Hydrogen and defects in first-principles molecular-dynamics-modeled *a*-Si:H

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We use *ab initio* pseudopotential local-density-approximation methods to create and study supercells of *a*-Si:H containing from 66 to 71 atoms. These supercells contain 0, 1, and, 2 well-localized defects. These geometrical defects are each associated with a unique localized state in the gap. The 0- and 1-defect supercells are particularly interesting because the defect banding present in all other theoretical supercells is missing. We study the properties of H in passivating dangling bonds, in bond-centered positions, in tetrahedral positions, and, in one case, as part of a floating-bond defect. Among other properties, we investigate band gaps, binding energies, relaxation effects, localization of defects, NMR linewidths and line shapes, and phonon spectra associated with the samples.

I. INTRODUCTION

There have been numerous theoretical studies addressing the topological structure, electronic structure, and defects of clusters or supercells of *a*-Si and *a*-Si:H.[1–9] To the best of our knowledge, all of these previous supercells have large numbers of spectral defects (localized states in the gap) and/or an unrealistically large amount of band tailing, when relaxed with a sufficiently accurate molecular-dynamics (MD) code and analyzed with a sufficiently realistic band-structure code. We remind the reader that in almost all computer-generated supercells, geometrical defects (a Si atom that is not fourfold coordinated) cannot be put into one-to-one correspondence with the spectral defects.[10] However, some of these supercells do not contain geometrical defects and some of them do not appear to contain spectral defects if analyzed with a sufficiently crude tight-binding theory.[10] These supercells routinely contain spatially extended defects of badly strained but still fourfold-coordinated Si atoms which show up as rather localized states in the gap and by excessive band tailing. We have shown that a few percent defects is enough to cause banding among the defects in supercell calculations. Thus these supercells are not representative of good experimentally grown device grade material. In fact many studies are on supercells that contain as many as 10–15 % defects. These supercells bear little relationship to any real *a*-Si. A similar state of affairs exists for amorphous-silicon hydride models.[11] We emphasize that the structures described in this paper have a realistic density of states with a high degree of spectral localization that is consistent with experiment.

In this paper we report on and give the coordinates[12] of a number of supercell samples that contain none of the extended defects alluded to above and where each spectral defect corresponds to a unique geometrical defect. These supercells were constructed with 0, 1, or 2 defects and contain 61 or 62 Si atoms and from 4 to 10 H atoms. Thus these supercells are appropriate for studying isolated defects or device grade *a*-Si:H. We have also introduced bond-centered (BC) H into these supercells and tried to introduce tetrahedral (T) interstitial H into them. Where appropriate, we have also prepared crystalline supercell samples of 64 Si atoms and one H atom for purposes of comparison. Various aspects of these supercells are extensively studied and, where possible, compared to experiments. These supercells are the best available within the constraints of present techniques and can be studied as they stand or combined into large supercells with a controlled number of defects. The primary tool in both the construction and analysis of the supercell samples is the *ab initio* alloy MD computer program of Sankey and Drabold[13–15] using four points in the supercell Brillouin zone. This program is well documented in the literature. These methods yield forces orders of magnitude more accurate than those obtained from pair potential and angular-dependent forces and are also far superior to codes based on tight binding. For many purposes, including tight-binding-induced defects, we have shown that the accuracy of *ab initio* methods is essential for an adequate description.[10]

In the rest of this section we shall discuss how we constructed the supercell samples and briefly characterize them. Section II contains the details of the binding energies associated with the supercells and their relaxation energies. Section III contains a discussion of the NMR linewidth and electric-field gradients. Localization of states and band tailing are explored in Sec. IV along with the phonon spectra.

The starting point for the group of supercell samples discussed in this paper is the 2-defect 63 Si atom supercell that we fabricated earlier and is discussed in the literature.[7,10] This cell has two geometrical defects that are both dangling bonds although one might be called a dangling-bond/floating-bond defect because if one defines a coordination radius greater than 2.78 Å, one of the dangling bonds becomes redefined as a floating bond. In addition, the supercell has two defects consisting only of fourfold-coordinated Si but with some badly strained bonds. This type of defect is seen in all supercells that we

have investigated including the Wooten-Weaire-Winer[16] (WWW) supercells, although they are usually not classified as defects by the authors. These defects are aggravated by relaxing the supercell with a good first-principles code instead of a Keating potential or various pair potential and angular-dependent force schemes.[17] We also note that rather poor supercells can be made to have a decent looking density of electronic states by using a sufficiently poor tight-binding theory. The easiest way to do this is by taking interparticle matrix elements that have a short enough range. We note that although the WWW supercells are generally believed to contain no defects, this is true only in a superficial sense.[9] First of all they exhibit horrendous band tailing which can be attributed to a rather small number of highly strained bonds whose bond angles deviate greatly from 109°. These bonds are too few to be noticed in the average and rms deviation of the bond angles but they can dominate the band tails. The connection of band tails, strains, and localization is discussed in Sec. IV. Further, these samples contain rather extended defects that cause states in the gap when analyzed with a decent band-structure code. However, with an appropriately defined coordination radius, they do not contain any geometrical defects.

The ancestral supercell and defects are well characterized in Ref. 10. It turned out that getting rid of the dangling-bond defects was exceedingly easy. We merely placed a H atom about 1.5 Å from the threefold-coordinated Si atom in the direction of the dangling bond and then let the supercell relax. The supercells relaxed very quickly with a minimum of reorganization of any of the Si atoms. The two badly strained bond defects were much more difficult to eliminate. We tried putting H atoms at various places in and around the defects but this usually nucleated more defects and never eliminated the original ones. Finally, we removed the Si that we considered to be the "center" of the defect and put H atoms by the four dangling bonds. When the supercell was allowed to relax, there was a substantial rearrangement of the atoms but the defect had disappeared. Interestingly enough, if the supercell was annealed before relaxing, the defects did not disappear. However, after quenching, the supercells are extremely stable upon annealing. The H atoms, which were quite close to each other before the supercell was relaxed, were all further than 2.2 Å apart after relaxation. As will be discussed later in Sec. III, the protons (H nuclei) from this procedure have a calculated NMR second moment that is in excellent agreement with the experimental measured linewidth from the so-called "broad NMR line" from the protons in good material. The addition of the H made our samples more stable and seemed to eliminate any memory effects of crystalline material.

Of course we do not believe that our procedure has very much in common with the way that hydrogenated *a*-Si is made in the lab. For that matter, because of the time scale of lab-fabricated supercells, no simulation has much in common with the manner in which samples are fabricated in the lab. Our goal here, as in earlier work, is to create supercell samples whose properties resemble the properties of good device quality material as much as is possible. This means a similar pair correlation function, a reasonable bond-angle distribution, a decent vibrational spectrum, and very few defects. The pair distribution functions for the Si-Si pairs for all of our supercells are similar to the pair distribution function of their ancestor which is given in Fig. 1 of Ref. 10. We have published electronic densities of states and distribution functions for these cells.[18] The same is true of the vibrational spectra. The bond-angle distributions (which are summarized later in this paper) are all about 109° with a variance of 10° and the number of defects is controlled. It turns out that when we removed the strained bond defects labeled $d4$ in Ref. 10, the defect labeled $d3$ also disappeared during the relaxation.

The labeling of the supercells discussed in this paper is as follows. The supercell sih $N.M$ has N atoms of Si and M atoms of H. The supercells sih 61.10, sih 61.9, sih 61.9.y, and sih 61.8 all have both of the strain defects ($d3$ and $d4$ of Ref. 10) removed and in addition both dangling bonds, the dangling bond $d1$, the dangling bond $d2$, and neither dangling bond passivated, respectively. Samples sih 62.6, sih 62.5, sih 62.5.y, and sih 62.4 have only the strained defect $d4$ removed but have the dangling bonds treated exactly the same as described above. In addition, supercell sih 64.0 is a perfect crystal supercell which we added H to for purposes of comparison. Further properties of these cells will be discussed in the next section.

II. PROPERTIES OF SUPERCELL SAMPLES

Some of the properties of the eight supercell samples described above are listed in Table I. Since the local-density approximation (LDA) and the minimal basis set cannot be expected to yield a reliable gap, the gap energies are meaningful only upon comparison to each other. As one can see, the gap generally increases as the hydrogen content rises. This is especially evident when comparing the first four samples in Table I to the second four samples. There are various calculations[19–23] showing that the gap of *a*-Si:H increases as the H content increases, at least for small concentrations of H. This effect is due to the valence band moving lower because of the Si-H bonds which are stronger than the Si-Si bonds. Coherent-potential-approximation (CPA) calculations[21] yield a value of an increase in the gap of 0.02 eV for every percent of H added. However, if we compare samples sih 62.6 and sih 61.10 (or any other comparable pair) we find that the gap increases by roughly twice the amount expected. The difference comes from the hydrogenation of one or more rather badly strained clusters that causes the conduction and valence bands to approach each other. This may well be the analog of band tailing for a finite supercell. We also note that, in general, the existence of dangling-bond localized states also increases the band gap, simply by repulsion of the band edges by the localized state. The bond-angle distributions of all of the samples are quite similar and are not remarkable.

We note that the relaxation energies associated with removing the H's from the dangling bonds are all quite small, of the order of tenths of an electron volt. This is consistent with our observation that the supercell sam-

TABLE I. Some properties of the eight basic supercell samples. The energy (in eV), including relaxation energies, is with respect to the appropriate sample that is fully passivated minus the appropriate number of free hydrogens. Thus the sample sih 62.5 (which has one unpassivated dangling bond) plus one free H atom has an energy of 4.6 eV greater than the fully passivated sample sih 62.6. The gap is the energy gap in eV and BAD is the mean bond angle and rms deviation in degrees for Si bonds. The relaxation energy (in eV) is also with respect to the passivated sample. Thus after removing both the H's passivating the two dangling bonds in sample sih 61.10, the sample loses an additional energy of 0.89 eV before coming to equilibrium as sample sih 61.8. The last column is the number of unpassivated dangling (or dangling/floating) bonds in the supercell sample.

Sample	Energy	Relaxation	Gap	BAD	Dangling bonds
sih 62.4	−7.82	0.57	1.43	109.2±11.5	2
sih 62.5	−4.6	0.26	1.31	109.5±10.2	1
sih 62.5.*y*	−4.7	0.46	1.43	109.3±10.2	1
sih 62.6	0.0	0.0	1.29	109.5±10.2	0
sih 61.8	−7.81	0.89	1.67	109.6±10.1	2
sih 61.9	−4.34	0.56	1.54	109.6±9.9	1
sih 61.9.*y*	−3.67	0.44	1.70	109.5±11.4	1
sih 61.10	0.0	0.0	1.54	109.2±9.9	0

ples undergo very little reorganization upon removal of these H atoms. We also note that the relaxation energy from removing the H's on both dangling bonds is less than the sum of the energies of removing them individually. The actual energies gained by passivating a dangling bond vary from 3.67 to 4.7 eV. These energies do not include spin polarization. Since energies with respect to the vacuum are slightly suspect, it is probably better to focus on the differences between the energies. These energy differences are considerable even for our rather small number of supercell sample. It suggests that assigning an energy to a hydrogenated dangling bond is not as meaningful as some investigators would wish. The energies are all definitely higher than the 2.0–3.0 eV that is associated with the passivating of a surface dangling bond in *c*-Si.[24–27] However, the energy associated with passivating dangling bonds is still controversial and could be significantly higher than 3 eV.[27]

We have also investigated putting of hydrogen in bond-centered positions and in tetrahedral positions. Some of our results are summarized in Table II. For these studies the supercell sample sih 62.6.*n* was formed by putting a H atom exactly between two Si atoms and then relaxing the sample. The letter *n* refers to different choices of BC positions and this will be discussed shortly. For sample sih 64.0.*a* we placed a H atom at a BC position of a 64-atom crystalline sample and then relaxed it, while for sample sih 64.0.*c*, we placed a H at the *T* position in the crystalline sample. The H at the *T* position in the crystal stayed there and relaxed only very slightly. As observed by others, we find that the BC hydrogen lies at a lower energy than the *T* hydrogen in the crystal.[28,29] We were unable to get a hydrogen to stay at a *T* or interstitial position in any of the amorphous samples. When this was tried the samples always rearranged themselves, usually into configurations with complicated defects including floating-bond configurations where a Si has four Si neighbors and one H neighbor. We believe that this failure is due to the fact that *a*-Si has no truly symmetric *T* sites and that the amorphous network can very easily rearrange itself to accommodate the bonding of an extra H. The crystalline network is very constrained by comparison. All of our attempts at forming interstitial H in the amorphous samples were accompanied by large rearrangements. The energy gaps of all of the *a*-Si samples with BC hydrogen were in the range of 1.32–1.34 eV. This was about the same gap as the supercell sih 62.5 which also has one defect but in the form of a dangling bond.

TABLE II. Some properties of supercell samples with BC and *T* hydrogen inserted. The energy (in eV) is with respect to sample sih 62.6 plus a free H atom and the relaxation energy (in eV) is with respect to a H atom put exactly between two atoms with no relaxation. The angle θ is the angle of the relaxed Si-H-Si bond and l_1 and l_2 are the Si-H bond lengths for the BC hydrogen. Sample sih 64.0.*c* refers to the crystalline supercell sample with hydrogen in a *T* site while all the rest of the entries refer to BC hydrogen.

Sample	Energy	Relaxation	θ	l_1	l_2
sih 61.6.1*a*	−1.61	3.03	164.0	1.67	1.58
sih 61.6.1*b*	−2.07	3.09	157.3	1.73	1.63
sih 61.6.1*e*	−1.67	2.83	157.2	1.62	1.57
sih 61.6.1*f*	−1.54	2.88	165.3	1.67	1.58
sih 64.0.1*a*	−1.40	2.48	179.9	1.62	1.62
sih 64.0.1*c*	−0.87	0.06			

From Table II we see that the binding energy of the H in the BC positions is about 3 eV less than the binding energies of the H's at dangling-bond sites but that the relaxation energies are of order 3 eV compared to the several tenths for the dangling-bond case. Given these energies, we think it is very unlikely that H will move between BC and dangling-bond sites in *a*-Si:H. Although we have not yet performed dynamical studies, our results indicate that it is unlikely that H is very mobile from one BC site directly to another. The huge relaxation energy would make this very difficult. That is, presumably the H would move from a relaxed BC position to a nearby unrelaxed BC position. This would require an energy of order the relaxation energy or would require the new site to fluctuate into a rare configuration that approaches the relaxed

configuration but without the H atom in it. In crystalline Si, the T site apparently plays a vital role in the motion of H.[28,30] Although the T site is not even metastable in our samples, this does not preclude a transient role in H motion.

Although BC hydrogen in c-Si lies in a symmetric position on the bond-center line, this is not the case in a-Si. We see from Table II that the Si-H bond lengths are not equal and that the Si-H-Si angle typically diverges from 180° by about 20°. In fact, BC hydrogen in a-Si has been theoretically investigated as a strain relief mechanism in earlier work.[31] Of special note here is that the H is distorted away from the bond-center line between two H's in all cases, and by about the same amount independent of the amount of strain relief. Sample sih 62.6.b, which has the large binding energy for the BC hydrogen, was also characterized by having a rather large bond-angle distortion involving the two Si's that were split by the H. In fact, a crude analysis from our limited data suggests a component of the binding energy that is proportional to the square of bond-angle distortion. Thus our work supports the contention that BC hydrogen can relieve strains, although the similarities in BC hydrogen at various sites seems to outweigh the differences. As discussed by Tarnow and Street,[31] Si vacancies that are hydrogenated are more efficient at relieving strain that BC hydrogen is. As will be discussed in the next section, there is reasonably strong experimental evidence that there is very little if any BC hydrogen in good a-Si:H.

Molecular hydrogen is also known to exist in most a-Si:H films. Much of this molecular hydrogen fills microvoids and has a very high density. However, some of the H_2 is in nanovoids that are well isolated from each other. We have not yet attempted to study these forms of hydrogen.

III. NMR PROPERTIES

In this section we consider some of the NMR implications of our supercells. First of all, consider the relationship of our clustered H to experimental measurements. NMR experiments on the H nuclei (protons) of good-quality a-Si:H show two rather distinct lines centered about the same origin.[32,33] There is a broad more or less Gaussian-shaped line and a narrow somewhat Lorentzian-shaped line. The broad line is unarguably due to rather highly clustered regions of the a-Si and multiple quantum NMR measurements suggest clusters of 5–7 H atoms.[32] This is the line of interest to us as the narrower Lorentzian-like line is due to dilute scattered H. We have analyzed our supercell samples by computing the average second moment, due to proton-proton interactions of the H atoms. If we assume that the NMR lines are Gaussian, then measurements on various samples yield the square root of the second moment of between 9.3 and 14.0 kHz. The square root of the second moment for our supercell samples is from 9.2 to 10.4 kHz with the larger second moment corresponding to the samples with more H. Given the assumptions about line shape, this is virtually perfect agreement. This is substantial evidence that the clustered H regions of good a-Si:H are similar to the clustered regions in our supercells. Thus the regions of high-density H in good a-Si:H films may be similar to our regions with one or more hydrogenated Si vacancies.

NMR on D in a-Si:H(D) yields entirely different information than the NMR on H. Since D has a small magnetic moment, the density of D has very little effect on the line shape. However, the D nucleus does have an electric quadrupole moment (which H does not) and thus is influenced by its electrical environment. Good device quality Si is characterized by three distinct deuterium NMR lines.[34–36] These lines can be characterized as a Pake doublet, a broad central, and a narrow central line. The (very sharp) Pake doublet is universally believed to arise from bonded D such as the type that passifies dangling bonds. We support this identification and note that the Si-H bond lengths in our sample generally vary by only 1–2%. This is entirely consistent with the very sharp Pake doublet which implies that the electric-field gradient (EFG) at the various sites varies by at most a few percent. Our calculated EFG's were computed by summing up the contribution from all nuclei and electronic charge from an extended sample made up by assuming a giant lattice of supercells. Unfortunately our code can be in error by 20% or more in the calculation of EFG's because this quantity is the second derivative of a potential. In fact all codes that we are aware of suffer similar shortcomings for the calculation of electric-field gradients or the frequencies of local modes. However, it is easily seen from the code that bond-length changes are much more important than bond-angle distortions in determining changes in EFG's. Thus a bond-angle distribution of say 10° is entirely consistent with an extremely sharp Pake doublet for H bonded in dangling-bond positions.

The narrow central line is composed of the molecular hydrogen in the form of HD and/or D_2 in microvoids and these volumes of molecular H are at densities comparable to liquid densities. These voids are not relevant to this paper. Finally there is a broad central line. The origin of this line is one of the major unsolved mysteries of a-Si:H and its existence is largely ignored by the a-Si community, probably because its origin is unknown. However, even in good device quality material, from 25% to 33% of the hydrogen resides in sites that contribute to this line. This is a very substantial fraction of the H to lie in an unknown form. Two possibilities that have been suggested and not discarded are that this signal is from isolated HD molecules in nanovoids or from H atoms that are part of a floating-bond configuration. It has been conclusively shown[34] that HD molecules sit in isolated nanovoids and that this form of hydrogen acts far differently than the liquidlike H_2 in the microvoids. Our calculations show that the EFG's that affect the D atoms at BC positions would be at least 30% larger than the EFG's that effect the normally bonded D. There is no substantial signal in any reported NMR experiments that corresponds to this and thus we tend to believe that little H or D exists in this configuration.

IV. LOCALIZATION

Next let us consider the localization of the defect states as well as the states in the conduction and valence bands.

Because of the finite size of our supercell, one cannot define precisely what a localized state is. However, in order to aid in assessing the character of a state, we define a "localized charge" $q(n,E)$ associated with the energy eigenvalue E and the atomic site centered at the atom number n. This charge is obtained from the density matrix and sp^3 orbitals of the computer program developed by Sankey *et al.* Because the orbitals possess significant overlap on neighboring sites, this is only an approximate definition of localization and is most meaningful when used in a comparative way rather than as an absolute number. The quantity $q(n,E)$ summed over all atoms is 1. We also define $Q(n,E)$ as $Nq(n,E)$, where N is the number of atoms in the supercell, and $Q_2(E)$ as

$$Q_2(E)=N\sum_n q(n,E)^2 . \tag{1}$$

Also note that $Q_2(E)$ will be 1 for an extended state that has the same amplitude at every site.

Figures 1(a), 1(b), and 1(c) show $Q_2(E)$ for eigenvalues near the Fermi surface for samples sih 62.6, sih 62.5, and sih 62.4, respectively. The conduction and valence bands are drawn as split off and localized states in the gap are also depicted as separated. The amount of localization of states deeper in the valence band and higher than the conduction band is similar to the localization in the valence band shown. We note that the states in the gap are quite well localized and that the localization is better when there are fewer states in the gap. Further, we note that the states at the edge of the conduction band are more localized than the states at the edge of the valence band. We noted this on earlier work on unhydrogenated Si.[10] The localization at a specific site for some of the samples is shown in Table III. We note that the excess localization of the conduction-band edge noted above is not easily associated with any particular sites. Although we do not fully understand this effect, we note that there are a number of ways in which the conduction-, and valence-band edges act very differently including the temperature dependence of the band tailing.[37,38] In this work as well as in earlier work, we have noticed that the defect states are less well localized in supercell samples with more defects of more strains. This effect cannot be entirely explained by banding of defect states since it is much more dependent on the amount of band tailing. For example, we found that about 70% of the defect state charge for the BC state in *c*-Si was located on the two Si sites that the H split. The number was about 55% for the *a*-Si samples, none of which had other defects. Even within tight binding the effect exists. For example, Bethe lattice calculations showed that the dangling bond has about 70% of its charge on one Si site[2,3] while calculations with the same tight-binding parameters on a strained supercell showed far less localization. Normally one expects disorder to lead to more localization, not less. However, here the defect states partially hybridize with the (conduction)-band tail states which are themselves quasilocalized. This leads to a spreading out of the defect-state wave function. Finally, we have analyzed the phonon spectra of a number of supercell samples. We find a vibrational density of states very similar to that

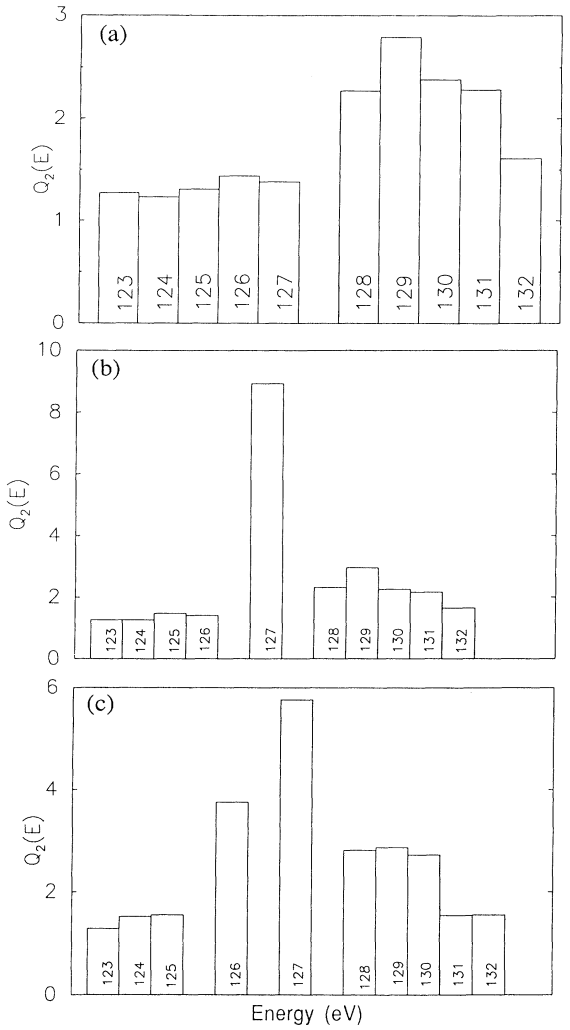

FIG. 1. The measure of localization $Q_2(E)$ for energy eigenvalues near the Fermi level for three supercell samples. (a) refers to sih 62.6 and the Fermi level lies in the gap between eigenvalues 127 and 128. (b) refers to sih 62.5 and the Fermi level lies on the eigenvalue 127 which belongs to the localized state in the gap. (c) refers to sih 62.4 and the Fermi level lies between levels 126 and 127 which are the two dangling-bond states in the gap.

TABLE III. Some properties concerning the localization of defect states. Here db, fb, and bc denote dangling bond, floating bond, and bond centered, respectively.

Sample	Defect	$Q_2(\lambda)$	$Q_2(\lambda,n)$
sih 61.9	db	14.0	30.3
sih 61.9.*y*	fb	6.5	16.6,11.7
sih 62.5	db	8.9	23.2
sih 62.5.*y*	db/fb	5.9	16.2
sih 62.6.1*a*	1bc	9.6	19.7,12.9
sih 62.6.1*b*	1bc	8.6	19.7,14.5
sih 61.8	db1	7.9	21.9
sih 61.8	db2	7.6	19.7
sih 62.4	db1	3.8	13.7
sih 62.4	db/fb	5.8	15.3

found in Ref. 9 with the addition of localized vibrational states for the H atoms. We find no localization of the rest of the modes as has sometimes been noted by other investigators.[39] We believe that these earlier reports are due to poor samples and/or an inadequate force code.

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