

H₈Si₈O₁₂ Clusters on Si(100)-2x1 and Gold: A Comparative Infrared Spectroscopic Study

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Introduction: The chemisorption of H₈Si₈O₁₂ (**1**) clusters on surfaces provides a facile method for the formation of a structurally well-defined layer of silicon oxide on a variety of surfaces. A number have been explored including Si(100)-2x1 and Si(111)-7x7,¹ and gold.² The cluster bonding geometries proposed for Si(100)-2x1 and gold based upon X-Ray Photoemission (XPS) and Reflection-Absorption Infrared Spectroscopy (RAIRS) are illustrated in **Figure 1**. In this paper, new synchrotron based RAIRS data in the 350-1000 cm⁻¹ region are discussed for both systems. The complete set of RAIRS data is compared for cluster adsorption on silicon and gold and the implications concerning the orientation of the cluster on the surface are examined.

Methods and Materials: Monolayers of **1** were prepared and analyzed using the following procedures. A Si(100)-2x1 wafer containing a buried metal layer (BML) was flashed to 1050°C and allowed to cool. These samples were purchased from S. Mantl, KFA-Julich. A background scan was collected before exposing the sample to a saturating dose of clusters. A second "sample" scan was then taken and ratioed to the background to arrive at a final plot. For the gold substrates, ~ 50 nm of Au was evaporated onto Cr/SiO₂/Si(100)-2x1 samples. RAIRS in the 350-1000 cm⁻¹ region was completed at U4IR at the NSLS using a liquid-He-cooled Cu/Ge detector.¹

Results: A comparison of the RAIRS data for **1** chemisorbed to Si(100)-2x1 and gold in the 350-1000 cm⁻¹ region is illustrated in **Figure 2**. The 750-2500 cm⁻¹ region has been discussed elsewhere.¹ In short, the spectra are very similar, exhibiting a similar pattern of ν(H-SiO₃), ν_{as}(Si-O-Si), and δ(Si-H) features at roughly 2280, 1180 and 890 cm⁻¹. The δ(Si-H) features are illustrated in Figure 2 and presented with the vibrational modes of the cluster framework (ν_s(Si-O-Si) at 571 (Au) and 576 (Si) cm⁻¹, δ(O-Si-O) at 411 (Au) and 414 (Si) cm⁻¹). These synchrotron data provide new support for the clusters remaining intact during the chemisorption process and are consistent with a single-vertex bonding geometry. Although the spectra are similar in a general fashion, there is one striking difference. The RAIRS data for **1** on silicon includes a distinct feature at 820 cm⁻¹ that is absent from the data for cluster on the gold surface. Upon deuteration of the cluster, the feature shifts to ~ 810 cm⁻¹ which suggests this peak represents a ν_s(Si-O-Si) vibrational mode of the cluster. The energy of the feature is significantly higher than expected based upon comparison to previous work by Calzaferri on O_n and C_{3v} symmetry cluster complexes.³ However, for zeolite A and other D_{2d} variations of the cluster, the region between 830-860 cm⁻¹ has been ascribed to ν_s(Si-O-Si) features.⁴ In summary, this peak suggests the cluster is offset from the silicon dimer row instead of oriented perpendicular. Molecular mechanics are also consistent with this assignment.

Conclusions: Synchrotron RAIRS measurements collected in the 350-1000 cm⁻¹ region for **1** chemisorbed to Si(100)-2x1 and evaporated gold films have permitted the direct comparison of a complete set of infrared data. Although these data support the same bonding geometry for **1** on Si and Au, the orientation of the cluster appears to be significantly different. The RAIRS data for **1** on gold is consistent with the Au-Si bond directed perpendicular to the surface (C_{3v}). However, the feature at 820 cm⁻¹ for **1** on Si(100)-2x1 suggests the cluster is offset.

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References: 1) J. Eng, K. Ragavachari, *et. al.*, *J. Chem. Phys.*, **109**, 8630, 1998 and references therein. 2) K. T. Nicholson, K.Z. Zhang, and M.M. Banaszak Holl, *J. Am. Chem. Soc.*, **121**, 3232, 1999. 3) C. Marcolli and G. Calzaferri, *J. Phys. Chem. B*, **101**, 4925, 1997. 4) M. Bartsch, P. Bornhauser, G. Calzaferri, *et. al.*, *J. Phys. Chem.*, **98**, 2817, 1994.

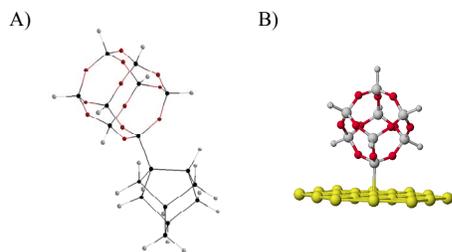


Figure 1. A) H₈Si₈O₁₂ bound to a Si-Si dimer on a nine atom silicon slab. B) H₈Si₈O₁₂ bound to a gold surface.

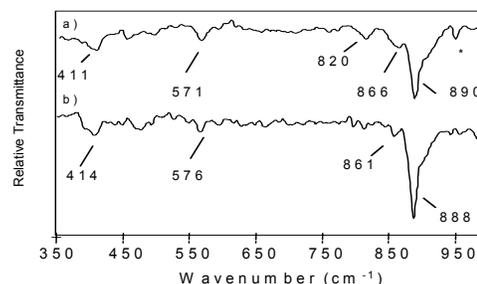


Figure 2. RAIRS of 350-1000 cm⁻¹ region of H₈Si₈O₁₂ chemisorbed to A) Si(100)-2x1 and B) gold surfaces. The * feature arises from noise within the synchrotron at the time of the experiment.