

# Molecular Surfaces— Photoionization Probes of Metal Clusters

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The intrinsic properties of isolated naked metal atom clusters ( $M_x$ ) in the size range from two to hundred atoms have been elusive to obtain yet this size range is of considerable scientific importance because the electronic, structural, magnetic and chemical properties of such clusters are expected to change from predominantly molecular to bulk character. In many ways these unsupported clusters exist as a state of matter which has been investigated very little. We produce isolated clusters of metal atoms by laser vaporization of a metal substrate within the throat of a pulsed supersonic nozzle source. The clusters are then identified and characterized by a combination of laser photoionization (both single and multiphoton ionization) and time-of-flight mass spectroscopy.<sup>1</sup> We report here early experimental results on clusters of iron ( $Fe_x$ ,  $x = 2-25$ ) and of nickel ( $Ni_x$ ,  $x = 2-25$ ) where careful analysis of the laser intensity dependence of each cluster ion signal as a function of ionizing laser frequency provides a coarse grained measure of the variation of ionization potential as a function of cluster size. As an example, consider Figure 1, where the iron data is displayed. This data shows that the ionization potential does not monotonically decrease from that of the atom to the bulk metal work function, but rather displays an oscillating behavior. Non-monotonic variations in ionization potential with cluster size have been seen in alkalis and other transition metals with filled  $d$  shells and one  $s$  electron such as copper and silver. These show even/odd alternation

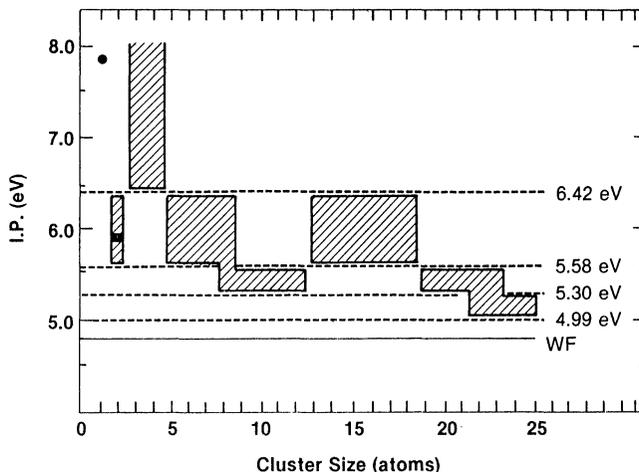


FIGURE 1 Iron cluster ionization potentials as a function of cluster size obtained from the intensity dependencies taken at the four ionizing laser photon energies indicated as dashed horizontal lines. Shaded areas indicate the regions in which the I.P.'s lie and overlapping boundaries show clusters for which intensity data gave inconclusive results. The point at cluster size one is the Fe atom I.P. and the solid horizontal line labelled WF is the bulk iron work function.

in IP up to  $x = 29$  due to the paired/unpaired nature of the  $s$  band. Fe ( $3d^6 4s^2$ ) represents a more complicated situation and no simple explanation can be offered. Currently theoretical calculations are underway using the  $X\alpha$ -SW method to provide an insight into the unique electronic nature of iron clusters in this size range.<sup>2</sup>

Our results for nickel show similarly that there is structure in the variation of ionization potential as a function of cluster size. These preliminary results are shown in Figure 2. For this open  $d$  shell system some theoretical calculations have been done.<sup>3</sup> Comparison of these results with theory suggest that qualitatively theoretical predictions and experimental measurements are in reasonable agreement and structural isomers of small clusters can be distinguished from the IP data. For example Ni ( $x = 3$ ) appears to prefer a bent configuration instead of a linear one. As calculations improve preferred structures of larger clusters may be similarly identified.

This avenue of research appears very promising. Similar results have been obtained for several other systems, for example, clusters

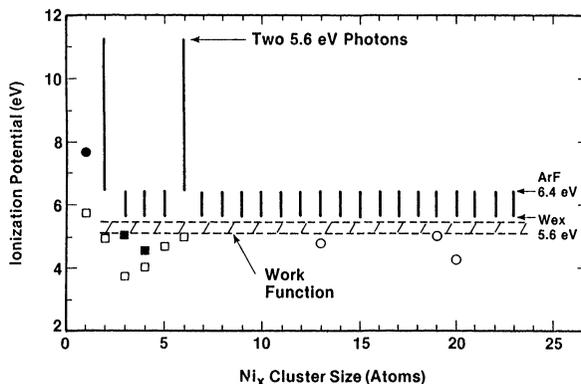


FIGURE 2 The maximum and minimum values of the ionization potentials for nickel clusters are plotted as a function of cluster size. The cross hatched area presents the range of values of the work function for nickel. The solid circle represents the value of the IP of atomic Ni (7.63 eV). The squares and circles are theoretical predictions [*JCP* **73**, 4492, 1980 and *J. Vac. Si. Tech.* **16**, 531, 1979 respectively]. The two theoretical values for  $\text{Ni}_3$  and  $\text{Ni}_4$  represent IP calculations for two different molecular structures.

of carbon, ( $\text{C}_x$ ,  $x = 2-200$ ) and  $\text{Pt}_x$  ( $x = 2-25$ ) which are currently being analyzed. It also opens up new opportunities to explore charge transfer reactions on cluster surfaces and other chemically important reactions.

## References

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