The Au(111) electrolyte interface: A DFT investigation TIMO JA-
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Germany — 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_2SO_4 electrolyte. At potentials of $E \geq +0.8\,V$ vs. SCE various surface sensi-
tive 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 coad-
sorption of H_3O^+ and/or H_2O has been studied [1]. The calculated binding energies
show that the coadsorption of a single H_3O^+ per sulfate (stabilizing the adlayer
by hydrogen bonds) is the most stable configuration. In addition, the charge den-
sity distribution within the adlayer well agrees with effective barrier heights deduced
from recent distance tunnelling spectroscopy measurements [2]. Afterwards we stud-
ied the interfacial structure that forms at negative electrode potentials and found
that water arranges near the electrode in an ice-like hexagonal structure with hy-
dronium 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   Electronic form version 1.4