

## Auger Electron Spectroscopy

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### Research Scope and Objectives

The overall goal of our research is to systematically develop the ability to identify the local chemical environment about adsorbed species. The program is structured to depend heavily on equivalent spectra for gas phase molecules in order to develop models for spectral analysis. The development of both a fingerprint level data base and the establishment of the classes of information content is necessary to understand the spectra of adsorbed species.

### Description of Research Effort

As a result of a systematic effort over the past few years, we have shown that the information content of Auger Electron Spectroscopy can be separated into three broad classes. First, the overall fingerprint character of the spectra carries information about the bonding symmetry local to a specific site. Second, the relative intensity of Auger transitions from different atomic sites carries information about the spatial distribution of electron density in the molecular orbitals. Third, the magnitude of the final state hole-hole interaction energy carries information as to the extent of chemical delocalization. We will give one example from recent work for each of these areas.

In collaboration with D. W. Goodman at Sandia we have investigated the active and inactive forms of carbon involved in CO methanation. On Ni(111) the active form of carbon yields a C(KVV) Auger spectrum which is identical in fingerprint to that for methylsilane and other C species in which the C is present with  $C_{3v}$  symmetry, implying that the carbon atom is bound in the three fold site. In contrast, the active carbon on Ni(100) yields a spectrum which is uniquely different from any known gas phase species consistent with bonding in the four fold site with a local symmetry for which no molecular analog exists. The inactive form of surface carbon gives a spectrum nearly identical to that of graphite. The only major difference is the existence of a high energy shoulder indicative of bonding via charge transfer from the metal to empty states of the graphite layer.

In collaboration with J. W. Rogers and J. S. Binkley at Sandia we have investigated the C(KVV) spectra of a series of nitro aromatic chemical explosives. For this class of explosives systematic changes are observed in the higher energy  $\pi$  region of the C(KVV) spectra as differing numbers of resonant electron withdrawing nitro groups or electron donating amino groups are added to the benzene ring. We suggest, in aromatic explosives such as 1,3,5-trinitrobenzene where hydrogen bonding is not important, that explosive sensitivity correlates directly with ring instability resulting from loss of  $\pi$  electron density relative to benzene. However, in aromatic explosives such as 1,3,5-triamino-2,4,6-trinitrobenzene where ring stability is decreased due to occupation of benzene like antibonding levels, shock sensitivity is mitigated by strong intra and intermolecular hydrogen bonding.

In collaboration with J. W. Rogers at Sandia and D. A. Ramaker of the Naval Research Laboratory we have investigated in detail the C(KVV) spectrum of graphite as an extension of our previous work on aromatic molecules. For this class of molecules, spectral transitions result from two distinct types of bonding orbitals: the delocalized  $\pi$  levels and the more localized  $\sigma$  levels. Transitions involving the  $\pi$  levels yield a value of the final state hole-hole repulsion energy indicative of the delocalized character of the orbitals. For graphite this value is zero while for the aromatic molecules the value is consistent with the limited size of the molecule. For transitions involving the  $\sigma$  levels, however, the value of the hole-hole repulsion is larger than for the  $\pi$  levels, indicative of localization to a more limited spatial extent. For graphite the hole-hole repulsion for the  $\sigma$  levels appears to be approximately 3.5 eV, implying that the holes are localized to a neighborhood of approximately 4 Å of the initial core hole.

#### Future Work

In the future this work will have a larger component in the area of solid surfaces and chemisorption, and will include photoelectron and low energy electron scattering spectroscopies. The molecular Auger studies will be more focused in terms of specific molecular problems or as models of solid state or chemisorbed systems.