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The structure of the Si9H12 cluster: A coupled cluster and multi-reference perturbation theory study

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Full geometry optimizations using both singles and doubles coupled cluster theory with perturbative triple excitations, CCSD(T), and second order multi-reference perturbation theory, MRMP2, have been employed to predict the structure of Si_9H_{12}, a cluster commonly used in calculations to represent the Si(100) surface. Both levels of theory predict the structure of this cluster to be symmetric (*not* buckled), and no evidence for a buckled (asymmetric) structure is found at either level of theory. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2176611]

The two most common approaches to computational studies of the Si(100) surface are to employ cluster or embedded cluster models or to use slab calculations with periodic boundary conditions. Both approaches have their advantages and disadvantages. Since the 100 surface after reconstruction is characterized by very reactive Si dimers, the simplest cluster that can properly represent this surface is the single dimer Si_9H_{12} cluster. Many computational studies of reactions that occur on the Si(100) surface, including those that employ the simple Si_9H_{12} cluster, rationalize the predicted or observed behavior in terms of buckling of the surface. This means that the two Si dimer atoms are not symmetrically equivalent (C_{2v} for the Si_9H_{12} cluster). Instead, one of these Si atoms moves up relative to the underlying atoms, while the other Si atom moves down, resulting in a polarization of the electron density and an increase in reactivity.

There have been many papers, both experimental and theoretical, that have debated whether the Si(100) surface is buckled or symmetric.[1–30] The focus of the present paper is on the Si_9H_{12} cluster, since the structure of this cluster, the most commonly used cluster for representing the Si(100) surface, has itself been the subject of intense controversy. In general, Hartree-Fock (HF)[22] and density functional theory (DFT)[22,25,27] calculations predict the Si_9H_{12} cluster to be buckled, while second order perturbation theory (MP2)[22] and multi-configurational self-consistent field (MCSCF)[21,22] wave functions predict this cluster to be symmetric. Other, more sophisticated methods have been applied to this question at geometries determined at lower levels of theory, but for these methods there are not currently analytical gradients available. Multi-reference second order perturbation theory (MRMP2)[22] calculations appear to support the symmetric structure, whereas quantum Monte Carlo[24] studies appear to support the buckled structure. A recent investigation using unrestricted density functional theory (UDFT) and the B3LYP functional illustrated that this level of theory finds potential energy minima at both the buckled and symmetric structures.[30] Although UB3LYP predicts the buckled structure to be the lower of the two in energy, MRMP2 calculations at the UB3LYP geometries predict the reverse order of stability. Similar trends are predicted by the same methods for larger clusters with up to five dimers.[22(d)]

Until now, the most sophisticated quantum chemistry methods have not been used to predict the structure(s) of Si_9H_{12}. Recently, an efficient, fully numerical gradient code has been designed and implemented into the GAMESS[31] electronic structure code.[32] This code has now been used to determine the minimum energy structures of the Si_9H_{12} cluster, using the 6-31G(d) basis set and coupled cluster and multi-reference perturbation theory methods. The singles and doubles coupled cluster method with perturbative triples, CCSD(T), was employed.

The MRMP2 and CCSD(T) geometry optimizations were initiated by first distorting the symmetric Si_9H_{12} cluster in C_{2v} symmetry along its buckling vibrational normal mode.[22(c)] The magnitude of the distortion was taken to be the classical amplitude of the vibrational mode. This distortion reduces the cluster symmetry to C_s. Full MRMP2 geometry optimization was then performed in C_1 symmetry, while C_s symmetry was retained in the CCSD(T) optimizations to conserve computer resources. In both cases, the geometry optimizations returned the structure to C_{2v} symmetry. No intermediate buckled structure was found in either case.

The final MRMP2 and CCSD(T) geometries for the Si_9H_{12} cluster are compared in Table I with those obtained using Hartree-Fock, B3LYP, and MP2. All calculations used the 6-31G(d) basis set. Because HF and DFT are unable to occupy the π^* orbital in the dimer, the dimer Si_d-Si_d distance is predicted by these methods to be somewhat shorter than that predicted by MRMP2. This is especially true for the HF method which predicts a Si_d-Si_d distance of 2.19 Å, about 0.04 Å shorter than the B3LYP distance and about 0.06 Å longer than the MRMP2 distance. The CCSD(T) method is able to recover most of this effect due to the inclusion of triple excitations, whereas MP2 predicts a bond distance that is very similar to the DFT value.

As has been illustrated previously, both HF and DFT predict the structure of Si_9H_{12} to be buckled. The amount of

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TABLE I. Calculated geometries for Si_9H_{12}.[a]

Coordinate[b]	HF	B3LYP	MP2	MRMP2	CCSD(T)
Si_d-Si_d	2.187	2.231	2.234	2.248	2.241
Si_d-Si_b	2.355	2.345	2.335	2.340	2.347
	2.355	2.362			
Si_b-Si_d-Si_d	107.1	100.7	106.3	106.4	106.5
	107.5	111.5			
Si_b-Si_d-Si_d-Si_b	0.8	8.9	0.0	0.0	0.0

[a]Bond lengths in Å, angles in degrees.
[b]Si_d refers to dimer Si, Si_b refers to bulk Si.

buckling predicted by DFT, as illustrated by both the Si_b-Si_d-Si_d bond angles and the Si_b-Si_d-Si_d-Si_b dihedral angle, is greater than that predicted by HF, where Si_d and Si_b refer to dimer and bulk Si atoms, respectively. For example, the HF and DFT dihedral angles are ~1° and ~9°, respectively. In contrast, MP2, MRMP2 and CCSD(T) all predict symmetric Si_9H_{12} structures. These three methods predict very similar geometries, with bond distances and angles differing by only 0.01 Å and 0.1°, respectively. It therefore appears to be very likely that Si_9H_{12} is symmetric. At present, the use of larger basis sets for MRMP2 and CCSD(T) geometry optimizations is not computationally practical. While it is unlikely that employing larger basis sets will qualitatively alter the results predicted here, such calculations should be done in order to fully validate these predictions.

The impact of this result on the predicted structure for bulk Si(100) is, of course, unclear. Arguments have been presented[25,27] that adjacent dimers increase the likelihood of buckling in order to reduce the inter-dimer repulsion. On the other hand, an analysis of this repulsion[22(d)] suggests that it is rather small, and MRMP2 at MCSCF geometries suggest that there is no buckling for up to five dimers. At present, geometry optimizations for multiple dimer structures using MRMP2 or CCSD(T) are not feasible.

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