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# An infrared study of $\text{H}_8\text{Si}_8\text{O}_{12}$ cluster adsorption on Si(100) surfaces

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Motivated by a controversy about the proper interpretation of x-ray photoelectron spectra of Si/SiO<sub>2</sub> interfaces derived from the adsorption of  $\text{H}_8\text{Si}_8\text{O}_{12}$  spherosiloxane clusters on Si(100) surfaces, we have studied the adsorption geometry of the  $\text{H}_8\text{Si}_8\text{O}_{12}$  clusters on deuterium-passivated and clean Si(100) surfaces by using external reflection infrared spectroscopy. Access to frequencies below 1450 cm<sup>-1</sup> was made possible through the use of specially prepared Si(100) samples which have a buried metallic CoSi<sub>2</sub> layer that acts as an internal mirror. A comparison of the infrared spectrum of the clusters on a deuterium-passivated Si(100) surface at 130 K with an infrared spectrum of the clusters in a carbon tetrachloride solution reveals that the clusters are only weakly physisorbed on the D/Si(100) surface and also provides evidence for the purity of the cluster source. We also present infrared spectra of clusters directly chemisorbed on a clean Si(100) surface and show evidence that the clusters are adsorbed on the Si(100) *via* attachment by one vertex. A complete assignment of the observed vibrational features, for both physisorbed and chemisorbed clusters, has been made based upon comparisons with the results obtained in *ab initio* calculations using gradient-corrected density functional methods. © 1998 American Institute of Physics. [S0021-9606(98)02820-7]

## I. INTRODUCTION

In recent years there has been a great deal of research on the structure of the Si/SiO<sub>2</sub> interface, due to the importance

of this interface in microelectronic devices.<sup>1</sup> One technique which has been widely used to study this interface is x-ray photoelectron spectroscopy (XPS),<sup>2,3</sup> because changes in the energy levels of the Si 2*p* core level can provide information about the local chemical environment of Si atoms at the interface. In particular, many XPS studies have focused on trying to understand the structure of Si/SiO<sub>2</sub> interfaces which are formed in industrially important processes, such as thermal oxidation.<sup>2,4</sup>

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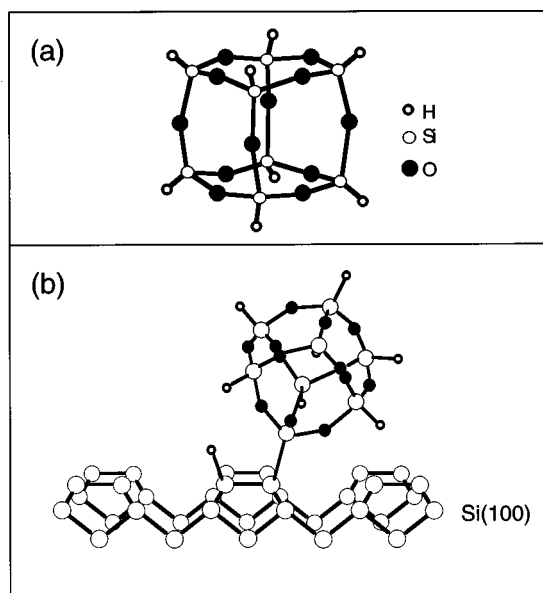


FIG. 1. (a) The free  $\text{H}_8\text{Si}_8\text{O}_{12}$  cluster. (b) Adsorption geometry proposed by Banaszak-Holl and McFeely in Ref. 5.

Recently, Banaszak-Holl and McFeely have used XPS to study the Si  $2p$  core levels of Si/SiO<sub>2</sub> interfaces that had been formed by the room temperature adsorption of a variety of siloxane clusters on Si(100) surfaces.<sup>5-7</sup> These studies were motivated by the observation that in previous studies of Si/SiO<sub>2</sub> interfaces, the Si  $2p$  features were assigned to SiO<sub>x</sub> structures on the basis of a “group-shift” model, which had never been experimentally shown to be applicable to Si/SiO<sub>2</sub> interfaces. Thus, the goal of their cluster studies was to provide a well-defined Si/SiO<sub>2</sub> interface with a known structure which could be used as a standard for assigning the XPS features of Si/SiO<sub>2</sub> interfaces generated by other methods, such as thermal oxidation.<sup>2,5</sup> Interestingly, on the basis of their XPS studies of these cluster-derived Si/SiO<sub>2</sub> interfaces, Banaszak-Holl and McFeely concluded that the “group-shift” model could not be used as a guiding principle to assign the features in the XPS spectra.<sup>8</sup> Their conclusions have generated a great deal of controversy in the literature.<sup>2,9,10</sup>

To address this controversy, we report in this paper our vibrational studies of a spherosiloxane cluster which has a chemical formula  $\text{H}_8\text{Si}_8\text{O}_{12}$  and a structure as shown in Fig. 1. In particular, we will focus on two key issues. The first issue is concerned with whether the clusters attach to the Si(100) surface in the manner proposed by Banaszak-Holl and McFeely.<sup>5</sup> This proposed adsorption geometry, shown in Fig. 1, simply involves the dissociative chemisorption of a cluster across a Si(100) dimer to form an  $\text{H}_7\text{Si}_8\text{O}_{12}$  species attached to one Si atom of the dimer and a hydrogen atom attached to the other. Indeed, since Banaszak-Holl and McFeely have based their controversial interpretation of the XPS studies of this class of clusters on this adsorption geometry, it is important to verify that this adsorption geometry is correct. The second issue is concerned with whether certain key features in the XPS spectrum of the clusters are due to contamination, rather than adsorbed clusters. More spe-

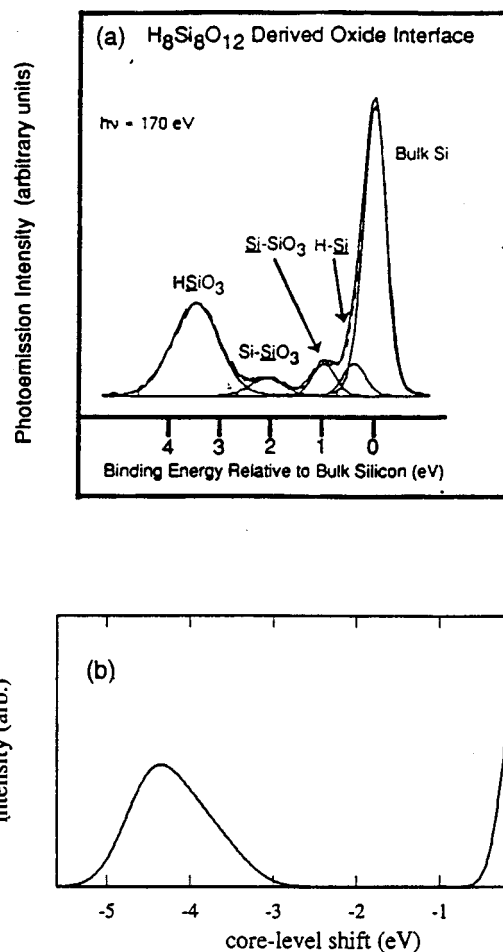


FIG. 2. (a) The XPS spectrum resulting from the chemisorption of the  $\text{H}_8\text{Si}_8\text{O}_{12}$  cluster on clean Si(100). This spectrum was taken from Ref. 5. (b) A calculated Si  $2p$  XPS spectrum of the clusters chemisorbed on a Si(100) surface, generated by density functional methods. This spectrum was taken from Ref. 9.

cifically, as shown in Fig. 2(a), the Si  $2p$  XPS spectrum of the clusters adsorbed on a Si(100) surface exhibits features shifted 0.4, 1.04, 2.19, and 3.64 eV relative to the bulk Si peak.<sup>5</sup> These features were assigned by Banaszak-Holl and McFeely as belonging to H-Si, Si-SiO<sub>3</sub>, Si-SiO<sub>3</sub>, and H-SiO<sub>3</sub> moieties, respectively, based upon a comparison of the relative integrated intensities of these features with the relative numbers of Si atoms in different chemical environments for clusters chemisorbed in the manner described above.<sup>2,5</sup> However, recent density functional calculations of the clusters in this adsorption geometry by Pasquarello, Hybertsen, and Carr have not predicted the existence of Si  $2p$  XPS features shifted 1.04 and 2.19 eV relative to the bulk Si peak, as shown in Fig. 2(b), suggesting that two of these features arise from contamination.<sup>9</sup> In particular, it has been suggested that the 1.04 eV feature arises from background water contamination,<sup>9</sup> and not from the existence of significant “second-nearest-neighbor” effects, as proposed by Banaszak-Holl and McFeely.<sup>5,8</sup> Additionally, it has been proposed that the 2.19 eV feature could be the result of nonselective decomposition of the cubes to form some type of suboxide species on the surface.<sup>9</sup>

In order to determine both the cluster adsorption geom-

etry on Si(100) surfaces and the importance of contamination effects from water or partially decomposed clusters, we have studied the adsorption of clusters on clean and D-passivated Si(100) surfaces by using external reflection infrared spectroscopy. Infrared spectroscopy can provide valuable complementary information to the XPS studies, because structural information about adsorbates on surfaces can be deduced by analyzing the features in an infrared spectrum. Additionally, since we have previously studied the dissociative adsorption of water on Si(100) with this technique,<sup>11</sup> we can provide estimates of the degree of water contamination in these particular studies by comparing with previously obtained data.

The remainder of this paper is organized as follows. In Sec. II, we will briefly describe details concerning the preparation of these Si(100) samples, the acquisition of the infrared spectra, and the handling procedures for the clusters and gases used in this study. We will also describe the density functional methods which were used to calculate the normal mode frequencies of free  $\text{H}_8\text{Si}_8\text{O}_{12}$  clusters and of related monosubstituted cluster compounds (i.e.,  $\text{RH}_7\text{Si}_8\text{O}_{12}$ , where  $\text{R}=\text{CH}_3$  or  $\text{SiH}_3$ ) which are relevant for the interpretation of the infrared spectra. In Sec. III, we report infrared experiments and calculations which demonstrate that the clusters are most likely adsorbed *via* attachment through a single vertex, as proposed by Banaszak-Holl and McFeely. We also discuss the role of water contamination and attempt to quantify the amount of water coadsorbed with the clusters.

## II. EXPERIMENT

### A. Sample preparation

The preparation and cleaning of the  $\text{Co}^+$ -implanted Si(100) samples have been described previously in detail.<sup>11</sup> Briefly, the Si(100) wafers (B-doped, 6–10  $\Omega\text{-cm}$ ) were heated to 650 K, bombarded with 200 keV  $^{59}\text{Co}^+$  ions (beam current density 15–20  $\mu\text{A}/\text{cm}^2$ , total dose  $\sim 2.3 \times 10^{17} \text{ cm}^{-2}$ ), and capped with a protective oxide. This implantation process was followed by a two-step annealing procedure which helped to reduce the surface damage caused by the ion bombardment. Next, the Si(100) samples were subjected to a series of wet chemical cleaning, oxidation, and etching steps which ultimately left a 1.0–1.5 nm thick protective oxide film on the surface. The samples were then inserted into a load-lock chamber, and a single sample was transferred to a manipulator that had been extensively outgassed previously in order to avoid contamination when annealing away the protective oxide layer. This entire transferring/annealing procedure has been described thoroughly elsewhere.<sup>11</sup> After the protective oxide was removed by annealing, a well-ordered Si(100) surface was obtained, as verified by low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and vibrational linewidth studies of the hydrogen-passivated surface.<sup>11</sup> Also, note that the Si(100) samples were never cleaned by *in-situ* ion bombardment, since this procedure would rapidly erode the thin Si layer above the  $\text{CoSi}_2$  layer. Whenever the sample was contaminated with carbon, as determined by Auger electron spectroscopy, it was replaced with a fresh sample.

### B. Infrared spectroscopy

The infrared experiments were performed at both the National Synchrotron Light Source of Brookhaven National Laboratories and at Bell Laboratories. The ultrahigh vacuum (UHV) chambers and the corresponding optical geometries have been described elsewhere in detail.<sup>11</sup> The infrared radiation was detected using two different types of detectors. At Brookhaven, a liquid-helium-cooled Cu:Ge detector, sensitive above  $330 \text{ cm}^{-1}$ , was used for studies in the mid- to far-infrared region, while at Bell Laboratories, a liquid-nitrogen-cooled HgCdTe/InSb sandwich detector, which is sensitive above  $720 \text{ cm}^{-1}$ , was used. The infrared spectra shown are the result of ratioing a series of coadded spectra of the adsorbate-covered surface against a series of coadded spectra for the clean surface. For the experiments that were performed at Brookhaven, typically 3–6 spectra of 256 scans were acquired at  $6 \text{ cm}^{-1}$  resolution and coadded prior to ratioing for both the clean and the adsorbate-coverage surfaces, while for the experiments at Bell Laboratories, typically 3 spectra of 512 scans at  $8 \text{ cm}^{-1}$  resolution were acquired prior to ratioing. The variation of the sample temperature during the acquisition of the infrared spectra was kept at  $\pm 0.2 \text{ K}$  or less by using a home-built heater feedback loop control. Such precise temperature control is critical since larger temperature fluctuations would cause a significant drift in the base line, rendering the spectrum unusable.

### C. Handling procedures for clusters and gases

The  $\text{H}_8\text{Si}_8\text{O}_{12}$  clusters were synthesized and purified according to a previously reported procedure,<sup>12</sup> and stored in a stainless steel vial which could be sealed by a metal bellows valve. Prior to performing any experiments, the cluster source was first conditioned by pumping extensively with a turbomolecular pump (for 24–36 hours) in order to remove potential contaminants, particularly water. Also, at the beginning of each day of experimentation, the cluster source was further conditioned by 30 min of pumping with a turbomolecular pump. This cluster handling procedure is similar to the one used previously by Banaszak-Holl and McFeely in their XPS studies of cluster adsorption on Si(100).<sup>6</sup> Exposures of the clusters are reported in langmuirs ( $1 \text{ L} = 1.3 \times 10^{-4} \text{ Pa}\cdot\text{s}$ ). These exposures were regulated by a precision sapphire leak valve and were made through a 3/8 inch outer diameter (o.d.) copper dosing tube that was directed at the Si(100) sample. The result of dosing through this tube was that the flux of clusters at the surface was higher than estimated from the measured partial pressure in the chamber. As determined by calibration experiments (not shown), a 0.4 L exposure cluster corresponds to a saturation layer on the clean Si(100) surface with this dosing method.

The deuterium used in these studies was purchased from Matheson (99.999% purity) and was used without further purification. Atomic deuterium used for passivating the Si(100) surface was generated by backfilling the vacuum chamber with  $\text{D}_2$  to  $1.3 \times 10^{-4} \text{ Pa}$  and then turning on a W filament ( $T_{\text{filament}} \sim 2100 \text{ K}$ , as measured by a disappearing filament pyrometer) which was located  $\sim 5 \text{ cm}$  from the Si(100) surface. During the D atom exposures, the Si(100)

sample temperature was held at 550 K to ensure that the surface would be passivated by the monodeuterated phase exclusively.<sup>13</sup> Although the exposures of atomic deuterium are reported in langmuirs, these exposures reflect the partial pressure of  $D_2$  in the chamber while the W filament was on, and not the actual flux of D atoms at the surface of the Si(100) sample. Typically, a 110 L dose of D atoms was sufficient to passivate the Si(100) surface completely by forming the Si-D monohydride phase, as verified by infrared spectroscopy.

The  $D_2O$  used in these experiments was stored in a quartz vial which was sealed by a metal bellows seal valve. Prior to use, it was purified by successive freeze-pump-thaw cycles. *In situ* mass spectrometry confirmed that the purity was greater than 95%.

#### D. *Ab initio* normal mode calculations

To assist in making vibrational mode assignments, *ab initio* calculations were performed to determine the normal mode frequencies of the free cluster and of monosubstituted clusters in which a hydrogen atom at one of the corners of the cluster was replaced by either a silyl group or a methyl group. We have chosen to use these monosubstituted clusters to model chemisorbed clusters on Si(100), because determining the normal modes of these monosubstituted clusters is computationally more tractable. However, we recognize that the use of silyl groups or methyl groups to represent the surface leads to a reduced mass which is substantially different than what would be obtained if the surface were fully represented. Nevertheless, the normal mode calculations for these simple model compounds can predict which cluster modes become infrared active if the octahedral symmetry of the free cluster is reduced to  $C_{3v}$ , as would be the case if the clusters attach to the Si(100) surface through a single vertex.

The *ab initio* calculations were performed using the B3-LYP gradient-corrected density functional method, which has been shown to be comparably accurate to methods which employ Gaussian basis sets, such as MP2, while being computationally less expensive.<sup>11,14,15</sup> The geometries of the free cluster and monosubstituted clusters were fully optimized prior to evaluating the matrix of force constants. The infrared intensities of all normal modes were determined as well, but we emphasize that these intensities are calculated using the total dynamic dipole of the mode. Thus, in making comparisons with the intensities of experimentally observed spectral features, one must be cautious because only the perpendicular component of the dynamic dipoles are observed for adsorbates on the  $Co^+$ -implanted Si(100) samples.<sup>16</sup>

### III. RESULTS

#### A. Cluster adsorption on deuterium-passivated and clean Si(100) surfaces

In Fig. 3(a), we present infrared spectra of clusters on deuterium-passivated Si(100) at 130 K. These spectra were taken as a function of exposure. For the sake of clarity, we have chosen to use an infrared spectrum of the deuterium-passivated Si(100) surface as the background spectrum, so that all of the spectral features in Fig. 3(a) are related to the

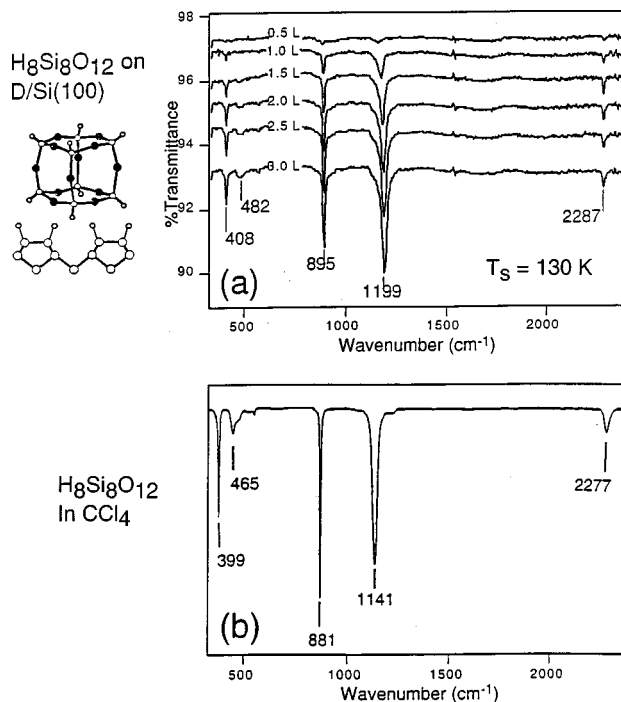


FIG. 3. (a) Infrared spectra of clusters on a D-passivated Si(100) surface taken as a function of cluster exposure. (b) Infrared spectra of clusters in a carbon tetrachloride solution. This spectrum was taken from Ref. 12.

vibrational modes of the clusters. The spectra show that five vibrational features gradually appear with increasing cluster exposure. Similar features are also observed for the clusters in a carbon tetrachloride solution,<sup>17</sup> as seen by a comparison of Figs. 3(a) and 3(b). This similarity is significant in that it provides evidence for the purity of the cluster source that was used in these studies. In particular, the five vibrational features observed in Fig. 3(a) clearly are characteristic of  $H_8Si_8O_{12}$  clusters, which implies the following: (1) the cluster source does not emit a mixture of structurally different siloxane molecules; and (2) during the dosing process, the clusters are not altered either by reactions with the interior wall of the chamber or by thermal cracking due to the ion gauge. These results will be especially important later, when we examine the infrared spectra of the clusters which are directly chemisorbed onto a Si(100) surface.

The vibrational mode assignments for the spectral features in Fig. 3(a) are summarized in Table I. These assignments were made by a straightforward comparison to the assignments previously reported for the clusters in a carbon tetrachloride solution,<sup>17</sup> as well as by a comparison to the results of our *ab initio* normal mode calculations for the free cluster. We note here that the calculations yield normal mode frequencies which agree quite well with the experimentally observed values reported in the literature,<sup>17</sup> differing by only 2%, on average. Additionally, the normal mode descriptions obtained from the calculations qualitatively agree with those previously proposed on the basis of a normal mode analysis using Wilson's *F* and *G* matrix method.<sup>17</sup> As an example, both the previously reported assignments and our *ab initio* calculations assign the features at 895 and 1199  $cm^{-1}$  to

TABLE I. Vibrational mode assignments for the major features in the infrared spectrum of molecular  $\text{H}_8\text{Si}_8\text{O}_{12}$  clusters. All frequencies are in wave numbers. The numbers in parentheses refer to the infrared intensities calculated using the total dynamic dipole, and not just the component perpendicular to the surface.

Mode description	Symmetry	Molecular $\text{H}_8\text{Si}_8\text{O}_{12}$ clusters		
		In $\text{CCl}_4^a$	On $\text{D}/\text{Si}(100)$	B3-LYP
$\delta_s(\text{Si}-\text{O}-\text{Si})$	$T_{1u}$	399	408	392 (173)
$\nu_s(\text{Si}-\text{O}-\text{Si})$	$T_{1u}$	465	482	451 (135)
$\delta_a(\text{O}-\text{Si}-\text{H})$	$T_{1u}$	881	895	894 (513)
$\nu_a(\text{S}-\text{O}-\text{Si})$	$T_{1u}$	1141	1199	1154 (2130)
$\nu(\text{O}_3\text{Si}-\text{H})$	$T_{1u}$	2277	2287	2361 (355)

<sup>a</sup>Reference 17.

threefold degenerate  $\delta(\text{Si}-\text{H})$  and  $\nu_a(\text{Si}-\text{O}-\text{Si})$  modes, respectively.

The close agreement between the frequencies observed in Figs. 3(a) and 3(b) suggests that the clusters are only weakly physisorbed on D-passivated Si(100) surfaces at cryogenic temperatures. This behavior is confirmed by infrared studies which monitor the thermal desorption of the clusters from a D-passivated Si(100) surface, as shown in Fig. 4. In these studies, a D-passivated surface was exposed to 16 L of clusters at 120 K, subsequently heated to each specified temperature for one minute (heating rate=3 K/s), and then recooled to 120 K. [For reference, a 16 L exposure of clusters corresponds to approximately 40 layers of clusters, as-

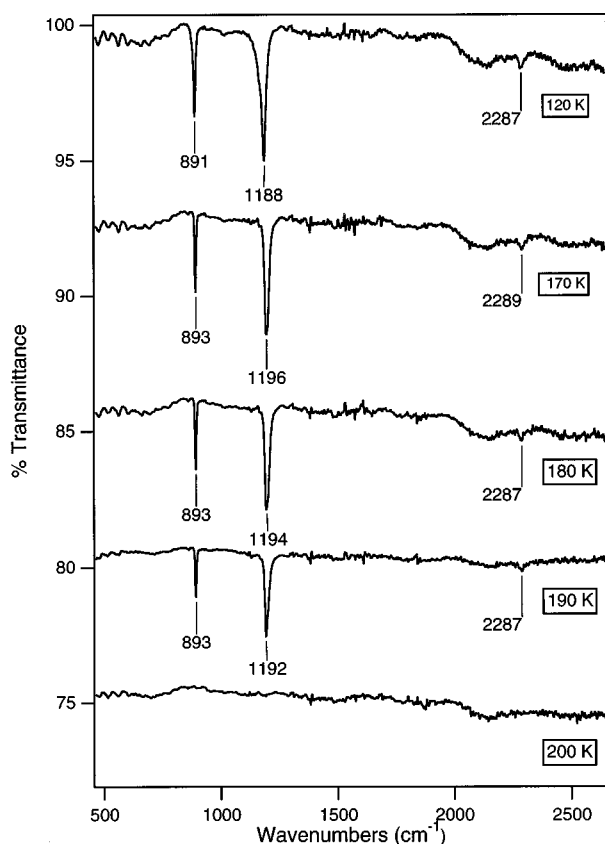


FIG. 4. Infrared spectra of clusters on a D-passivated Si(100) surface taken as a function of substrate temperature.

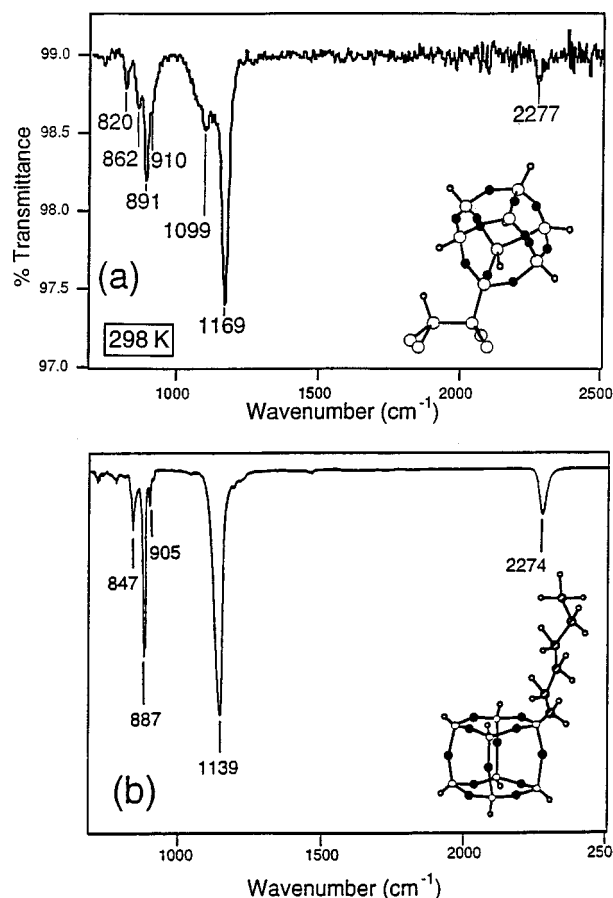


FIG. 5. (a) Infrared spectrum obtained following a saturation exposure of clusters on a clean Si(100) surface at room temperature. (b) Infrared spectrum of a hexyl-substituted cluster in a pentane solution. This spectrum was taken from Ref. 13.

suming that the sticking probability of the clusters on the D-passivated Si(100) surface at 120 K is the same as that for clusters on a clean Si(100) surface at room temperature.] From the series of spectra shown in Fig. 4, it is evident that all of the clusters have desorbed from the D-passivated surface by 200 K, indicating that the clusters interact only weakly with the D-passivated surface. This result is important because it sets an upper limit for the multilayer desorption temperature of the clusters. Thus, in later infrared experiments where the clusters adsorb directly on a Si(100) surface at room temperature, we can exclude the possibility that the corresponding infrared spectra are the result of a superposition of vibrational features originating from both chemisorbed and physisorbed clusters.

Figure 5(a) shows an infrared spectrum obtained after exposing a Si(100) surface at room temperature to a saturation exposure of clusters. By comparing with the spectra of physisorbed clusters in Fig. 3, it is evident that several additional spectral features appear following the reaction of the clusters with the clean Si(100) surface. For example, the feature at  $891\text{ cm}^{-1}$ , which corresponds to a  $\delta(\text{O}_3\text{Si}-\text{H})$  mode in the physisorbed cluster, is also present in Fig. 5(a), but splits to produce satellite features at  $862$  and  $910\text{ cm}^{-1}$ . Additionally, the feature at  $1169\text{ cm}^{-1}$ , corresponding to a triply degenerate  $\nu_a(\text{Si}-\text{O}-\text{Si})$  mode in the physisorbed clus-

TABLE II. Vibrational mode assignments for the major features in the infrared spectrum of  $\text{H}_8\text{Si}_8\text{O}_{12}$  clusters adsorbed on Si(100). All frequencies are in wave numbers. The calculated infrared intensities refer to intensities which are calculated using the total dynamic dipole, and not just the component perpendicular to the surface plane. The different  $\delta(\text{Si-H})$  and  $\nu_a(\text{Si-O-Si})$  modes correspond to different collective motions of Si-H and Si-O-Si groups within the cluster.

Mode description	Symmetry $C_{3v}$	$\text{H}_8\text{Si}_8\text{O}_{12}$ clusters			
		Hexyl-substituted <sup>a</sup>	$\text{CH}_3$ -substituted B3-LYP	On Si(100) IR data	$\text{SiH}_3$ -substituted B3-LYP
$\delta(\text{Si-H})$	$E$	847	874 (427)	862	842 (125)
$\delta(\text{Si-H})$	$A_1$	887	900 (1000)	891	890 (1016)
$\delta(\text{Si-H})$	$E$	905	921 (78)	910	900 (625)
	$A_1$				918 (132)
$\nu_a(\text{Si-O-Si})$	$E$	...	1044 (18)	1099	1037 (52)
	$A_1$		1114 (8)		1112 (54)
$\nu_a(\text{Si-O-Si})$	$E$	...	1141 (33)	...	1136 (313)
	$A_1$		1141 (83)		1141 (270)
$\nu_a(\text{Si-O-Si})$	$E$	1139	1152 (4182)	1169	1151 (3851)
	$A_1$		1152 (2206)		1151 (1988)
$\nu(\text{O}_3\text{Si-H})$	$E$	2274	2360 (591)	2277	2362 (624)
	$A_1$		2366 (65)		2360 (128)

<sup>a</sup>Reference 18.

ter, now has a shoulder at  $1099\text{ cm}^{-1}$  in Fig. 5(a). Finally, we observe a rather weak feature at  $820\text{ cm}^{-1}$ , which is in the frequency range expected for a  $\nu(\text{Si-OH})$  mode of a hydroxyl group on a Si(100) surface.<sup>11,15</sup> This feature will be discussed in detail below.

A comparison of the infrared spectrum shown in Fig. 5(a) with an infrared spectrum of hexyl-substituted clusters in a carbon tetrachloride solution [Fig. 5(b)]<sup>18</sup> reveals that these two spectra are fairly similar, suggesting that the vibrational assignments for the hexyl-substituted cluster can be used as a guide for assigning the vibrational features observed in Fig. 5(a). These assignments, which are confirmed by our *ab initio* calculations described below, are summarized in Table II. However, we note that the feature observed at  $1099\text{ cm}^{-1}$  in Fig. 5(a) does not appear to have an analog in the spectrum of the hexyl-substituted clusters [Fig. 5(b)]. Based solely on a comparison between the spectra in Figs. 5(a) and 5(b), it is impossible to determine whether this feature is intrinsic to molecularly chemisorbed clusters on Si(100), or whether it arises from other surface species, such as partially decomposed clusters.

Motivated by these issues, we performed *ab initio* calculations to determine which normal modes of a cluster would become infrared active if the octahedral symmetry of a cluster were reduced to  $C_{3v}$ , by substitution of either a silyl or methyl group at one vertex. Importantly, the frequencies calculated for the  $\text{SiH}_3$ -substituted cluster, which are summarized in Table II, agree rather well with *all* of the experimentally observed frequencies for the clusters chemisorbed on a Si(100) surface. For example, as shown in Table II, the calculations predict that substituting a hydrogen at a corner of the cluster by a  $\text{SiH}_3$  group causes  $\delta(\text{O}_3\text{Si-H})$  vibrations at 842 and  $\sim 900\text{ cm}^{-1}$  to become infrared active, which accounts for the features at 862 and  $910\text{ cm}^{-1}$  in Fig. 5(a). Additionally, the calculations predict that infrared active features occur at 1112, 1136, and  $1141\text{ cm}^{-1}$  for the  $\text{SiH}_3$ -substituted cluster, which most likely gives rise to the

broad shoulder at  $\sim 1099\text{ cm}^{-1}$  in Fig. 5(a). Interestingly, although the calculations predict that similar infrared active modes should appear in the infrared spectrum of the methyl-substituted cluster, such modes would possess a weaker infrared intensity than the analogous modes of the  $\text{SiH}_3$ -substituted cluster (cf. Table II). These differences in infrared intensity may be related to subtle differences between the vibrational coupling of the cluster modes to the Si- $\text{CH}_3$  and Si- $\text{SiH}_3$  vibrations. In an analogous fashion, the presence of a feature at  $1099\text{ cm}^{-1}$  in the infrared spectrum of the clusters on a Si(100) surface [Fig. 5(a)], but not in the infrared spectrum of hexyl-substituted clusters [Fig. 5(b)], may be related to subtle differences in vibrational coupling of the Si(100) surface and the hexyl group to the modes of the cluster.

The close agreement between the frequencies observed in Fig. 5(a) and those predicted from the normal mode calculations for the  $\text{H}_7\text{Si}_8\text{O}_{12}$ - $\text{SiH}_3$  cluster compound strongly suggest that the  $\text{H}_8\text{Si}_8\text{O}_{12}$  clusters attach to the Si(100) surface through one vertex. Such a cluster adsorption geometry is consistent with the one proposed by Banaszak-Holl and McFeely on the basis of XPS studies of clusters on Si(100) surfaces, as described above. However, if each cluster dissociatively chemisorbs across a single Si(100) dimer, as shown in Fig. 1, the hydrogen atom that is adsorbed on the same dimer as the  $\text{H}_7\text{Si}_8\text{O}_{12}$  cluster fragment should give rise to a vibrational feature at  $\sim 2090\text{ cm}^{-1}$ . This feature is expected based on comparisons with infrared studies of analogous systems. For example, a moderately intense  $\nu(\text{Si-H})$  feature is observed at  $2088\text{ cm}^{-1}$  following the dissociative chemisorption of water across a single Si(100) dimer to form surface-bound hydrogen and a hydroxyl group.<sup>11</sup> Similarly, a moderately intense  $\nu(\text{Si-H})$  feature is observed at  $2088\text{ cm}^{-1}$  following the dissociative chemisorption of ethanol across a single Si(100) dimer to form surface hydrogen and ethoxy.<sup>14</sup> Thus, the complete absence of such a  $\nu(\text{Si-H})$  feature in Fig. 5(a) is somewhat surprising. However, one possible explanation

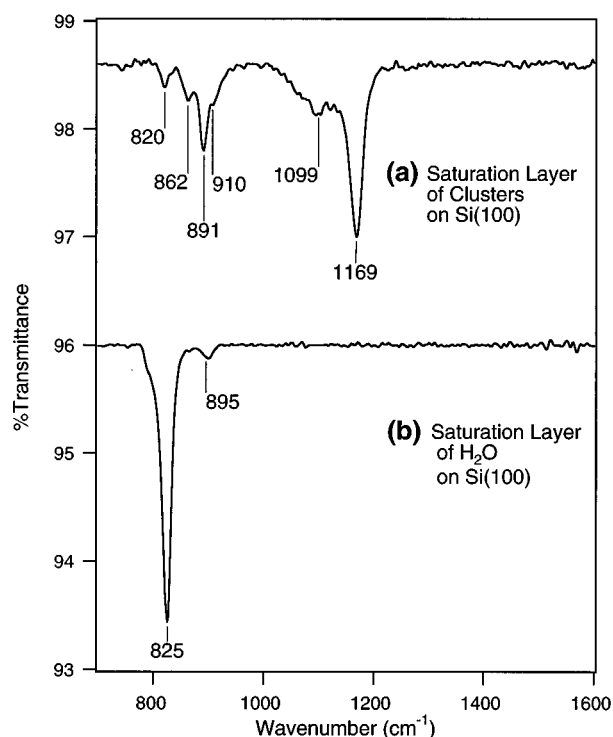


FIG. 6. (a) The infrared spectrum obtained after a saturation exposure of clusters on a Si(100) surface. The feature at  $820\text{ cm}^{-1}$  could result from the  $\nu(\text{Si-O})$  feature of dissociated water which is present as a contaminant. (b) Infrared spectrum obtained following a saturation exposure of  $\text{H}_2^{16}\text{O}$  on a clean Si(100) surface.

tion is that the surface concentration of hydrogen may too low to give this mode appreciable intensity. In other words, since the clusters are rather bulky, a saturation coverage of chemisorbed clusters only generates one  $\text{H}_7\text{Si}_8\text{O}_{12}$  group and one H atom per three Si(100) dimers,<sup>6</sup> leading to a surface hydrogen coverage that is only one-third of that obtained for a saturation coverage of either water or ethanol.

## B. Identification and quantification of water contamination

Although the results of the normal mode calculations for the  $\text{SiH}_3$ -substituted cluster reproduce the experimentally observed frequencies for the clusters adsorbed on a clean Si(100) surface rather well, we note that the calculations do not predict the presence of any spectral features at  $820\text{ cm}^{-1}$ . This result suggests that this feature does not arise from a vibrational mode of the cluster, but rather from a vibration of some contaminant on the surface. In fact, based upon our previous infrared studies of water chemisorption on Si(100), we believe that this feature is consistent with the  $\nu(\text{Si-OH})$  vibration of surface hydroxyl groups generated by the dissociative chemisorption of water on the Si(100) surface,<sup>11</sup> though we do not have enough signal-to-noise near  $2100\text{ cm}^{-1}$  to detect the  $\nu(\text{Si-H})$  vibration that would accompany the  $\nu(\text{Si-OH})$  mode.

However, assuming that the  $820\text{ cm}^{-1}$  feature results from water contamination, we can place a lower limit on the amount of water coadsorbed with the clusters by comparing the integrated intensity this feature [Fig. 6(a)] with the inte-

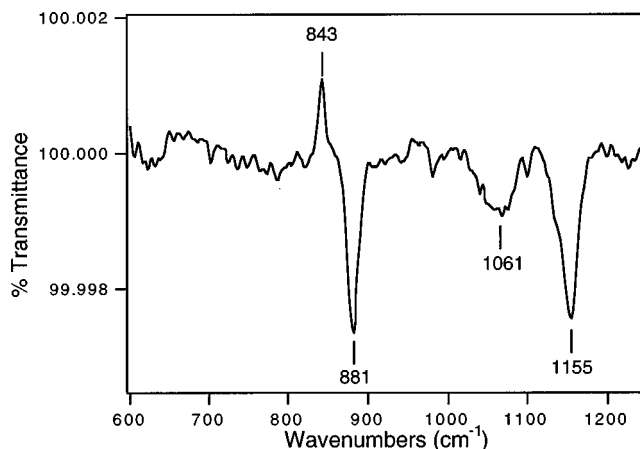


FIG. 7. Difference spectrum obtained by subtracting the spectrum of a  $\text{D}_2\text{O}$  passivated Si(100) surface from the spectrum taken after the same surface was exposed to 1.2 L of clusters.

grated intensity of the  $\nu(\text{Si-OH})$  feature for a saturation coverage of water on the Si(100) surface [Fig. 6(b)]. Such a comparison reveals that the integrated intensity of the  $820\text{ cm}^{-1}$  feature is only 5% that of the  $\nu(\text{Si-OH})$  feature for a saturation coverage of water, suggesting that the amount of coadsorbed water is rather small. However, we emphasize that this comparison only provides a rough estimate which is good to within a factor of  $\sim 1.5$ , due to uncertainties in the reproducibility of the optical alignment.<sup>19</sup> Additionally, it appears that the clusters can react with a water-treated Si(100) surface, so that the  $820\text{ cm}^{-1}$  feature might be attenuated and might not account for all of the water contamination. Although this point will be addressed in detail in a future publication,<sup>20</sup> we merely illustrate it here by showing that the clusters can react with a  $\text{D}_2\text{O}$ -treated (i.e.,  $\text{D}_2\text{O}$  saturated) Si(100) surface. Figure 7 shows a difference spectrum obtained by subtracting the spectrum of a  $\text{D}_2\text{O}$ -treated Si(100) surface from the spectrum of a  $\text{D}_2\text{O}$ -treated Si(100) surface after a cluster exposure sufficiently large to saturate a clean Si(100) surface. This difference spectrum clearly shows a positive-going feature at  $843\text{ cm}^{-1}$ , indicating an attenuation of the  $\nu(\text{Si-OD})$  mode of the chemisorbed  $\text{D}_2\text{O}$ . The integrated intensity corresponds to a 30% decrease of the  $\nu(\text{Si-OD})$  feature. Additionally, strong features appear at  $881$  and  $1155\text{ cm}^{-1}$ , and are assigned to  $\delta(\text{O}_3\text{Si-H})$  and  $\nu(\text{Si-OSi})$  modes of the cluster, respectively, based on a comparison with the spectra in Fig. 3(a). We also observe a broad, relatively intense feature at  $1061\text{ cm}^{-1}$ , which is *not* observed for clusters weakly physisorbed on D/Si(100) [Fig. 3(a)]. The presence of this feature suggests that at least a fraction of the clusters interacts strongly with a water pre-covered surface at room temperature, and possibly even reacts.

## IV. DISCUSSION

### A. The adsorption of $\text{H}_8\text{Si}_8\text{O}_{12}$ clusters on Si(100)

As mentioned in the Introduction, one key part of the controversy concerning the proper interpretation of the XPS spectrum of the chemisorbed clusters is whether the clusters attach to the Si(100) surface by one vertex. Indeed, several



alternative scenarios to the single vertex adsorption geometry proposed by Banaszak-Holl and McFeely have been suggested in an effort to explain the XPS spectrum of the clusters.<sup>2</sup> For example, one possible scenario is that the clusters decompose during the dosing process, so that the XPS spectra reflect the presence of various suboxide species. A second possible scenario is that a fraction of the clusters which adsorb initially on the Si(100) surface completely decomposes, causing artifacts in the XPS data, yet subsequent clusters attach to the surface via one vertex.<sup>9</sup> Also, it has been suggested that each cluster can react with more than one Si surface dimer, leading to either double vertex attachment or the partial destruction of the siloxane cage.<sup>2</sup>

However, based on our infrared data and *ab initio* calculations, we can clearly exclude some of these scenarios. For example, the infrared spectrum of clusters physisorbed on a D-passivated Si(100) surface [Fig. 3(a)] is completely consistent with intact, molecular clusters, and allows us to rule out the possibility that the cluster source emits a variety of structurally different clusters. Additionally, as mentioned above, this result argues against the possibility that the surface is contaminated by cluster fragments formed during the dosing process by thermal cracking due to a hot filament in the chamber, such as that of an ion gauge, or by reacting with the stainless steel inner walls of the chamber to evolve structurally different clusters. Our infrared studies also argue against the possibility that an initial fraction of the clusters that adsorb on the surface *completely* decomposes, because in such a scenario, the resulting suboxide would very likely have low symmetry on the surface, causing dipole active features not predicted by the calculations. Indeed, the good agreement between the frequencies observed in the infrared experiments on the chemisorbed clusters with the frequencies calculated for the SiH<sub>3</sub>-substituted cluster suggests that the spherosiloxane cage of the clusters must remain fairly intact upon adsorption and is completely consistent with a single vertex adsorption geometry. However, we emphasize that a surface  $\nu(\text{Si-H})$  feature, which should result from cluster dissociation across Si(100) dimers [Fig. 1(b)] was not observed. Furthermore, we have not performed exhaustive calculations to characterize the normal modes of a partially decomposed cluster, due to the multitude of different possible ways that the cluster can decompose, so that we cannot say definitively that no other possibilities exist other than single vertex attachment. Additionally, we note that the structurally similar H<sub>10</sub>Si<sub>10</sub>O<sub>15</sub> cluster, which has a solution infrared spectrum similar to that of the H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> cluster,<sup>21</sup> also reacts with the Si(100) surface to yield a spectrum similar to that of a dissociatively chemisorbed H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> cluster [Fig. 5(a)].<sup>20</sup> Thus, the spectrum shown in Fig. 5(a) is not necessarily unique to a H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> cluster bound by a single vertex, and on this basis, we cannot rule out the possibility that the siloxane cage of a surface-bound H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> cluster may be slightly decomposed on the Si(100) surface, though largely intact and similar in structure to that of the unbound cluster.

## B. The role of water contamination

The role of water contamination in the XPS studies of clusters chemisorbed on a Si(100) surface has been debated strenuously in the literature.<sup>2,6,9</sup> At the core of this debate is uncertainty over the proper interpretation of the Si 2*p* feature shifted 1.0 eV relative to the bulk Si feature in the XPS spectrum of clusters on Si(100) [Fig. 2(a)]. Banaszak-Holl and McFeely have claimed that this feature arises from strong “second-nearest-neighbor” effects, although Pasquarello, Hybertsen, and Car have suggested that this feature arises from surface hydroxyl groups present due to water contamination.<sup>9</sup> However, it has been argued by McFeely *et al.* that, if the 1.0 eV feature does indeed result from dissociatively chemisorbed water, then the integrated intensity of this 1.0 eV feature, relative to the integrated intensities of the other features, implies that there is a 1:1 ratio of chemisorbed clusters to chemisorbed water on the Si(100) surface.<sup>2</sup> In other words, since one cluster and one dissociated water molecule together would occupy three surface dimers, a 1:1 ratio of clusters to water on the Si(100) surface means that 33% of the dimers must be occupied by water.

Thus, one critical challenge for the infrared experiments is to determine whether coadsorbed water occupies at least 33% of the Si(100) surface. A comparison of integrated intensities in Fig. 6 indicates that the amount of coadsorbed water is significantly smaller than the amount required to assign the 1.0 eV feature in the XPS studies (Fig. 2) solely to coadsorbed water. However, it should be emphasized that these infrared experiments were not performed in the same chamber as the XPS experiments, so that the level of contamination in these experiments is not necessarily the same as in the XPS experiments. An additional complication arises from the ability of the clusters to react with a Si(100) surface that is precovered with water, because the surface species generated by exposing a water-precovered surface to clusters has not yet been identified. More experiments are underway to examine the interactions of the clusters with coadsorbed water.<sup>20</sup>

## V. CONCLUSIONS

In order to address the controversy concerning the adsorption geometry of H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> clusters on Si(100), we have performed infrared experiments and *ab initio* calculations. By studying the adsorption of clusters on a deuterium-passivated Si(100) surface, we have shown that molecularly intact clusters can be dosed onto the surface, and that no decomposition occurs during the dosing process. After exposing a clean Si(100) surface to the clusters, we obtain an infrared spectrum which is consistent with a cluster adsorption geometry in which the spherosiloxane cage is attached to the surface through a single vertex, though we do not observe the corresponding  $\nu(\text{Si-H})$  that is expected if the clusters dissociate across the Si(100) dimers, as shown in Fig. 1(b). The *ab initio* calculations accurately reproduce the vibrational features observed for weakly physisorbed clusters on a D-passivated surface, as well as those observed for clusters directly chemisorbed on the Si(100) surface. On this

basis, we have been able to provide a complete mode assignment for the vibrational spectrum of the chemisorbed clusters.

We have also attempted to quantify the amount of dissociated water which is coadsorbed with the clusters during the dosing process. Based upon a comparison with the results from previous studies of water chemisorption on Si(100), we conclude that the amount of dissociated water coadsorbed after exposing the clusters to the surface is quite small. However, infrared studies of cluster adsorption on a water pre-covered surface indicate that a fraction of the clusters interacts strongly with the surface, possibly even reacting with the surface hydroxyl groups at room temperature.

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