

Characterization of a Keggin Polyoxometalate on Metal and Semiconductor Surfaces

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Previous work has shown that the Keggin polyoxometalate α -[SiW₁₂O₄₀]⁴⁻ self assembles to form a monolayer on Ag and Au surfaces.^{1,2} The T_d symmetric α -[SiW₁₂O₄₀]⁴⁻ species orients with an S₄ axis perpendicular to the surface,^{1,3} and the interaction between α -[SiW₁₂O₄₀]⁴⁻ and Ag surfaces was shown to be strong.^{1,3,4} In addition, the first redox wave of α -[SiW₁₂O₄₀]⁴⁻ was absent on Ag surfaces but present on Au surfaces.⁴

In this work, surface sensitive vibrational spectroscopies are utilized to elucidate details of the strong interaction between α -[SiW₁₂O₄₀]⁴⁻ and Ag surfaces. Assignment of vibrational modes and correlation with solid and solution spectra yields valuable information regarding the nature of the surface interactions, particularly as the potential is varied. The results indicate that vibrational modes arising primarily from different parts of the molecule exhibit different potential dependent behaviors.

Polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS) was utilized to obtain IR of α -[SiW₁₂O₄₀]⁴⁻ at the Ag(111) surface as the surface potential was varied. One band found in the IR of solid α -H₄SiW₁₂O₄₀ is not found in the PM-IRRAS. Of the other four bands in the PM-IRRAS, two bands shift with potential and two bands disappear on the cathodic potential sweep.

Surface enhanced Raman spectroscopy (SERS) was utilized to obtain Raman of α -[SiW₁₂O₄₀]⁴⁻ on Ag and Au surfaces as the potential was varied, as shown in Figure 1. On Ag, one band in the SERS is not present in the normal Raman of solid α -H₄SiW₁₂O₄₀. Most bands exhibit a linear shift in energy as the potential is varied but only over a specific potential range. Furthermore, the intensities of the bands show different behavior as the potential is varied. Bands in the SERS of α -[SiW₁₂O₄₀]⁴⁻ on the Au surface usually showed a good energy match for bands observed on the Ag surface, but much less potential dependence in the SER spectra was exhibited on the Au surface.

In both the PM-IRRAS and the SERS, most bands exhibited a good energy match with bands from solid α -H₄SiW₁₂O₄₀, indicating that the polyoxometalate was intact on the surface. Assignment of the vibrational modes⁵⁻⁷ revealed that different parts of the molecule behaved in different ways as the potential was varied on the Ag surface. Furthermore, the polyoxometalate interacts with the surface primarily through W-O-W bridging moieties.

A model outlining the molecular behavior as a function of potential was set forth. In this model, the polyoxometalate was already reduced to α -[SiW₁₂O₄₀]⁵⁻ on the Ag

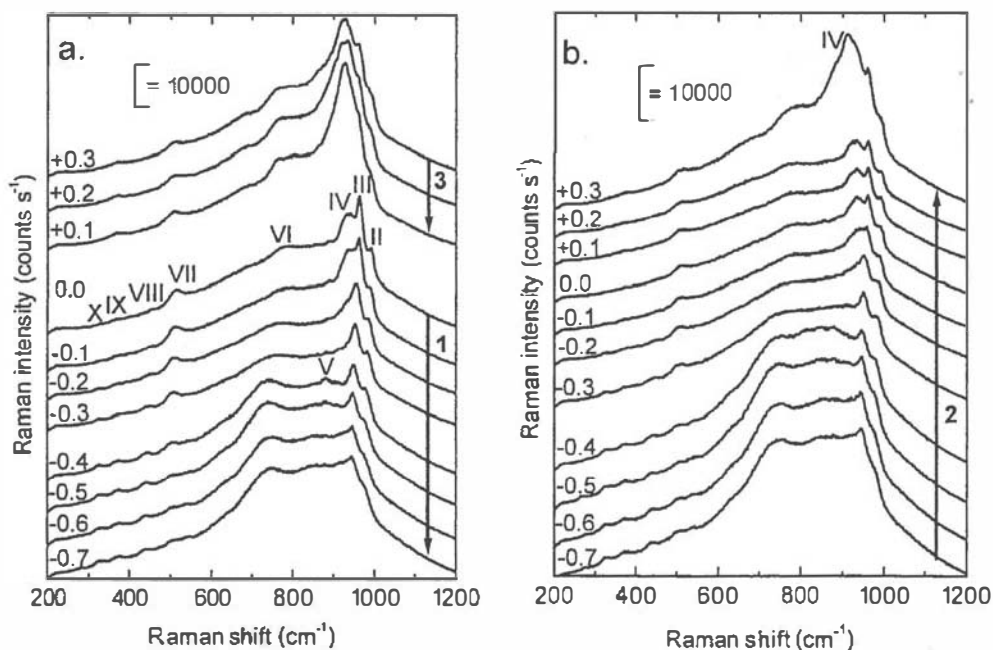


Figure 1. SERS of 0.5 mM α -[SiW₁₂O₄₀]⁴⁻ + 0.1 M HClO₄ on Ag. Potentials on the left in the panels are versus Ag/AgCl.

surface. Previous studies of polyoxometalates on Ag have indicated that polyoxometalate species are reduced upon association with the Ag surface.^{8,9} As the potential is moved in the negative direction, the molecule reorients as shown in Figure 2. This behavior can account for the potential dependent changes in peak energy and peak intensity in both the PM-IRRAS and the SERS in addition to accounting for the missing first redox wave on Ag. Furthermore, comparison of the spectroscopy obtained from Au surfaces is consistent with a weaker interaction between α -[SiW₁₂O₄₀]⁴⁻ and Au, as suggested from previous work.^{2,4}

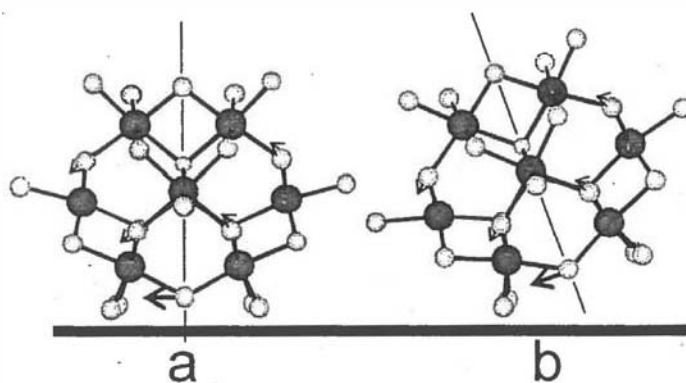


Figure 2. Side view of the polyoxometalate on the Ag surface showing the configuration a) before and b) after rotation at negative potentials on the Ag surface.

Most studies of polyoxometalates on surfaces have focused on metal or carbon surfaces. Because of the technological relevance of semiconductor surfaces, it would be

worthwhile to examine polyoxometalates on these surfaces as well. To this end, studies of α -[SiW₁₂O₄₀]⁴⁻ on Si surfaces were undertaken. One type of study involved derivatizing a Si surface with an aminosilane, yielding amino groups above the surface. When this surface with an aminosilane, yielding amino groups above the surface. When this surface was immersed in an acidic solution of α -[SiW₁₂O₄₀]⁴⁻, the amino groups protonated and the polyoxometalate was assembled on this layer via electrostatic attraction. Characterization of this layer by x-ray photoelectron spectroscopy indicated that there was a substantial amount of W^{VI} present on the surface, and IR through the sample indicated that α -[SiW₁₂O₄₀]⁴⁻ was intact on the surface.

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