

***Ab initio* calculations for the $c(2 \times 2)$ structure of the Br/Ag(100) and Br/Au(100) surfaces**

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The adsorption of bromine on the Ag(100) and Au(100) surfaces both in vacuum and in solution have been extensively investigated by experiments and classical simulations. One of the interesting properties of the Br-chemisorbed Ag(100) and Au(100) surfaces is that bromine occupies different bonding sites on the Ag and Au surfaces. Various experimental measurements have demonstrated that while bromine occupies the four-fold hollow site on the Ag(100) surface, it prefers the two-fold bridge site on Au(100). However, previous theoretical studies have not reproduced these different chemisorption structures. In fact, *ab initio* calculations employing small cluster models failed to predict the preferred bonding site of bromine on Au(100) [1].

We performed *ab initio* total-energy density-functional pseudopotential calculations with periodic supercell models for the $c(2 \times 2)$ structure of the Br/Ag(100) and Br/Au(100) surfaces. The metal surface was modeled by repeated slabs with seven and nine metal layers separated by a vacuum region equivalent to seven metal layers. Three bonding configurations with the bromine adsorbates at the hollow, bridge, and on-top bonding sites for each of the surfaces were investigated. All the configurations were optimized, and the detailed geometric and electronic structures for each configuration were determined. The convergence of the total energies was carefully checked so that the errors of the total-energy differences were within 10 meV [2].

The obtained results are in agreement with the experimental data. The calculations show that while the hollow configuration is more stable than the bridge configuration by 210 meV/adatom for the Br/Ag(100)- $c(2 \times 2)$ surface, it is less stable by 60 meV/adatom for the Br/Au(100)- $c(2 \times 2)$ surface. The on-top configuration for both the surfaces is found to be the least stable (560 meV/adatom and 300 meV/adatom higher in total-energy than the corresponding most stable configuration for the Br/Ag(100) and Br/Au(100) surfaces, respectively).

The bond between Br and the substrate is found to be covalent with a slight polarization due to a small charge transfer from the substrate to the bromine. The chemical bonding between Br and the substrate is shown to be stronger in the hollow configuration than in the bridge configuration for both the Br/Ag(100) and Br/Au(100) surfaces. Compared with the Br/Ag(100) surface, however, the Br/Au(100) surface exhibits a reduced difference in the bonding strength between the hollow and bridge configurations. The core-core Coulomb interaction is found to be higher for the hollow configuration than for the bridge configuration. The detailed balance between the electronic and the core-core contributions to the

total energy determines hollow and bridge as the preferred bonding site on the Ag(100) and Au(100) surfaces, respectively.

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[1.] A. Ignaczak et al., J. Electroanal. Chem. 420 (1997) 71; 450 (1998) 715.

[2.] S. Wang and P.A. Rikvold, Submitted to Phys. Rev. B.