# Calculation of Phonon-Phonon Interactions and Two-Phonon Bound States on the Si(111):H Surface

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The Si(111):H surface is studied within the framework of density-functional theory using the local-density approximation. In particular, the Si-H stretch mode is investigated in detail. The phonon-phonon interaction strength is found to be $2\Gamma = -76.6$ cm$^{-1}$ and the phonon bandwidth to be 7.2 cm$^{-1}$. Two-phonon bound states are found to exist with a binding energy of 86.4 cm$^{-1}$, in excellent agreement with the recent experimental result of 90 cm$^{-1}$.

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The Si(111):H surface, in which all of the silicon dangling bonds are saturated by a single monolayer of hydrogen atoms, is undoubtedly one of the most ideal semiconductor surfaces obtainable. It has been extensively studied both experimentally [1,2] and theoretically [3-9] in the past. Since the flat, stable Si(111):H surface was synthesized recently using wet chemical methods [10,11], interest in this surface has been renewed [12-14]. Recently, Guyot-Sionnest [14] reported that for the hydrogen vibration, the experimentally measured frequency shift between the $v_{0\text{-}1}$ and the $v_{1\text{-}2}$ transitions is 90 cm$^{-1}$, indicating very strong phonon-phonon interactions and the existence of two-phonon bound states.

Two-phonon bound states were first discussed by Cohen and Ruvalds [15] and later explored by many authors [16,17]. The Si(111):H surface is probably the best system in which to look for two-phonon bound states for several reasons. The system is so simple that other complications will not enter the problem; it is a two-dimensional system, so that two-phonon bound states are more likely to exist; and the vibrational amplitude of the hydrogen atom is large and therefore the anharmonicity is strong. Of course, Guyot-Sionnest's experimental work is also a strong motivation. We studied the Si(111):H surface using density-functional theory within the local-density approximation (LDA), focusing on frozen-phonon calculations of the hydrogen vibrations. It is found that two-phonon bound states do exist. The energy of a two-phonon bound state is lower than the energy of two free phonons by 86.4 cm$^{-1}$, in excellent agreement with the experimental result of Guyot-Sionnest.

The surface is modeled by a slab consisting of eight layers of silicon atoms and four layers of vacuum. The dangling bonds on each surface of the slab are saturated by a layer of hydrogen atoms. Norm-conserving pseudopotentials [18] are employed to eliminate the core electrons of silicon and to soften the potential of hydrogen. The exchange-correlation energy used is the Ceperley-Alder form [19] parametrized by Perdew and Zunger [20]. The wave functions are expanded in a plane-wave basis with a kinetic-energy cutoff of 20 Ry. Six Monkhorst-Pack [21] special $k$ points in the irreducible surface Brillouin zone are used to carry out the integration in $k$ space. The size of the slab, the plane-wave energy cutoff, and the number of $k$ points are all very well converged. An iterative algorithm [22] is used to obtain eigenvectors.

The positions of all the atoms are allowed to relax. The relaxation is very small as expected because of the lack of dangling bonds. The Si-H bond length is found to be 1.524 Å, slightly longer than the ideal bond length, 1.480 Å, in a $SiH_4$ molecule. The first-to-second layer spacing of Si atoms contracts by 0.025 Å, while all the Si atoms deeper inside the bulk hardly relax at all. These results are in reasonably good agreement with those of Kaxiras and Joannopoulos [7].

Following the method of Meade and Vanderbilt [23], we found the surface stress of the Si(111):H surface to be 0.21 eV/(1×1 cell). As expected, this stress is very small compared to the stresses calculated for other Si surfaces, e.g., 2.6 eV/(1×1 cell) for Si(111)7×7 or −1.1 eV/(1×1 cell) for Si(111):Ge [23]. This result suggests that Si(111):H may be a useful fiducial surface for experimental surface stress measurements [24,25], which are only sensitive to stress *differences* on opposite sides of a wafer. Moreover, it suggests that surface stress is unlikely to have a major influence on the frequency of Si-H vibrations in the vicinity of surface steps [26].

Since silicon is much heavier than hydrogen, the hydrogen stretching and wagging modes are almost completely localized on the hydrogen atom. In fact, our test calculations show that the vibrational amplitude of the first-layer silicon atom is only about 2% of that of the hydrogen atom for both the Si-H stretching and wagging vibrations. Therefore, all the silicon atoms are kept fixed in the frozen-phonon calculations reported below. This simplification introduces a well-defined error of about −1% to the phonon frequencies. This error also exists in other first-principles calculations [7,9].

In the harmonic approximation, the frequencies of the Si-H stretching and wagging vibrations are found to be $\omega_{\text{stretch}} = 250.8$ meV (2023.2 cm$^{-1}$) and $\omega_{\text{wag}} = 69.4$ meV (559.3 cm$^{-1}$), in satisfactory agreement with the LDA calculations of Ref. [7] ($\omega_{\text{stretch}} = 245$ and $\omega_{\text{wag}} = 71$

meV) and Ref. [9] ($\omega_{\text{stretch}}=246$ and $\omega_{\text{wag}}=79$ meV). The differences are probably because of the differences in the energy cutoff and the $k$-point sampling. The bandwidth of the Si-H stretching mode is also calculated. It is very small, only 7.2 cm$^{-1}$, or 0.9 meV, in reasonable agreement with the experimental estimation [14] of 11 cm$^{-1}$.

In order to study the anharmonic effects of the hydrogen vibration, we have done a large number of frozen-phonon calculations to map out the energy surface for the hydrogen atom. The polynomial expansion of the potential felt by a hydrogen atom is truncated after the fourth-order term, and has the form

$$V(x,y,z)=V_0+\tfrac{1}{2}m\omega_z^2z^2+\tfrac{1}{2}m\omega_x^2(x^2+y^2)+a_3z^3+b_3(x^2+y^2)z+a_4z^4+b_4(x^2+y^2)z^2+c_4(x^2+y^2)^2. \tag{1}$$

Azimuthal symmetry is assumed, which is expected to be a good approximation for small vibrations, and indeed our calculations show that the error due to this approximation is less than 1%. A typical example of our frozen-phonon calculations is shown in Fig. 1, where the hydrogen atoms are displaced in the $z$ direction ($x=y=0$), and the three coefficients $\omega_z$, $a_3$, and $a_4$ are determined. Both the energies and the forces are used in the least-squares fit, and the largest displacement is about 0.15 Å. All the coefficients in Eq. (1) as determined by our frozen-phonon calculations are listed in Table I.

The truncation of the polynomial causes a problem, in that the potential in Eq. (1) is not bounded from below. In fact, when $z^2$ tends to infinity while keeping $0.071<z^2/(x^2+y^2)<1.126$, the potential tends to minus infinity. Higher-order terms in the polynomial, which would correct this problem, are difficult to obtain with reasonable accuracy. Fortunately, we can get useful information out of the potential in spite of this problem. We diagonalize the one-particle Schrödinger equation with the potential in Eq. (1) by expanding the wave functions in a basis of a three-dimensional anisotropic harmonic oscillator with frequencies $\omega_x$ and $\omega_z$. We first restrict the basis set such that no excitations in the $x$ and $y$ directions are included, and increase the number of excitations (basis functions) in the $z$ direction until the lowest few eigenstates converge. (In this subspace, the potential is stable.) Then we repeat the above procedure while systematically increasing the number of excitations in the $x$ and $y$ directions included in the basis set. It turns out that the lowest few eigenstates converge quite precisely before the instability sets in.

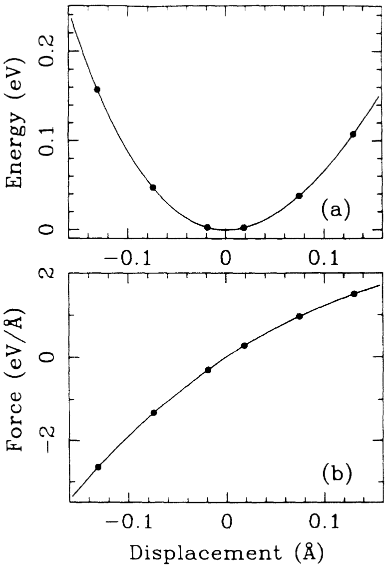

FIG. 1. An example of frozen-phonon calculations corresponding to displacing the hydrogen atoms in the $z$ direction ($x=y=0$). (a) Energy and (b) force vs displacement. The lines are the result of a least-squares fit.

The results for the phonon energies of the hydrogen stretching and wagging modes are listed and compared with experimental results [27,28] in Table II. It is interesting to note that the anharmonicity decreases the frequency of the Si-H stretching mode while increasing that of the wagging mode. The effective phonon-phonon coupling strength $\Gamma$ is defined as $2\Gamma=(E_2-E_1)-(E_1-E_0)$, where $E_0$, $E_1$, and $E_2$ are the lowest three eigenvalues of the Si-H stretching phonon mode. $2\Gamma$ is found to be $-76.6$ cm$^{-1}$. We find that the coupling to the wagging mode is as important as the anharmonicity in the stretching mode; the contribution to $2\Gamma$ from the latter alone ($b_3=b_4=c_4=0$) is only 39.9 cm$^{-1}$.

To study the two-phonon bound state, we use a Hubbard-type model Hamiltonian,

$$H=\epsilon_0\sum_i a_i^\dagger a_i+\Gamma\sum_i a_i^\dagger a_i^\dagger a_i a_i+t\sum_{\langle ij\rangle}a_i^\dagger a_j\,, \tag{2}$$

to describe the coupling of the Si-H stretching excitations at the surface; here $\langle ij\rangle$ denotes nearest neighbors on the triangular lattice. Equation (2) is to be regarded as an effective Hamiltonian; that is, $a_i^\dagger$ is the quasiparticle creation operator which raises the system of Eq. (1) on site $i$ from its ground to first excited state. Thus, $\epsilon_0=E_1-E_0$ and $\Gamma$ are just the quantities introduced

TABLE I. Parameters in the potential felt by a hydrogen atom, as defined in Eq. (1).

| | |
|---|---|
| $\omega_z$ (meV) | 250.84 |
| $\omega_x$ (meV) | 69.35 |
| $a_3$ (eV/Å$^3$) | −11.13 |
| $b_3$ (eV/Å$^3$) | 4.00 |
| $a_4$ (eV/Å$^4$) | 9.94 |
| $b_4$ (eV/Å$^4$) | −11.66 |
| $c_4$ (eV/Å$^4$) | 0.78 |

TABLE II. The frequencies of the Si-H stretching and wagging phonon modes, the bandwidth, the phonon-phonon coupling strength, and the binding energy of the two-phonon bound state of the Si-H stretching mode, compared with experiments. All are at the $\bar{\Gamma}$ point, and in units of $\mathrm{cm}^{-1}$.

| | Present theory | Experiment |
|---|---|---|
| Si-H stretching frequency | 1957.8 | 2083.7 [a] |
| Si-H wagging frequency | 573.9 | 637 [b] |
| Bandwidth $t$ | 7.2 | |
| Phonon-phonon coupling strength $2\Gamma$ | −76.6 | |
| Binding energy of two-phonon bound state | 86.4 | 90 [c] |

[a] Ref. [27].
[b] Ref. [28].
[c] Ref. [14].

above, and implicitly include the renormalization due to coupling with wagging modes and three- and four-phonon interactions considered there. The last term in Eq. (2) represents the nearest-neighbor harmonic hopping; because $t$ is already the smallest energy in Eq. (2), it is reasonable to use the unrenormalized coupling obtained from the harmonic bandwidth calculation. For a triangular lattice (the first Brillouin zone of which is shown in the inset of Fig. 2), $\omega(\bar{\Gamma})-\omega(\bar{M})=8t$. From our frozen-phonon calculations, we find that $\omega(\bar{\Gamma})-\omega(\bar{M})=6.40\ \mathrm{cm}^{-1}$, and therefore $t=0.80\ \mathrm{cm}^{-1}$. The dispersion curves along some high-symmetry lines are plotted in Fig. 2(a), where $\epsilon_0$ has been artificially shifted to $\epsilon_0=-6t$ so that the phonon bands are relative to $\omega(\bar{\Gamma})$.

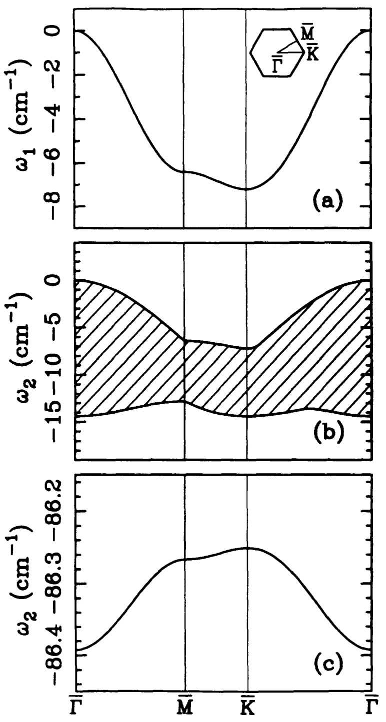

FIG. 2. Phonon dispersion curves along some high-symmetry lines, for the model of Eq. (2). Inset: The surface first Brillouin zone. (a) One-phonon dispersion. (b) Two-phonon continuum corresponding to two free phonons. (c) Dispersion of two-phonon bound state.

We then solve the model Hamiltonian in Eq. (2) with two phonons in the system. Equation (2) is rewritten in $k$ space as

$$H=\sum_{\mathbf{k}}\omega_1(\mathbf{k})a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+\frac{\Gamma}{N}\sum_{\mathbf{K},\mathbf{k},\mathbf{k}'}a_{\mathbf{k}}^{\dagger}a_{\mathbf{K}-\mathbf{k}}^{\dagger}a_{\mathbf{k}'}a_{\mathbf{K}-\mathbf{k}'}\,, \tag{3}$$

where $\omega_1(\mathbf{k})$ is the one-phonon energy at lattice momentum $\mathbf{k}$, as plotted in Fig. 2(a). Notice that $\mathbf{K}$, the total lattice momentum of two phonons, is a good quantum number. Following Cooper [29], we find that for a given $\mathbf{K}$, the exact condition for a solution is

$$\frac{1}{N}\sum_{\mathbf{k}}\frac{1}{\omega_1(\mathbf{k})+\omega_1(\mathbf{K}-\mathbf{k})-\omega_2(\mathbf{K})}=-\frac{1}{2\Gamma}\,, \tag{4}$$

where $\omega_2(\mathbf{K})$ is the total energy of two phonons. The solutions of Eq. (4), which consist of a continuum and a two-phonon bound state band, are found numerically and plotted in Figs. 2(b) and 2(c). Notice that the bandwidth of the continuum is $14.4\ \mathrm{cm}^{-1}$, twice the bandwidth of the one-phonon band, as expected. The bandwidth of the two-phonon bound state, however, is only $0.14\ \mathrm{cm}^{-1}$, i.e., much smaller than that of the one-phonon band. This is expected because two one-phonon states are averaged over in Eq. (4). In Guyot-Sionnest's two-color sum-frequency generation experiment [14], the frequency shift measured is at the $\bar{\Gamma}$ point, since both the pump and the probe beams are in the infrared. From our calculation, the binding energy of the two-phonon bound state at the $\bar{\Gamma}$ point is $86.4\ \mathrm{cm}^{-1}$, in good agreement with Guyot-Sionnest's experimental result [14], $90\ \mathrm{cm}^{-1}$.

Two-phonon bound states are known to exist in molecular solids and liquids [30]. However, to our knowledge, Si(111):H is the first covalently bonded system in which the existence of a two-phonon bound state has been confirmed both experimentally and theoretically. The two-phonon bound state arises in this system from the fact that the Si-H bond is very similar to a tightly bonded molecule in the sense that the Si-H stretch frequency is much higher than all other vibrational frequencies, and the coupling between neighboring oscillators is weak. Our results suggest that two-phonon bound states are likely to exist on other surfaces covered with light atoms or molecules. The Si(111):H surface, although simple, exhibits many interesting properties, including the long lifetime of the Si-H stretching phonon mode [12] and an electron energy-loss peak [31] at $795\ \mathrm{cm}^{-1}$ which is yet to be accounted for. In the future, we will try to understand these properties from first-principles calculations, as well as to study steps on the Si(111):H surface and their effects on the electronic and vibrational properties.

In conclusion, we have studied the Si(111):H surface from first principles. The stress on this surface is found to be very small. The structure and the hydrogen vibrational frequencies agree with other LDA calculations. The emphasis of the study is on the anharmonic effects associated with the Si-H stretching mode. A very strong phonon-phonon coupling is found, and a narrow band of two-phonon bound states is found to exist with a binding energy of 86.4 $\mathrm{cm}^{-1}$, in excellent agreement with the recent experimental result of 90 $\mathrm{cm}^{-1}$.

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