

Experimental and Theoretical X-ray
Photoemission Studies of Island Decorated
Platinum Single Crystal Electrodes - P. Bagus
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Data will be presented on XPS results of spontaneously deposited adlayers of ruthenium and osmium on the Pt(111) electrode. When such an electrode is brought in contact with RuCl₃ or OsCl₃-containing solutions, highly oxidized layers of either ruthenium or osmium are formed. Upon the potential scan in the negative-going direction in 0.1 M H₂SO₄ solution, the oxidized layers are reduced, and nanosized, pure metallic Ru or Os islands are formed on the platinum surface. These layers have been studied experimentally by XPS at Urbana-Champaign, and theoretically at College-Station. Comparison of the data obtained by XPS to those obtained by the use of electrochemical NMR (EC-NMR) will be made.

In this context, a comprehensive review of different mechanisms, which contribute to chemical shifts of core-level binding energies, BEs, in XPS measurements is made. A principle focus is on showing how the mechanisms can be used to relate the BE shifts to features of the chemical bonding and chemical interactions in the studied system. Several initial state mechanisms are identified; while some are well known, the importance of others has been only recognized fairly recently. A theoretical framework is presented which places the analysis and interpretation of these BE shifts on a firm foundation. A rigorous definition and distinction of initial and final state effects are presented. This definition is applied to show that initial state effects are often the dominant factors for the chemical BE shifts. It is also shown that, in many cases, theoretical approaches involving the use of constrained variations can permit a clear and definitive separation of the contributions of the different mechanisms. Several representative applications to the analysis and interpretation of core-level BE shifts are described which show how the theoretical methods of analysis can be used to identify the mechanisms important for the BE shifts. Often more than one mechanism makes an important contribution to the shifts and it is common that the contributions will be canceling. When all of the relevant mechanisms are taken into account in the analysis of the BE shifts, these shifts do provide valuable information about the chemical bonding and electronic structure of the materials being studied. The mechanisms presented and the theoretical frameworks described provide a unified view of BE chemical shifts.