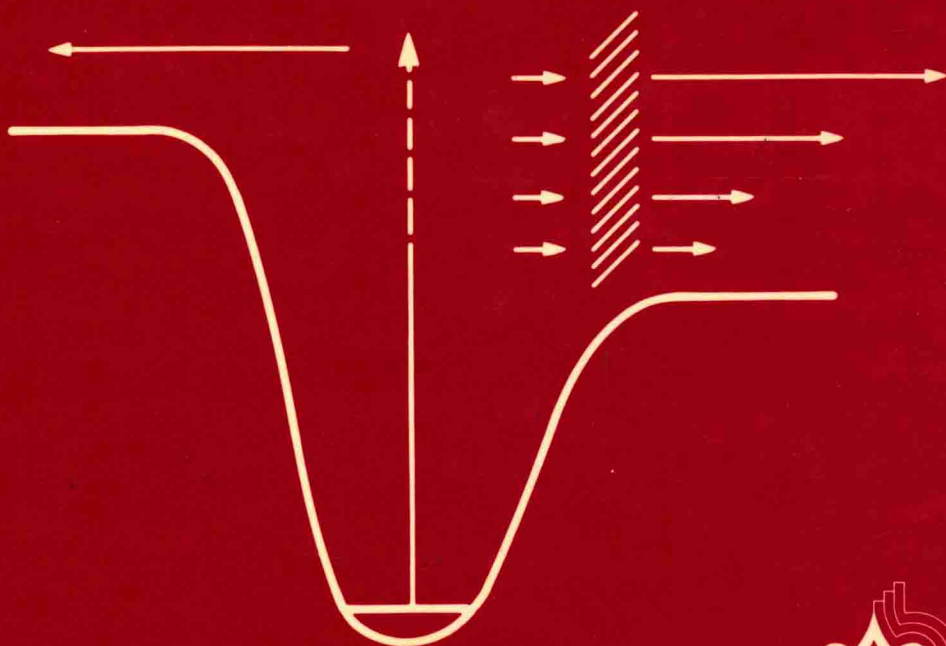


Chemistry and Structure at Interfaces

New Laser and
Optical Techniques

Edited by

Richard B. Hall and Arthur B. Ellis



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Chemistry and Structure at Interfaces

New Laser and Optical Techniques

Preface

This volume is a collection of review articles on recent investigations of chemistry and structure at interfaces. The collection stems from a three-day symposium entitled "Photoprocesses at Solid Surfaces" held at the National Meeting of the American Chemical Society in Seattle, Washington in March, 1983. One of the highlights of the symposium was a session on new laser and optical techniques at which each of the contributing authors was an invited speaker. There was a keen interest in this session for obvious reasons. Techniques based on stimulus and response involving photons are applicable to the study of surfaces in high pressure and condensed phase environments, including many of great technological importance such as catalysts, electronic materials, lubricants, surfactants, and biological cells and membranes. At the meeting, the authors described new and promising, but in some cases immature, methods. Considerable progress has been made since that time and the current works review these areas in depth. In most cases, efforts through mid-1985 are included in the reviews.

Each of the chapters gives an overview of the experimental techniques employed, however the emphasis is on what has been learned about surface chemistry and bonding. The first three chapters describe investigations of interactions at gas-solid interfaces. These investigations supplement conventional ultra-high-vacuum surface science studies, providing new information on bonding and configurations in the near surface region and on the dynamics and kinetics of molecular interactions at the surface. The next three chapters describe investigations of interactions at liquid-solid interfaces. These studies break new ground in the study of bonding, molecular orientation, electron transfer and chemical interactions at surfaces in the presence of fluid overlayers.

We have made no attempt to provide a complete survey of works in this field. Rather, we have tried to provide an in depth sampling of selected efforts. We believe the studies reviewed here exemplify the rapidly expanding effort in the application of laser and optical methods to the study of interfacial processes.

We would like to thank the contributors to this volume for their extended efforts. We would also like to thank Mrs. Marianne Kane and Mrs. Claudette Desiato for their skill and extreme patience in preparing the camera-ready copy for this book.

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**1. EXAMINATION OF THE GAS-SOLID AND METAL-SUPPORT
INTERFACES IN SUPPORTED CATALYSTS BY NEAR EDGE
X-RAY ABSORPTION SPECTROSCOPY**

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1.1. Introduction

Catalysts consisting of small metal particles dispersed on a high-surface-area oxide support are of great technological importance and scientific interest. The local coordination geometry and the electronic structure of the metal particles, which can be as small as 10 Å in diameter, may differ significantly from the coordination geometry and electronic structure of the bulk metal. In order to understand the catalytic properties of these materials, it is necessary to determine exactly how the metal particles differ from the bulk metal. In some cases the properties of the metal particles may be modified by interaction with the support, so information on the metal-support interface is also required. Chemisorption may also cause changes in the particle structure. X-ray absorption spectroscopy is an ideal technique for investigating the particle structure of these metals because it is element-specific and it is sensitive to the local environment around the absorbing atom.

With the availability of synchrotron radiation, X-ray absorption spectroscopy has been increasingly used to obtain information on the local structure of materials. Extended X-ray Absorption Fine Structure (EXAFS) is now

established as an important tool for investigating the local structure of complex disordered systems, including catalysts [1]. The region of the X-ray absorption spectrum used in EXAFS lies far above (> 100 eV) the absorption edge of the excited atom. However, the near edge region, within 50 eV of the absorption edge, can also provide information, largely complementary to the information that is obtained from EXAFS. In the case of catalysts, an analysis of the near edge region has given information about changes in the electronic structure of the catalyst caused by the support or by chemisorption and has also been used to determine the local structure around a particular site. Near edge spectroscopy of this region has been referred to by a number of different acronyms including NEXAFS (Near Edge X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Structure).

In the EXAFS region of the X-ray absorption spectrum, the emitted electron has a high kinetic energy and is weakly scattered by the surrounding atoms, whereas in the near edge region the kinetic energy of the emitted electron is fairly low and the scattering much stronger. The amplitude of the intensity oscillations in the absorption spectrum in the near edge region is therefore much larger than in the EXAFS region. Near edge structure, however, may be more difficult to interpret than EXAFS because multiple scattering of the emitted electron becomes more important as the kinetic energy of the electron is reduced. The standard EXAFS single scattering formalism has recently been extended to include these multiple scattering effects [2,3], thus allowing this formalism to be used to analyze the near edge region. Multiple scattering theory has for some time been used to carry out molecular orbital calculations on molecules and clusters with the Scattered Wave $X\alpha$ (SW- $X\alpha$) method [4]. The same technique can also be used to calculate continuum states, and $X\alpha$ calculations have quite accurately reproduced the near edge structure of small molecules [5] and ions [6]. A somewhat different formalism for multiple scattering in molecules and clusters, based on Low Energy Electron Diffraction (LEED) theory, has been developed by Durham et al. [7,8] and has been used to analyze the near edge structure of metals [9], compounds [10] and adsorbates [11]. The near edge structure in metals has been shown to reflect the local density of states obtained in band structure calculations in the region above the Fermi level [12].

A number of different theoretical techniques therefore are now available for the analysis of near edge structure. Multiple scattering effects, while complicating the theory, can provide important information on the local structure around the excited atom. We will now review what has been learned about catalysts from an analysis of their near edge structure with the aid of multiple scattering theory.

1.2. Electronic Structure of Catalysts from L Edge Resonances

At the L_2 and L_3 edges of transition metals and their compounds, there are usually found fairly sharp, intense resonances sometimes known as "white lines." The resonances at the L edges of osmium metal are shown in Figure 1.1. Since transitions at the L_2 and L_3 edges must originate in the $2p_{1/2}$ and $2p_{3/2}$ core orbitals, the upper state must have d or s orbital character. Calculations have shown that transitions from the 2p core orbital to s valence orbitals are much weaker than the corresponding transitions to d orbitals [13], and can effectively be ignored. The L edge resonance lines therefore correspond to transitions to empty states in the d band in metals and to transitions to exciton levels having some d character in compounds. There was found to be an approximate correlation between the intensity of the L_3 edge resonance in a series of metals and the d orbital occupancy obtained from band structure calculations [14]. This led to the suggestion that the white line intensities could be used to follow changes in the electronic structure of catalysts.

There have been a number of attempts to obtain an accurate analysis of the relationship between d orbital occupancy and white line intensity. Lytle et al. [15] measured the area of the L_3 edge resonance in the absorption spectra of a series of platinum and iridium compounds. They subtracted the L_3 edge area in a pure metal from the area of the L_3 resonance in the given compound and were able to correlate the difference in area with the amount of charge transferred from the d orbitals on the metal atom to the ligands in the various compounds. Estimates of the extent of charge transfer were obtained from the metal and ligand electronegativities using Pauling's empirical relationship between ionic character and electronegativity [16]. A