

Chemisorption of $H_8Si_8O_{12}$ Clusters on Gold: A Novel Si–H Bond Activation

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Monolayer assembly of discrete inorganic cage molecules has been reported during the past decade by a number of groups.¹ Single and multiple layer coverage have been observed for polyoxoanions on metal and graphite surfaces,^{2–4} metal halide and polyhedral borane clusters on gold,^{5,6} and hydridosilsesquioxane clusters on silicon,⁷ germanium, and zinc selenide.⁸ Controlled formation of inorganic interfaces has led to new insights into the spectroscopic interpretation and structure of commercially important solid/solid interfaces.^{7,9} This line of research is also being utilized to elucidate the surface role of cage complexes in important technological areas such as catalysis, corrosion protection, low-temperature dielectric formation, and lithography.¹

The interaction of $H_8Si_8O_{12}$ with an evaporated gold surface in ultrahigh vacuum (UHV) is described in this communication. The reaction provides a simple approach for the generation of a ~ 6 Å thick hydrophobic silicon oxide film on gold. Surface binding is proposed to consist of a silicon vertex of the cage chemisorbed to a gold surface atom, in contrast to the oxygen, halogen, or sulfur binding suggested for previous inorganic cage complex self-assembled monolayers (SAMs) (Figure 1).^{4–6} The reaction appears to occur via addition of a Si–H bond followed by reductive elimination of H_2 . Si–H activation by the gold surface at 20 °C is a surprising and novel aspect of this chemistry.

Soft X-ray photoemission spectroscopy (XPS) of a clean, freshly evaporated gold surface exposed to a saturating dose of $H_8Si_8O_{12}$ revealed two Si $2p_{3/2}$ core-level features with binding

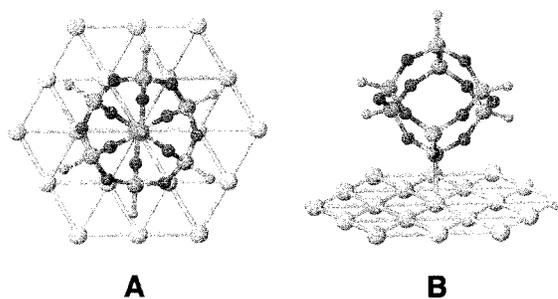


Figure 1. Proposed structure of the $H_8Si_8O_{12}$ cluster on the gold surface. The orientation of the cluster is based on a mechanics minimization of the $H_8Si_8O_{12}$ cluster on an Au(111) crystal face. The three oxygens attached to the gold-bound silicon atom are oriented away from the Au–Au bond vectors and over the triangular holes. Note the remarkable registration of the cluster Si–O 12-membered ring with the six gold atoms surrounding the binding site.

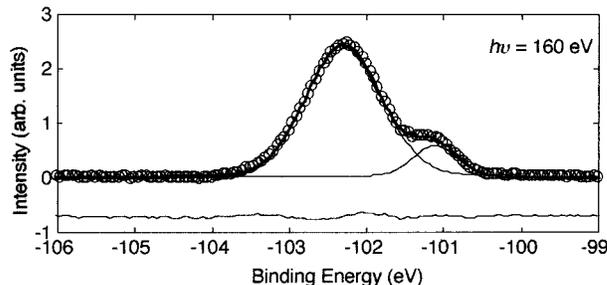


Figure 2. Soft X-ray Si $2p_{3/2}$ core-level spectra of the interface derived from $H_8Si_8O_{12}$ chemisorbed to gold.

energies of -101.1 and -102.3 eV (Figure 2).^{10,11} Full-widths at half-maximum (fwhm) for these peaks are 0.57 and 1.14 eV, respectively. The area ratio is 1:7.3.¹² Valence band spectra were also obtained. The spectra show six key features between 7 and 17 eV that are identical with data previously obtained for $H_8Si_8O_{12}$ on Si(100).^{7b}

The relative peak positions in the XPS suggest that a cluster silicon atom is directly bound to the gold substrate and the 7.3:1 area ratio indicates that just one cluster vertex is surface bound. Binding of additional cluster vertices to the surface would result in a dramatic change in the area ratio. For example, a two-vertex binding mode would give a 3:1 peak ratio. The valence band spectra are also consistent with monovortex binding.

The peak area ratio and binding energy separation are constant as a function of cluster exposure,¹³ providing evidence against multilayer formation. Upon multilayer formation at low temperature in other systems, both the peak area ratio and binding energy separation are observed to change dramatically.^{7d} Previous XPS and IR studies performed on silicon substrates indicate $H_8Si_8O_{12}$ multilayers are not present at 20 °C at UHV conditions.^{7d,7e}

(10) The gold substrate consisted of a silicon wafer containing a thin Cr barrier layer and an evaporated gold film. Immediately prior to use, in situ formation in UHV of a fresh gold surface was achieved by evaporation of gold from a tungsten filament. XPS characterization was used to determine that the surface was pure gold.

(11) Experimental apparatus for synchrotron soft X-ray photoemission spectroscopy and approaches to fitting Si $2p$ core level spectra have been previously described in ref 7b. Binding energies are referenced to Au $4f_{7/2}$ at 84.0 eV.

(12) Esca-Tools and Matlab Version 4.0 was employed for curve fitting purposes. The error is estimated to be $\pm 10\%$.

(13) Spectra were taken at a variety of cluster exposures ranging from 0 to > 10 L ($1 \text{ L} = 1 \times 10^{-6}$ Torr s). The gold surface became totally saturated after ~ 5 L of exposure.

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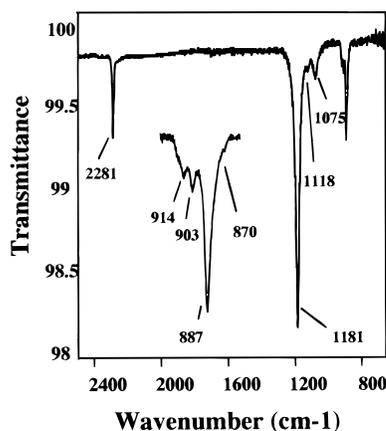


Figure 3. RAIRS of the interface derived from $\text{H}_8\text{Si}_8\text{O}_{12}$ chemisorbed to gold.

Reflection absorption infrared spectroscopy (RAIRS) at 1 cm^{-1} resolution was also used to characterize the adsorbed clusters (Figure 3).¹⁴ The spectrum has the following clearly resolvable peaks: $\delta(\text{H}-\text{SiO}_3)$ 887, 903, and 914 cm^{-1} , $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ 1075, 1118, and 1181 cm^{-1} , and $\nu(\text{H}-\text{SiO}_3)$ 2281 cm^{-1} . There are also shoulder features at 2274 and 870 cm^{-1} . The $\delta(\text{H}-\text{SiO}_3)$, $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$, and $\nu(\text{H}-\text{SiO}_3)$ features shift a total of 8, 15, and 0 cm^{-1} , respectively, between 1 and 5 L of cluster exposure to the surface ($1\text{ L} = 1 \times 10^{-6}\text{ Torr s}$). No accompanying surface $\nu(\text{Au}-\text{H})$ is observed; however, at $20\text{ }^\circ\text{C}$ hydrogen should recombine on the Au surface to form dihydrogen, similar to proposals made for alkanethiol SAMs.^{1a}

The frequencies and intensities of the features observed in the RAIRS experiment suggest a lowering of cage symmetry from O_h to C_{3v} upon surface binding. The features are consistent with the data collected for other monosubstituted clusters in solution such as $(\text{CO})_4\text{CoH}_7\text{Si}_8\text{O}_{12}$, $\text{C}_6\text{H}_{13}-\text{H}_7\text{Si}_8\text{O}_{12}$, and $\text{Ph}-\text{H}_7\text{Si}_8\text{O}_{12}$.¹⁵ The RAIRS results are also qualitatively similar to those observed for monovortex binding of $\text{H}_8\text{Si}_8\text{O}_{12}$ to $\text{Si}(100)$.^{7e,f}

Infrared band positions and intensities were calculated by using nonlocal density functional theory to further support the proposed model for bonding at the surface.¹⁶ On the basis of the aforementioned comparison, C_{3v} symmetric $\text{Au}-\text{H}_7\text{Si}_8\text{O}_{12}$ was used as a model structure for the calculation. Table 1 illustrates a comparison between the experiment and theory as well as the assignments of each spectral feature.

There are two major error sources for this theoretical method. It does not account for vibrational anharmonicity and it calculates the total dynamic dipole for the intensity prediction. Due to the surface selection rule, only the perpendicular component of the induced change in the net dipole moment will be observed experimentally.^{7e,17} Thus, low-intensity vibrations with significant components in the xy plane will be extremely difficult to detect. Furthermore, resolution of the predicted 1177 and 1176 cm^{-1} modes in the $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ region as well as the 2299 and 2302 cm^{-1} in the $\nu(\text{Si}-\text{H})$ region is not expected as these intense bands will overlap experimentally.

(14) The RAIRS apparatus and experimental methodologies have been described in detail in ref 7f. Both p and unpolarized light were used for these experiments. No difference was observed consistent with the expected metal surface selection rules. A trace peak was detected at $\sim 1174\text{ cm}^{-1}$ when using s-polarized light (coincident with the most intense feature in the p-polarized spectrum). This may simply result from imperfections in the polarizer.

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Table 1. Vibrational Mode Assignments for RAIRS of $\text{H}_8\text{Si}_8\text{O}_{12}$ Clusters Adsorbed to Gold^a

| mode description and symmetry | $\text{H}_7\text{Si}_8\text{O}_{12}$ on gold 1 cm^{-1} resolution | $\text{AuH}_7\text{Si}_8\text{O}_{12}$ B3-LYP freq (intensity) | % diff between theory and expt | |
|---|--|--|--------------------------------|------|
| $\delta(\text{Si}-\text{H})$ | E | 870 vw | 873 (71) | 0.34 |
| $\delta(\text{Si}-\text{H})$ | A_1 | 887 m | 923 (665) | 4.1 |
| $\delta(\text{Si}-\text{H})$ | E | 903 w | 927 (331) | 2.7 |
| | A_1 | 914 vw | 941 (36) | 3.0 |
| $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ | E | 1075 w | 1090 (1) | 3.2 |
| | A_1 | | 1109 (286) | |
| $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ | E | 1118 w | 1159 (17) | 2.4 |
| | A_1 | | 1145 (543) | |
| $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$ | E | 1181 vs | 1177 (1911) | 0.34 |
| | A_1 | | 1176 (1945) | |
| $\nu(\text{Si}-\text{H})$ | E | 2274 vw | 2298 (20) | 0.92 |
| | A_1 | 2281 m | 2295 (5) | |
| | E | | 2302 (342) | |
| | A_1 | | 2299 (192) | |
| | A_1 | | 2308 (27) | |
| av % diff | | | | 2.1 |

^a The presented intensities are calculated using the total dynamic dipole, not just the component perpendicular to the surface plane.

There is good agreement between theory and experiment which further supports the proposed single-vertex model. The average error in the range $2300-800\text{ cm}^{-1}$ is 2.1%. This is consistent with the errors described for other theoretical models of cluster/surface interfaces.^{7e} An additional calculation with gold atoms attached to two cluster vertices (C_{2v} symmetry) was completed for comparison. Features with moderate intensities were predicted in the $\delta(\text{Si}-\text{H})$ and $\nu(\text{Si}-\text{H})$ regions that are not observed experimentally.

The peak shifting detected in RAIRS as the surface becomes saturated with clusters is ascribed to intercluster hydrogen bonding. Hydrogen bonding is observed in the solid state for $\text{H}_8\text{Si}_8\text{O}_{12}$.¹⁸ Since the number of intermolecular interactions is expected to increase as a function of surface coverage, the peak shifting suggests clusters are in close contact with each other on the surface, especially at saturation. Peak shifting of this kind is frequently taken as evidence of self-assembly.^{1a,6,19}

The stability of the $\text{H}_7\text{Si}_8\text{O}_{12}$ layer on gold was also investigated. Treatments of $>36\text{ 000 L}$ oxygen ($1\text{ L} = 1 \times 10^{-6}\text{ Torr s}$) caused no observable change in the Si 2p core levels or RAIRS. A similar lack of reactivity toward water was also noted by RAIRS. By way of comparison, the Au-Si bond in $\text{MePh}_2\text{P}-\text{Au}-\text{SiPh}_3$ is also stable toward water.²⁰ The Si-Au linkage is also stable to extended UHV exposure. No change is observed by XPS after 24 h in a vacuum. These tests support the chemisorption of $\text{H}_8\text{Si}_8\text{O}_{12}$ to gold and suggest a fairly robust Si-Au bond.

A surprising Si-H activation at $20\text{ }^\circ\text{C}$ resulting in the chemisorption of $\text{H}_8\text{Si}_8\text{O}_{12}$ clusters to gold has been presented. Combined XPS and RAIRS studies indicate the surface consists of $\text{H}_7\text{Si}_8\text{O}_{12}$ clusters attached via one vertex to a surface gold atom (Figure 1). The infrared assignments have been supported by nonlocal density functional calculations. The generality of the gold mediated Si-H activation is being further studied. STM experiments are underway to elucidate the orientation and packing of the clusters on the surface.²¹

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