr>
<th>Active space size</th>
<th>Isomer 2s</th>
<th>Isomer 3s</th>
<th>Isomer 1t</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1s core¹</td>
<td>No core²</td>
<td>1s core¹</td>
</tr>
<tr>
<td>(8.8[9])</td>
<td>0</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>(10,10)</td>
<td>0</td>
<td>0</td>
<td>7.7</td>
</tr>
<tr>
<td>(12,12)</td>
<td>0</td>
<td>0</td>
<td>5.7</td>
</tr>
<tr>
<td>(14,14)</td>
<td>0</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>FORS (16,16)</td>
<td>0</td>
<td>0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

¹ The four 1s core orbitals were kept doubly occupied.
² Excitations from all orbitals, including the four 1s core, were included.
³ Effect of excitations from 1s core orbitals upon relative energies estimated using results from MRPT2 (14,14) calculations.

discussed 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 predictions 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 SiC₃ 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 SiC₃ 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.32 However, this is not universally the case (see, for example, O₂ and o-benzylene in Ref. 32), and use of SD orbitals has not been tested for energy gaps between structural isomers having different spins. The CCSD technique between structural isomers having different spins. The CCSD method is sometimes referred to as the “gold standard” for single reference calculations, but it is well known that this method can lose accuracy for multireference problems (see, for example, N₂O₂ 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 SiC₃ is indeed a challenge.

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38This code is based upon the ideas presented in the following papers: B. H. Lengsfeld I, J. Chem. Phys. 73, 382 (1980); D. R. Yarkony, Chem. Phys. Lett. 77, 634 (1981).
43Quote attributed to T. H. Dunning.