Quantum Mechanics Calculations of the Thermodynamically Controlled Coverage and Structure of Alkyl Monolayers on Si(111) Surfaces

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Supporting Information

1. Pseudopotentials and basis sets

The pseudopotentials used in these calculations are standard norm-conserving, non-separable pseudopotentials[1] generated using Hamann's methods. [2,3] The carbon and silicon pseudopotentials included up to $l=1$ and $l=2$ projectors, respectively (with standard settings), with the $l=1$ and $l=2$ potentials, respectively, used as the local potential in each case. The hydrogen atom was also treated as a pseudopotential (rather than with a bare-core potential), with only an $l=0$ potential. Multiple tests with

hydrogen atoms, H_2 molecules and water molecules verified that the energetics of the bare core hydrogen potential and the hydrogen pseudopotential were almost indistinguishable.

The basis functions were double-zeta plus polarization quality, formed from contracted Gaussians. Hence the *occupied* orbitals Si-*s* and Si-*p*, and the H-*s*, for example, had two radial degrees of freedom, and the Si-*d* and H-*p* *unoccupied* angular polarization orbitals had only one. The basis sets for hydrogen, carbon, and silicon were contracted (4s1p/2s1p), (5s4p1d/2s2p1d), and (4s3p1d/2s2p1d). This nomenclature denotes, for H for example, that four Gaussian *s*-functions were contracted into two independent functions, and one Gaussian *p*-function was used as one independent radial degree of freedom. The *d*-functions (for carbon, and silicon) were made up of the five pure $l=2$ functions, i.e., the *s*-combination as excluded. Tables S-1, S-2, and S-3 list the Gaussians and contraction coefficients for hydrogen, carbon, and silicon.

Table S-1: *Basis set for hydrogen. The Gaussian decay constants* α *($1/bohr^2$), and associated contraction coefficients* c_α *for the contracted Gaussian basis functions (unnormalized).*

s-functions			p-function	
α_s	c_α (1st zeta)	c_α (2nd zeta)	α_p	c_α
0.102474	0.087388	0.075281	1.100000	1.000000
0.372304	0.405344	0.120939		
1.230858	0.485455	0		
4.783324	0.397563	0		

Table S-2: *Basis set for carbon. The Gaussian decay constants α ($1/bohr^2$), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).*

	s-functions			p-functions			d-function	
α_s	C_α (1st zeta)	c_α (2nd zeta)	α_p	c_α (1st zeta)	c_α (2nd zeta)	α_d	c_α
0.155830	0.219500	1.000000	0.154701	0.107631	1.000000	0.770000	1.000000
0.458320	0.695623	0	0.523908	0.524630	0		
1.40253	0.362537	0	1.442267	1.002503	0		
2.805200	-1.296428	0	4.604695	1.675411	0		
5.610400	0.450261	0					

Table S-3: *Basis set for silicon. The Gaussian decay constants α ($1/bohr^2$), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).*

	s-functions			p-functions			d-function	
α_s	c_α (1st zeta)	c_α (2nd zeta)	α_p	c_α (1st zeta)	c_α (2nd zeta)	α_d	c_α
0.104600	0.209953	1.0	0.094241	0.067616	1.0	0.450000	1.000000
0.272263	0.559782	0	0.317679	0.318212	0		
1.300508	-0.991282	0	1.561145	-0.066383	0		
2.601030	0.334871	0					

2. K-points and wave function grid settings

The number of k-points for each calculation was varied according to the unit cell size. 8 k-points were used in the direction of each of the two unit cell vectors for 1x1 unit cells (there are only two unit vectors because the models used are only 2D periodic). The number of k-points for other structures was set to the closest integer, *inversely* proportional to the cell dimension along each unit vector. Thus, the 2x2 and 3x3 unit cells had 4 and 3 k-points in each direction, respectively. The relationship between the number of k-points and the unit cell dimensions was determined through calculations on the silicon crystal (containing 8 atoms) with increasing number of k-points in each direction until the crystal energy variation for adjacent numbers of k-points was below 0.001 eV.

The wave function grids in real space were set to 0.5 Bohr in each of the unit vector directions. This value was also determined through tests on the silicon crystal and ensures that the crystal energy has converged to within 0.005 eV of the asymptotic value. Thus, the 1x1 unit cell, whose unit vectors are 7.230 Bohr long, has 15 grid points in each direction parallel to the surface. The number of grid points was adjusted *directly* proportional to the unit cell dimensions for larger unit cells.

3. Spin polarization

Calculations of singlet states were performed with restricted (closed shell) DFT. Calculations of doublet (radical) states or dissociated triplet states, necessary for the computation of bond energies and dissociated surface states, were performed with unrestricted (spin-polarized) DFT, in which the N_α spin-up and N_β spin-down orbitals are optimized independently.

4. References

1. A. Redondo, W.A. Goddard III and T.C. McGill, Phys. Rev. B 15, 5038 (1977)

2. D.R. Hamann, Phys. Rev. 40, 2980 (1989)

3. D.R. Hamann, pseudopotential generation program PUNSLDX, unpublished.