Electronic Properties of Disilane: An ab initio Calculation

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We calculate from first principles the electronic ground and excited state, geometrical and vibrational properties of the staggered and eclipsed disilane (Si_2H_6) conformations. We find that, due to the rotation of a silyl group around the Si–Si axis, significant changes of the physical properties are induced. Therefore, depending on the conformation, the reactivity of disilane may be strongly altered.

Introduction Simple molecules do rotate around one or more internal bonds, going through stable and unstable conformations as a 360° rotation is performed. Ethane is the best known and most widely studied example [1, 2]. In fact, the central C–C bond is a threefold symmetry axis, and thus as one of the two methyl groups rotates around this axis the molecule goes through (stable) staggered and (unstable) eclipsed conformations (see Fig. 1). The preferred staggered structure is attributed to steric effects [1–4], more precisely to increased repulsion since the bond electrons are located closer together [2].

Recently, in addition to ethane, disilane (Si_2H_6) has also attracted attention [5, 6] due to its importance in the production of silicon based semiconductor devices. In particular, the fundamental processes in the disilane decomposition on silicon surfaces is relevant to the understanding and optimization of the growth of epitaxial Si on Si substrates. The morphological parameters of the eclipsed and staggered silane conformations were recently calculated by Pophristic et al. [5]. They concluded that the origin of the eclipsed to staggered relaxation can be attributed to preferential hyperconjugative stabilization (i.e. energy stabilization through electron excitation to a delocalized state). This charge delocalization changes the electronic properties of the molecule, as a function of the conformation it adopts.

The main purpose of this paper is to provide a detailed report on the geometric and electronic structure differences between the staggered and eclipsed disilane conformations. The possible differences become relevant when the disilane molecule interacts with an environment, in particular with the Si[100] surface we mentioned above. A full calculation of this interaction process is in progress [7].

This paper is organized as follows. After this introduction we discuss technical aspects of our calculation. Next, we present the optimized geometries and vibrational frequencies of the two disilane conformations, and provide details of the ground and excited state electronic properties. Finally, we close the paper drawing conclusions.

Technical Details Our computational approach is an implementation of the density functional theory (DFT) in a plane wave basis set as performed by CPMD [8]. This

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implementation makes use of the norm conserving pseudopotential approach [9] in the framework of the Becke-Lee-Yang-Parr (BLYP) gradient correction approximation for the exchange-correlation functional [10, 11]. Wave functions are expanded in plane waves, with an energy cutoff of 40 Ry. We have tested the convergence of the total energies as function of the cutoff and box size (we used a 10.58 Å cubic box) to confirm that our conclusion are accurate to within 0.1 eV per molecule.

In our analysis we also used the concept of maximally localized Wannier functions, as introduced by Marzari and Vanderbilt [12]. The Wannier functions are obtained as the unitary transformation, in the subspace of the occupied Kohn-Sham orbitals, which minimizes the spread [13].

It is well known that DFT is not sufficient to provide accurate excited states. However, a generalization of the theory furnishes us with a tool capable of reliably describing many of the excited state properties. In the CPMD code an implementation of the Tamm-Dancoff approximation to time-dependent density functional theory (TDDFT) has been performed. This approximation has been shown to yield reliable results for small molecules and clusters [14].

Geometrical and Vibrational Properties As discussed in the previous section, we have optimized the geometries using a standard minimization method of the ionic forces, as obtained from the electronic structure calculation. A summary of our results, as well as a comparison with similar ab initio methods and experimental observations, is given in Table 1. We obtain a global overestimate of the Si-Si distance which does not exceed 1%. Our results agree favorably with similar methods reported in the accurate work by Cho et al. [6]. From the optimized geometries we conclude that the magnitude of the rotational energy red-shift is 0.043 eV (1.0 kcal/mol), which is comparable to the experimental result of 1.26 kcal/mol [15] and to the theoretical calculations of Pophristic et al. [5] and of Cho et al. [6]. This energy corresponds to a temperature of around 500 K, which is much higher than the typical experimental temperatures (as in CVD [16]), and implies that at low temperatures a mixture of both conformations will be found. The relative fractions depend on temperature and on the annealing. The results reported in Table 2 focus on the differences between the two possible disilane conformations. For the staggered conformation the vibrational frequencies agree successfully with experimental values [15] and the results computed by Cho et al. [6]. The major difference is noticed for the A_{1g} rotation symmetry, whose blue-shift is an indication

Computed and experimental results for disilane				
conformation	geometry	CPMD	other authors	experiment
staggered	d (Si–Si) d (Si–H) ∠ (Si–Si–H) ∠ (H–Si–H)	2.352 Å 1.489 Å 110.4° 108.5°	2.364 Å [5], 2.350 Å [6] 1.478 Å [5], 1.489 Å [6] 110.62° [6] 108.5° [6], 108.3° [6]	2.331 Å [17] 1.492 Å [17] 110.3° [18] 108.6° [18]
eclipsed	d (Si–Si) d (Si–H) ∠ (Si–Si–H) ∠ (H–Si–H)	2.364 Å 1.488 Å 110.6° 108.3°	2.376 Å [5], 2.361 Å [6] 1.478 Å [5], 1.489 Å [6] 110.8° [6] 108.5° [5], 108.08 [6]	

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Computed and	experimental	results for	disilane

Table 1

symmetry	staggered (CPMD)	staggered (experiment [15])	eclipsed (CPMD)
$\begin{array}{c} \\ A_{1g} \\ E_{g} \end{array}$	430	432 [15]	461
	628	628 [15]	615

Table 2	
Computed and experimental values of the vibrational frequencies ($(in cm^{-1})$

that the molecule in the eclipsed conformation requires more oscillation energy. Instead, for the Si–Si stretching mode we obtain a frequency red-shift of only $10-20 \text{ cm}^{-1}$ relative to the staggered conformation, indicating an increase of Si–Si bond length (less rigid bond).

Thus, our calculations are in good agreement with experiment for all the geometrical properties we computed. This agreement puts our calculations on a strong footing for the analysis of the the electronic structure.

Ground State Electronic Properties Geometrical changes of the atomic arrangements and of the distances between atoms induce modifications of the electronic charge distribution, which leads to hyperconjugation. Thus, after elucidating the molecular geometry, we present our results for the ground state electronic properties in Table 3. In this context Mulliken population analysis is a useful tool, since it allows to describe relevant electronic changes. We notice that the valence charge in the eclipsed and staggered conformations is almost the same, but accompanied by a significant change on the electronic distribution. This becomes even clearer when we compare the spread of the maximally localized Wannier functions, given in Table 4, which indicates an increased spread, and thus an augmented bond length of the Wannier function localized along the Si–Si axis. But, no difference between the Wannier functions for the two disilane ground state conformations is observed.

Mulliken popula	tion ana	lysis of the	disilane	molecule
		Mullik	en	valence charge
staggered	Si	0.502		3.665
	Н	-0.143		0.955
eclipsed	Si	0.496		3.666
_	Η	-0.141		0.956
conformation	shune w		spread	d function [Å]
			-1	[]
staggered	S	Si-Si	1.124	
	S	Si–H	0.970	
eclipsed	S	Si-Si	1.128	
	S	Si–H	0.970	

Table 3



Fig. 1. HOMO (top) and LUMO (bottom) electronic densities of the disilane eclipsed and staggered conformations

Excited States In contrast with the ground state, geometric changes generate drastic variations of the excited state electronic properties. As mentioned above, the main reason for the minimal energy of the staggered conformation is hyperconjugation [3]. In Fig. 1 we notice that, after excitation, electrons prefer the sylil structure of the staggered conformation, instead of the eclipsed geometry. In fact, we computed the energies of the singlet state, using TDDFT, to obtain 6.654 and 6.396 eV for the eclipsed and staggered comformations, respectively. This is consistent with Fig. 1, where we notice that the electron density in the LUMO is localized between two Si atoms in the eclipsed conformation, while it is shared by three H and one Si atom in the staggered case. All of this shows that internal rotation induces changes of the excited spectra, which may noticeable modify the reactivity of the molecule.

Conclusions We calculated geometric and electronic structure differences between staggered and eclipsed conformations. We conclude that the electronic properties of disilane depend strongly on geometry and consequently, that the reactivity is also affected. This is relevant to model more complex physical systems, as it is the case of disilane deposition on Si[100], since usually disilane has been modeled [19] using the "wrong" eclipsed conformation.

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