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Vibrational properties of alkyl monolayers on Si(111) surfaces: Predictions from *ab-initio* calculations

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Vibrational properties of Si(111) surfaces terminated by different functional groups have been investigated using density functional theory (DFT). The variations in methyl-related frequencies in different chemical environments, e.g., in methane, methylsilane and ethylsilane, and the methyl- and ethyl-terminated Si(111) surfaces are well predicted by DFT within the local density approximation. In particular, DFT calculations provide useful information on trends and mode assignments in cases where the surface coverage and morphology are not well established experimentally, e.g., in the case of the ethyl-terminated Si(111) surface. Influences of DFT exchange-correlation functionals and anharmonic effects on computed vibrational frequencies are discussed. © *2012 American Institute of Physics*. [doi:10.1063/1.3685489]

Akylated Si(111) surfaces exhibit a better air stability than those of the H-terminated Si(111) surface and desirable electrical properties for potential applications as photoelectrodes for solar energy-conversion.[1,2] The surface morphology, relative coverage, and electronic properties of chemically stable species on Si(111) surfaces, e.g., hydrogen, methyl and ethyl, and their derivatives, have been extensively explored by scanning tunneling microscopy,[3–5] high-resolution synchrotron photo-emission,[6,7] low-energy electron diffraction,[6] and electrical junction barrier measurements.[8] Although the geometrical arrangements of well-ordered functionalized Si(111) surfaces, such as H- and CH$_3$-Si(111), are now well established, open questions remain on the chemical properties, orientation, and coverage of the adsorbates on semi-disordered or more complex surfaces.

In this paper, we present density functional theory (DFT) calculations of the vibrational frequencies of a series of functionalized Si(111) surfaces and compare them with transmission infrared spectroscopy (TIRS) data.[9,10] We evaluate the accuracy and robustness of DFT-based calculations in describing trends in vibrational properties of alkyl-terminated Si surfaces as a function of chemical environment and coverage. In particular, we analyzed the errors arising from the harmonic approximation often used in periodic DFT calculations and from the influence of the chosen exchange-correlation functional.

DFT calculations within the local density approximation (LDA) were carried out with the plane-wave package QUANTUM ESPRESSO (Ref. 11) with norm-conserving pseudopotentials, and a plane wave basis sets with a kinetic energy cutoff of 100 Ry. Functionalized Si(111) surfaces were modeled by six-layer slabs with the experimental bulk equilibrium lattice constant (5.43 Å), with the bottom layer terminated by hydrogen atoms. All atoms except the bottom hydrogen layer were relaxed during geometry optimization until the maximum force was smaller than 0.03 eV/Å. A (1 × 1) unit cell and a 8 × 8 k-grid were used for full coverage; partial cover-

ages at 25%, 50%, and 75% were modeled by using a (2 × 2) supercell and a 4 × 4 k-grid, with the remaining atop Si sites terminated with hydrogen atoms.

Table I lists the computed bond lengths and harmonic vibrational frequencies of H-, Cl-, and CH$_3$-Si(111) surfaces at full coverage. The results were found to be almost identical with those obtained with 12-layer slabs and are consistent with our previous results[12] on the rapid convergence of structural and energetic properties as a function of slab thickness. The agreement with experiment is in general satisfactory, with errors within ±50 cm^{-1}, except a difference of 67 cm^{-1} for the asymmetric CH$_3$ stretching frequency. However, the deviation of LDA results from experiment is not a systematic shift, therefore, the application of a global scaling factor is in general not recommended throughout the whole frequency range. The lack of a universal trend in LDA frequencies can be traced back to an incomplete error cancellation arising from the choice of a local exchange-correlation functional and the use of the harmonic approximation, as we discuss in detail below.

Influence of exchange-correlation functionals. Table II lists harmonic vibrational frequencies of gas phase methane computed with LDA, Perdew-Burke-Ernzerhof (PBE) and B3LYP (Beck's three-parameter hybrid functional with the Lee-Yang-Parr correlation functional) approximations, and

TABLE I. Bond lengths (Å) and harmonic vibrational frequencies (cm^{-1}) of H-, Cl-, and CH$_3$-Si(111) computed using plane-wave basis sets with E_{cut} = 100 Ry.

−R	Mode Assignment	ν (cm^1)		r_{Si-R} (Å)
		LDA	Exp. [9]	
-H	δ(Si-H)	589	627	1.50
	ν(Si-H)	2072	2083	—
-Cl	δ(Si-Cl)	506	528	2.06
	ν(Si-Cl)	564	583	—
-CH$_3$	ρ(C-H)	732	757	1.90
	δ_s(C-H)	1208	1257	—
	ν_s(C-H)	2929	2909	—
	ν_a(C-H)	3032	2965	—

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TABLE II. Bond lengths (Å) and harmonic vibrational frequencies (cm^{-1}) of methane computed within DFT with the cc-pVTZ basis set. Experimental harmonic frequencies are given for comparison.

	LDA	PBE	B3LYP	Exp. (Ref. [16])
r_{CH}	1.095	1.096	1.088	1.086
δ_s (C-H)	1255	1287	1342	1367
δ_a (C-H)	1486	1512	1560	1584
ν_s (CH$_3$)	2974	2972	3029	3026
ν_a (CH$_3$)	3105	3086	3132	3157

the correlation-consistent polarized valence triple-zeta (cc-PVTZ) basis set, using the GAUSSIAN09 package.[13] The predicted frequencies differ by only a few cm^{-1} from those computed using the quadruple-zeta (cc-PVQZ) basis set or plane wave basis sets with a kinetic energy cutoff of 100 Ry, therefore, they are considered to be well converged. Clearly, hybrid functionals such as B3LYP greatly improve over local and semi-local functionals for the vibrational frequencies. The C-H bond length predicted by B3LYP is also in better agreement with experiment.

Influence of anharmonic effects. Experimental data on vibrational frequencies contains both harmonic and anharmonic contributions. The latter are highly nontrivial to evaluate for complex systems like the functionalized Si(111) surfaces considered here, and are often ignored in practice. Below, we evaluate the anharmonic effect in methylsilane, which has a similar C-Si bonding structure as CH$_3$-Si(111), thus providing an estimate of the influence of anharmonic effects for the methyl-terminated surface. Table III shows that B3LYP frequencies are significantly larger than LDA ones as in the case of methane. In addition, the inclusion of anharmonic effects substantially decreases the symmetric and asymmetric CH$_3$ stretching modes. A change of less than 0.01 Å in bond lengths is observed between the equilibrium structure and the vibrationally averaged structure. As expected, best agreement with experiment is found for the B3LYP anharmonic frequencies. However, the LDA harmonic frequencies are within ±4% of the experimental values. This small deviation comes from an error cancellation between two approximations: the neglect of anharmonic effects and the choice of the local functional. An important question is whether similar error cancellations may be

expected when the physical or chemical environment of the adsorbed functional groups changes, so that the trend of the frequency variations may still be reliably reproduced. This is discussed in detail below.

Influence of chemical environment and coverage. Fig. 1 shows the comparison of LDA harmonic frequencies for CH$_3$ deformation and stretching vibrations in methane, methylsilane, CH$_3$-Si(111), ethylsilane, and C$_2$H$_5$-Si(111), in comparison with measured anharmonic frequencies. Note that for C$_2$H$_5$-Si(111), the measured peak at 2930 cm^{-1},[10] which was assigned to the symmetric CH$_3$ stretching, is here assigned to the antisymmetric CH$_3$ stretching according to our eigenmode analysis. Fig. 1 shows that we can reproduce the correct variation of methyl-related frequencies in different chemical environments, with errors in the absolute values between -60 and $80\,cm^{-1}$. In particular, the splitting of both the antisymmetric CH$_3$ deformation and antisymmetric stretching frequencies in ethylsilane and C$_2$H$_5$-Si(111) surfaces, due to Fermi resonance interactions, is very well captured. Therefore, for more complex surface conditions, e.g., mixed functionalization or partial coverage, harmonic frequencies predicted by DFT within local or semilocal approximations are expected to provide qualitatively accurate information; in particular, we expect the trend of frequency variation as a function of the adsorbate environment to be correctly predicted. In Fig. 1, we also plot the LDA prediction for the CH$_3$-Si(111) surface at 25% coverage. As the coverage decreases to low coverages, the methyl groups gradually rotate to the expected staggered configuration with respect to the Si(111) substrate, due to the release of surface strain among neighboring methyl groups. As a consequence, the symmetric and antisymmetric CH$_3$ stretching frequencies both increase, with $\nu_s = 2929$, 2935, 2943, and 2949 cm^{-1} and $\nu_a = 3029$, 3034, 3041, and 3043 cm^{-1} at 100%, 75%, 50%, and 25% coverages, respectively. In contrast, the frequencies for CH$_3$ deformation ($\delta_{s,a}$) show a weak variation with the coverage, as such modes are less influenced by neighboring adsorbates.

TABLE III. Bond lengths (Å) and vibrational frequencies (cm^{-1}) of methylsilane from DFT/cc-pVTZ calculations, compared with experimental anharmonic (anh.) frequencies.

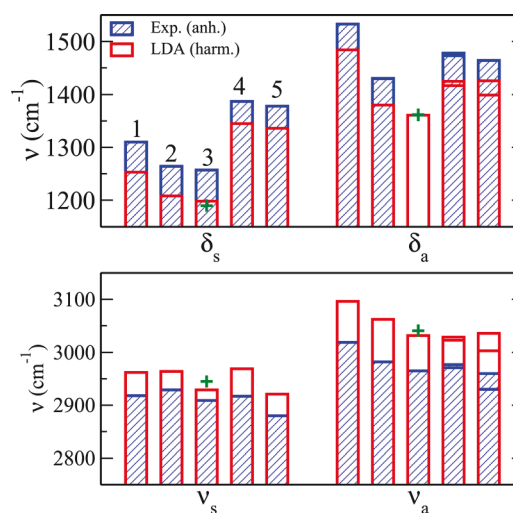|	LDA		B3LYP		Exp. (Ref. [17])
	harmonic	anh.	harmonic	anh.	
r_{CH}	1.098	1.097	1.090	1.090	1.093
r_{SiH}	1.497	1.502	1.486	1.492	1.485
r_{CSi}	1.863	1.870	1.885	1.893	1.867
δ_s (C-H)	1215	1180	1295	1262	1264
δ_a (C-H)	1384	1361	1466	1451	1403
ν_s (C-H)	2984	2862	3035	2961	2929
ν_a (C-H)	3076	2931	3108	2963	2982
ν (Si-C)	706	696	688	678	701

FIG. 1. (Color online) LDA harmonic frequencies (empty bars) for CH$_3$ deformation ($\delta_{s,a}$) and stretching vibrations ($\nu_{s,a}$) in comparison with measured anharmonic frequencies (shaded bars) for methane (1),[16] methylsilane (2),[17] CH$_3$-Si(111) (3),[9] ethylsilane (4),[15] and C$_2$H$_5$-Si(111) (5).[10] Crosses correspond to LDA frequencies for CH$_3$-Si(111) at 25% coverage.

TABLE IV. Vibrational frequencies and mode assignment of the C_2H_5-Si(111) surface.

$\nu_{exp.}$ (cm^{-1})	assignment	$\nu_{theo.}$ (cm^{-1})	assignment
2960	$\nu_{a,CH3}$	3036	—
2930	$\nu_{s,CH3}$	3003	$\nu'_{a,CH3}$
2905	$\nu_{a,CH2}$	2984	—
2880	$\nu_{s,CH3}$	2921	—
2850	$\nu_{a,CH2}$	2939	$\nu_{s,CH2}$
2080	ν_{Si-H}	2068	—
1464	$\delta_{a,CH3}$	1426, 1399	$\delta_{a,CH3}, \delta'_{a,CH3}$
1378	$\delta_{s,CH3}$	1334	—

Finally, we analyze the vibrational frequencies of the C_2H_5-Si(111) surface and compare them with TIRS experiments.[10] In contrast to the methyl termination, the strain energy of C_2H_5-Si(111) was found to increase significantly when the surface coverage is equal to or larger than 75%.[14] Such a high coverage is possible due to the highly favorable thermodynamics for the reaction of R-MgCl with Cl-Si during the alkylation process.[5] Indeed, based on scanning tunneling microscopy (STM) measurements,[5] a surface coverage of 80% was estimated for the C_2H_5-Si(111) surface produced from the two-step chlorination/alkylation procedure.

Table IV lists the vibrational frequencies and mode assignment of C_2H_5-Si(111) computed at full coverage. Overall, in comparison with $\nu_{exp.}, \nu_{theo.}$ for both CH_3 and CH_2 stretching modes are blue-shifted by roughly 70-90 cm^{-1}, while those of the deformation modes are red-shifted by 40 cm^{-1}. A similar trend, but with different magnitude, is found for CH_3-Si(111). We note that some of the theoretical mode assignments disagree with those in Ref. 10. For example, our vibrational eigenmode analysis reveals only one symmetric CH_3 stretching mode but two antisymmetric CH_3 stretching modes; this is consistent with the modes measured for ethylsilane[15] but not with the peak assignment in Ref. 10. Therefore, we suggest that the measured peak at 2930 cm^{-1} should be labeled as $\nu'_{a,CH3}$ instead of $\nu_{s,CH3}$. Similarly, we have found only one antisymmetric CH_2 stretching mode instead of the two reported in Ref. 10, so that the measured peak at 2850 cm^{-1} should be labeled as $\nu_{s,CH2}$ instead of $\nu_{a,CH2}$. Finally, our eigenmode analysis suggests that in addition to the measured peak at 1464 cm^{-1} for $\nu_{a,CH3}$, there should be another one ($\nu'_{a,CH3}$) at a frequency about 30 cm^{-1} smaller. We emphasize that the reassignment of vibrational modes in Table IV is still fully consistent with the observed mode polarization in Ref. 10.

In summary, we have presented DFT/LDA results for vibrational frequencies and mode assignment of the CH_3- and C_2H_5-Si(111) surfaces and estimated the errors arising from the choice of the local exchange-correlation approximation and the neglect of anharmonic effects. Overall, LDA harmonic frequencies are in reasonable agreement with experiments and the trend of frequency variation upon changes in chemical environment and surface coverage is correctly predicted. In particular, the one to one correspondence between calculated and measured frequencies can be established based on vibrational eigenmode analysis and measured mode polarization, thus providing a promising, useful tool for assigning peak positions in IR spectra of semi-ordered and complex surfaces.

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