

## Rules controlling sulfur chemisorption to gold surfaces and gold nanoparticles

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### Abstract

In situ STM imaging of thiol monolayers on single-crystal Au(111) surfaces, combined with VASP and SIESTA density-functional-theory calculations for surfaces and nanoparticles, reveal the key qualitative features controlling sulfur-gold bonding. Sulfur-linked alkyl and aryl groups RS to gold surfaces and nanoparticles are commonly referred to as being “thiolates”, assuming that the gold *s* electrons form covalent bonds to the sulfur, as occurs in gold molecular clusters and thin films. However, surface atoms of bulk gold and gold nanoparticles take on noble character, pacifying them by making the *s* orbitals unavailable for bonding. Instead, very strong van der Waals interactions between S and the gold *d* orbitals dominate the bonding. Exposure of SAMs to thiolates or to conditions in which they could form results in destruction of the SAM, not surface passivation. Superatom theories for the structure of nanoparticles, which assume thiolate character, are shown to be inapplicable to the description of chemical properties. Gold adatoms above surfaces are also passivated through direct links to the surface and through superexchange via sulfur and therefore take on the Au(0) valence state of bulk gold. Sulfur may bind either to adatoms or directly to flat surfaces, and the rules controlling which motif is generated are described. These can be used to avoid the intense surface pitting associated with adatom-containing AMs. Examples are shown in which both motifs pack together in the same SAM. The factors controlling SAM chirality, with implications for chiral syntheses, are determined.

### Biography

Jeff Reimers studied organic spectroscopy under Ian Rodd and Gad Fischer before doing a PhD with Bob Watts on the structure, thermodynamics, and spectroscopy of water and ice. He then studied semiclassical quantum mechanics in USA under Kent Wilson and Rick Heller before returning to Australia to be an ARC Research Fellow from 1985 to 2010 at the University of Sydney. There he collaborated extensively with Noel Hush and Max Crossley on problems involving electron transfer, molecular electronics, porphyrin chemistry, and photosynthesis. Last year he moved to a joint appointment at UTS and Shanghai University, focusing on protein crystallography. His work spans a wide range of chemical applications, from mutagenesis to electrical engineering to the origins of consciousness. He has received the RACI Physical Chemistry Division Medal and the H.G. Smith Medal, and is a Fellow of the RACI and the Australian Academy of Science.