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Response to "Comment on 'An *ab initio* cluster study of the structure of the Si(001) surface'" [J. Chem. Phys. 113, 9353 (2000)]

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The main point of the Comment by Hess and Doren (HD) (Ref. 1) is that a MCSCF wave function cannot adequately represent the potential energy surface (PES) for the Si_9H_{12} cluster, because dynamic correlation is required for an accurate description of the PES. A second issue, not directly addressed in the Comment, but perhaps more important at the end of the day, is whether the Si_9H_{12} cluster is particularly relevant to the structure of the Si(100) surface. We will mostly focus on the first issue, then comment briefly on the second one.

HD's approach for incorporating dynamic correlation is to use density functional theory (DFT). Their conclusion is that "MCSCF calculations do not reliably identify the minimum energy structure." Their verification of this conclusion is that if one optimizes the buckled structure using DFT with a large basis set, optimizes the symmetric structure using a four orbital, four electron multiconfigurational SCF (MCSCF) with an effective core potential (ECP) valence basis, and then performs single point calculations at these two geometries using a form of second order multireference perturbation theory (MRMP), the buckled structure is favored by 0.9 kcal/mol (see their Table I).

Of course, one would like to fully optimize both structures (if indeed they both exist) using the MRMP level of theory, but this is difficult without the availability of MRMP analytic gradients. Nonetheless, performing single point calculations at a pair of geometries that were obtained using such different levels of theory seems a bit inconsistent. We therefore have undertaken two additional types of calculations, in order to help sort out this small controversy.

First, since the MCSCF calculations of Hess and Doren give essentially the same geometries as did our original calculations,² we reoptimized the symmetric Si_9H_{12} structure with a two orbital, two electron MCSCF (TCSCF) using the 6-31G(*d*) basis set.³ As reported in Ref. 2, this structure is positive definite at the TCSCF level of theory, and the smallest buckling frequency that emerges from the corresponding Hessian is $\approx 190\text{ cm}^{-1}$. Then, using MacMolPlt,⁴ we displaced the molecule along this buckling normal mode. At each displaced geometry, MRMP calculations were performed using three different MRMP methods. These are the same CASMP2 methods in GAUSSIAN98 (Ref. 5) used by

Hess and Doren, the MCQDPT2 (Ref. 6) method in GAMESS,⁷ and the CASPT2 (Ref. 8) method in MOLPRO.⁹ The results of these calculations are summarized in Table I, together with the TCSCF results. Three important points may be gleaned from this table. First, the three MRMP methods are all in very close agreement with each other. Second, all four methods, including TCSCF, predict a monotonic *increase* in energy as the molecule buckles. Third, the buckling potential along this normal mode becomes somewhat, but not greatly, flatter when dynamic correlation is included. At the largest buckling angle, the MRMP energy increase is about 10–11 kcal/mol, as compared with the TCSCF value of about 14 kcal/mol. This is about a 25% decrease. So, while the introduction of dynamic correlation does have a quantitative effect on the TCSCF results, as indeed one would expect, there is no qualitative difference between the two types of calculation. Now, one could argue, with some merit, that the foregoing analysis is flawed, since it is not based on a true geometry optimization and since the more one deviates from the energy minimum, the less reliable a normal mode becomes. In the absence of analytic MRMP gradients, this is a bit of a dilemma. On the other hand, if dynamic correlation is truly needed to obtain the correct structure, one simple approach is to use single reference MP2.^{10(a)} For this method, one does have analytic gradients, and in GAMESS these gradients are highly scalable,^{11,12} so the calculations may be run efficiently on highly parallel computers.^{10(b)} While we maintain that an adequate representation of the Si_9H_{12} structure requires a multireference wave function, a MP2 optimization will certainly provide a test of the importance of dynamic correlation. Because the DFT method used by Hess and Doren contains parameters that are fitted to experimental data, the origin of that method's behavior is less definitive.

First, the MP2 geometry optimization was performed on the symmetric structure with the 6-31G(*d*) basis set. This optimized structure is positive definite, even though the dimer Si–Si distance of 2.234 Å is closer to the DFT value than the MCSCF value. A second optimization using the 6-311G(*d*) basis set³ gave essentially identical results. The value of the lowest buckling frequency for this structure is $\approx 130\text{ cm}^{-1}$, somewhat smaller than the TCSCF value. It is likely that a MRMP frequency will be somewhere between

TABLE I. Energies along the TCSCF buckling coordinate.

HSiSi angles ^a	Relative energies (kcal/mol)			
	TCSCF	CASMP2	MCQDPT2	CASPT2
106.1, 106.1	0.0	0.0	0.0	0.0
105.5, 106.7	0.04	0.03	0.02	0.03
104.9, 107.3	0.15	0.10	0.10	0.11
104.2, 107.8	0.33	0.23	0.21	0.24
103.0, 109.0	0.93	0.65	0.60	0.67
99.7, 111.6	3.68	2.58	2.40	2.69
92.7, 115.8	14.06	10.22	10.08	10.84

^aThese are the HSiSi and SiSiH angles at the surface dimer.

130 and 190 cm⁻¹. Since it is possible that the symmetric dimer is a higher energy local minimum on the MP2 PES, a second geometry optimization was performed, starting from the most distorted structure in Table I. The result of this reoptimization was the symmetric dimer structure. While we cannot claim to have exhaustively examined the MP2/6-31G(d) PES, these results are rather suggestive that TCSCF, MP2, and MRMP all predict just one, symmetric, minimum for Si₉H₁₂. This would then further suggest that DFT predicts a buckled structure for a reason that is *not* connected to dynamic correlation.

As to how relevant the Si₉H₁₂ structure and PES are to the actual Si(100) surface, the conclusion at this juncture must be that the connection is tenuous. As noted by both HD (Ref. 1) and ourselves,² the overwhelming experimental evidence is that the surface is buckled. If this is the case, the behavior must be due somehow to dimer–dimer interactions, dynamic effects or the conditions under which the clean Si(100) surface is prepared. There are, of course, no dimer interactions in Si₉H₁₂. Paulus¹³ has shown that a multireference wave function predicts the two-dimer species Si₁₅H₁₆ to be symmetric. Our preliminary MCSCF(4,4) calculations agree with this conclusion. On the other hand, as noted in Ref. 2, the buckling frequency of 190 cm⁻¹ is small enough to suggest that any asymmetric attack on the surface, by a substrate or a probe, will be likely to cause buckling. It is possible that high temperatures will have a similar effect. So, the *chemistry* that occurs on the surface may be somewhat independent of the exact structure of Si₉H₁₂, especially since it is calculated at 0 K. Nonetheless, the origin of the surface

buckling is certainly of interest. We have therefore initiated a series of calculations, using the parallel MCSCF (Refs. 14, 15) method, in which the structure of clusters of increasing size and with increasing numbers of dimers will be determined. This will be augmented by MRMP energetics, in order to understand the nature of the PES.

At this point, we conclude that, given the agreement among TCSCF, MP2, and MRMP methods, the structure of Si₉H₁₂ is symmetric, that dynamic correlation does *not* play a major role in determining the structure, and that DFT incorrectly predicts Si₉H₁₂ to be buckled.

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