

Structures of Adsorbate Layers and Electronic
Configurations of Metal Clusters

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Research Scope and Objectives

A fundamental problem in heterogeneous catalysis is to understand the structure and bonding of adsorbates to substrates. The transformation of adsorbate molecules from reactants to intermediates and finally to desorbed products from catalyst surfaces is the result of bond making and breaking processes whose favorable outcome depends on subtle and poorly known surface electronic structural rearrangements.

Our aim is to achieve insights into these questions by

- (1) developing a sensitive new technique to determine in a facile way certain geometrical features of adsorbate structures, and
- (2) determining the electronic structures of small ligand-free metal clusters before and after reaction with molecules important in catalysis.

Description of Research Effort

(1) Primary Structure and Composition of Adsorbate Layers via "Static" Mode Laser Fluorescence and Auger Spectroscopy

Laser fluorescence spectroscopy of sputtered species (LFS) is being developed in our laboratory as a new tool for determining the primary structure of adsorbates on metal surfaces. Without significantly changing the adsorbate/metal ratio during a measurement ("static" mode), it is now possible to determine in a facile way whether adsorbates, such as oxygen and nitrogen, form overlayer or underlayer assemblies and to follow aspects of surface reconstruction as a function of surface coverage. LFS results for nitrogen adsorption on polycrystalline Ti metal have confirmed earlier LEED observations by others of underlayer formation at coverages not exceeding one monolayer. Oxygen adsorption, on the other hand, proceeds to form two full underlayers with surface reconstruction occurring between the first and second underlayer. Sequential dosing of a Ti surface with nitrogen and oxygen or dosing with N₂O, NO, and NO₂ results in mixed composition layers, each composition being reproducibly dependent either on dosing sequence or on the particular nitrogen oxide used as the adsorbate.

(2) Spectroscopy of Ligand-Free Metal Clusters in Noble Gas Matrices

The fact that metal clusters containing of the order of 100 atoms display catalytic activity raises questions concerning catalyst action, and in a more general sense, the evolution of bulk metal properties as a

function of cluster size. Intense theoretical and experimental effort has been devoted in the last few years to determine the electronic structures of the smallest clusters, the transition metal diatomic molecules, which with their densely packed manifolds of low-lying states are the simplest systems to display many of the subtle effects of d-bonding.

The chromium dimer molecule Cr_2 , has come to occupy a central role in this field. We have studied this molecule in Ar and Kr matrices using absorption, excited state absorption, and laser fluorescence techniques. On irradiating a resonance transition of Cr atoms, one finds that photo-diffusion leads to bleaching of the atomic bands revealing for the first time a higher energy dimer transition at 340 nm which is assigned to the $1\Sigma_g \rightarrow 1\Pi_u$ transition. Laser stimulated fluorescence is observed from a trap level to lower-lying level, possibly $3\Sigma_u$, which shows a vibrational progression at 241 cm^{-1} . The $1\Pi_u$ state appears not to be predissociated in contradistinction to the $1\Sigma_u$ state, and it will be of interest to do a rotational analysis of this state using RIMS in seeded expanded jet experiments. An energy level diagram has been constructed based on the earlier RIMS data of Riley, *et al.* (CHM Division) which incorporates our latest matrix isolation data and which is consistent with all of the spectroscopic and thermodynamic data available on this important molecule.

Future Research

(1) Primary Structure and Composition of Adsorbate Layers

The LFS results on oxygen and nitrogen covered Ti surfaces will be extended to Ag and Fe surfaces.

The use of resonance ionization spectroscopy (RIS) for the study of sputtered atoms is expected to give a 10^5 gain in sensitivity versus laser fluorescence. This enhancement results from the ability to extract and then count each ion produced during the laser light pulse. Photons, on the other hand, are isotropically emitted giving, with detector considerations, a 10^{-5} counting efficiency (photons emitted/photons counted). In the Surface Analysis by Resonance Ionization of Sputtered Atoms (SARISA) technique, surface damage and surface compositional changes will be negligible because of the requisite low ion beam currents (10^{-12} amps).

(2) Spectroscopy of Ligand-Free Metal Clusters in Noble Gas Matrices

Further elucidation of the electronic structures of small ligand-free metal clusters will continue using absorption, laser fluorescence, excited state absorption and optical-optical double resonance techniques. These will be compared with e.p.r., MCD, and EXAFS data as well as with theoretical calculations.

Work on the photochemical formation of molybdenum atom-dinitrogen complexes will be extended in new directions. We plan to investigate the thermal stabilities of $\text{Mo}(\text{CO})_{6-x}(\text{N}_2)_x$ species in an attempt at isolating these interesting complexes as crystalline solids.