A UPD Surface Compound:
Structure and Energetics

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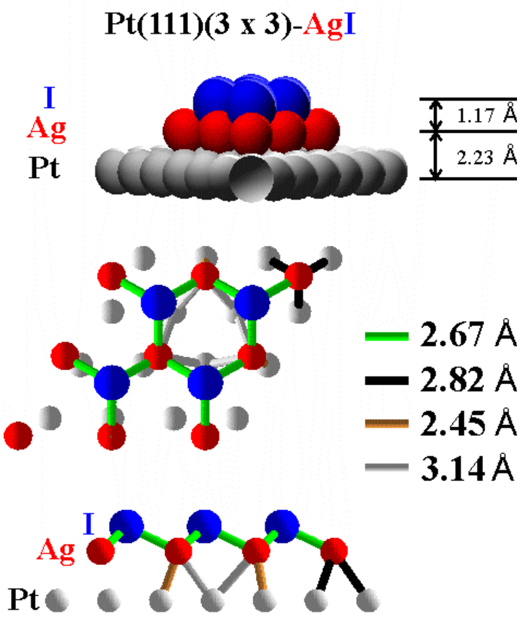

The initial stage of underpotential electrodeposition of Ag on Pt(111)(√7 x √7)R19.1°-I gives a Pt(111)(3 x 3)AgI surface compound (AgI(ads)) containing 4/9 ML Ag and 4/9 ML I in a structure that is like a slice of bulk AgI laid on the surface but laterally contracted by 10%. By combining detailed structural data with the cohesive energy determined by a thermodynamic analysis, insight into the nature of the bonding can be obtained.

The atom locations in this structure have recently been determined by tensor LEED [1]. A layer of Ag atoms lies above the surface Pt atoms, but shows no significant corrugation. One Ag atom in the unit cell occupies an f.c.c. hollow site on the Pt, but the other three atoms occupy asymmetric “near atop” sites. A layer of I atoms lies above the Ag layer, bonded to it with bonds that are locally tetrahedral and whose lengths are consistent with bond orders of 4/3. That is, these covalent bonds are similar to those in bulk AgI, after correcting for the fact that the iodine atoms have one less bond owing to the surface termination. We suggest that the directional preference of the Ag-I bonds forces some of the Ag atoms into the unusual asymmetric sites with respect to the Pt underlayer, and explains why these Ag-Pt bonds are anomalously short.

The energetic rationale for this was found by studying the energetics of the AgI(ads). We combined experimental thermodynamic data from electrochemistry (AgI(ads) → I(ads) + Ag(s)), iodine thermal desorption spectroscopy (I(ads) → I(g)) and contact-angle measurements (for immersion of AgI(ads) and emersion of I(ads)). The cohesive energy of the AgI(ads) surface structure was thereby estimated as 530 ± 20 kJ/mol. Simple bond-energy addition suggests that about two-thirds of the bond energy of the structure is in the Ag-I bonds and one-third in the Ag-Pt bonds. Thus we see the energetic rationale for the dominance of the Ag-I interactions – they contain the majority of the bond energy

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[1] M. Labayen, D.A. Harrington, M. Saidy, and K.A.R. Mitchell, *Surface Science*, 490 (2001) 256).

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