**The Au(111) Electrolyte Interface: A DFT Investigation**

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Density functional theory calculations have been performed to derive a detailed model of the electric double layer for Au(111) in contact with an aqueous H$_2$SO$_4$ electrolyte. At potentials of $E \geq +0.8$ V vs. SCE various surface sensitive techniques found evidence for a ($\sqrt{3} \times \sqrt{7}$)R19.1° (bi)sulfate structure, but the nature of coadsorbates remains still unclear. Focusing on a sulfate adlayer, the coadsorption of H$_3$O$^+$ and/or H$_2$O has been studied [1]. The calculated binding energies show that the coadsorption of a single H$_3$O$^+$ per sulfate (stabilizing the adlayer by hydrogen bonds) is the most stable configuration. In addition, the charge density distribution within the adlayer well agrees with effective barrier heights deduced from recent distance tunnelling spectroscopy measurements [2]. Afterwards we studied the interfacial structure that forms at negative electrode potentials and found that water arranges near the electrode in an ice-like hexagonal structure with hydronium ions being located in the second water layer and non-specifically adsorbed. Again the calculated charge density distribution shows a perfect correspondence to distance tunnelling spectroscopy measurements. [1] S. Venkatachalam and T. Jacob, Z. Phys. Chem., 221, 1393 (2007). [2] S. Venkatachalam et al., Angew. Chem. Int. Ed., 46, 8903 (2007).

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Date submitted: 27 Nov 2007