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The Atomic Structure of Transition Metal Clusters

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Chemical reactions are used to probe the atomic (geometrical) structure of isolated clusters of transition metal atoms. The number of adsorbate molecules that saturate a cluster, and/or the binding energy of molecules to cluster surfaces, are determined as a function of cluster size.

Systematics in these properties often make it possible to propose geometrical structures consistent with the experimental observations. We will describe how studies of the reactions of cobalt and nickel clusters with ammonia, water, and nitrogen provide important and otherwise unavailable structural information. Specifically, small (less than 20 atoms) clusters of cobalt and nickel atoms adopt entirely different structures, the former having packing characteristic of the bulk and the latter having pentagonal symmetry. These observations provide important input for model potentials that attempt to describe the local properties of transition metals. In particular, they point out the importance of a proper treatment of d-orbital binding in these systems, since cobalt and nickel differ so little in their d-orbital occupancy.

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1. Introduction

While considerable work has been reported on the electronic structure of metal clusters, little has been said about cluster geometrical structure. An understanding of the way the atoms pack in a cluster will provide insight into the transition from molecular behavior to bulk behavior as cluster size increases. It is also possible that amorphous metal systems are composed of clusters, i.e., the properties are dominated by the kinds of short-range forces found in small clusters. The traditional method of determining cluster structure (both geometrical and electronic) has been the observation and identification of magic numbers in cluster mass spectra. These magic numbers arise from cluster sizes having enhanced stability, hence enhanced intensity in the mass spectra. Perhaps the best known examples include clusters of alkali metal atoms [1], where stability is dominated by closed electronic shells, and rare gas clusters [2], where the closings of icosahedral, i.e., geometrical, shells and subshells determine cluster stability. For these traditional magic numbers to appear, cluster formation must be under equilibrium or quasiequilibrium conditions, since only then will the amount of a given cluster produced in the source be dependent on its stability. Such conditions are usually found in the high-temperature-oven alkali cluster sources and the adiabatic-expansion rare gas cluster sources.

Clusters of refractory materials such as transition metals cannot generally be made by these techniques. Instead, pulsed laser vaporization of a metal target located in a flow tube has proven to be an extremely useful and general method for transition metal cluster generation [3]. In this procedure, the initially white hot plume of vaporized metal atoms is

quickly cooled by a background (~ 20 Torr) of inert carrier gas. Nucleation and cluster growth quickly occur, with the ultimate cluster sizes achieved largely governed by diffusional loss of metal atoms to the walls of the flow tube. Such a growth process is far from an equilibrium one. Instead, growth is kinetically controlled, with the amount of a given cluster size produced governed primarily by the statistical probability that enough cluster-atom collisions occur to form that cluster. Cluster stability plays little role in determining mass spectral intensity. This is illustrated in Fig. 1, which shows an extensive mass spectrum of nickel clusters generated by laser vaporization. As can be seen, no magic number patterns appear. As another example of this effect, when sodium clusters are generated by laser vaporization the magic numbers characteristic of electronic shell closings disappear [4].

Another procedure for determining cluster stability, and hence perhaps providing some information on cluster structure, is to fragment the clusters in the mass spectrometer ionization process. Magic numbers have been characterized for rare gas [5] and alkali [6] clusters in this manner. However, once again the technique does not work for transition metal clusters. It appears that, due to the relatively strong binding energies in transition metal systems, the clusters may actually melt before they will evaporate atoms, and thus will lose any geometrical structural stability they might have had.

In recent years we have developed a technique for probing the geometrical structure of isolated (i.e., gas phase) transition metal clusters that is based on their chemical reactivity [7]. It seems evident that the chemical properties of clusters will depend on structure, so we in a sense turn the tables and use their chemical properties to divine their structure.

One property is the number of binding sites on a cluster for a particular adsorbate molecule, determined by counting the number of molecules that saturate the cluster. A systematic dependence of this number on cluster size may point to a particular structural motif. The primary molecular probes that we have used in this saturation scheme are ammonia and nitrogen. Another probe is based on the equilibrium reaction of clusters with a single water molecule. For a reaction at equilibrium the relative amount of a reaction product is a strong function of the cluster-molecule binding energy, which might be sensitive to cluster structure. We will present examples of such studies, using the reactions of nickel and cobalt clusters with these three reagents.

2. Experimental

As mentioned above, clusters are generated by pulsed laser vaporization of a metal target located in a flow-tube reactor (FTR) [8]. At a point downstream of the target where cluster growth has terminated and the clusters have thermalized to the FTR temperature, reagent gas is introduced, either as pure gas or as mixtures in inert gas (helium). All gas flows are continuous, so such reaction conditions as pressure, temperature and interaction time can be controlled and measured. At the end of the FTR the clusters and their reaction products expand out of a nozzle into vacuum and are formed into a molecular beam. The clusters are detected via pulsed laser ionization and time-of-flight mass spectrometry. The basic experimental procedure is to monitor changes in the mass spectra, i.e., changes in the distribution of reaction products, with changes in such

reaction conditions as temperature, reagent partial pressure, and reaction time.

For reagent saturation studies, the most convenient procedure for illustrating the interaction of a given cluster with a given molecule is to determine the coverage of the cluster, as measured by the average number $\bar{m}$ of molecules on the cluster, as a function of the reagent partial pressure in the FTR. $\bar{m}$ is calculated from the intensity-weighted average of the product peaks in the mass spectrum. A plot of $\bar{m}$ vs $\log(\text{pressure})$, what we call an *uptake plot*, describes in detail the way a cluster becomes covered with an adsorbate molecule [9]. While coverage generally increases with pressure, in some cases plateaus appear in the uptake data, where coverage is independent of pressure. The identification of such plateaus provides the most important structural information, particularly if the plateaus correspond to a single peak (having, say, m adsorbed molecules) in the mass spectra. This means that the m primary binding sites are occupied (i.e., the cluster is saturated), and the binding energy for the molecule to the $(m+1)$ th site is significantly lower than to the m th site. This implies that the $(m+1)$ th site is different in nature from the m th site, a fact that carries structural information. Sometimes a cluster will have more than one plateau in its uptake plot, meaning that more than one type of site exists on the cluster surface. Other times, different plateaus will be seen at different temperatures, implying different binding energies for the different sites. Such observations convey additional structural information.

For the equilibrium reaction with water, the important thermodynamic measurement of reactivity is the equilibrium constant K_{eq} . Since $kT \ln K_{eq} = -\Delta G^\circ = -\Delta H^\circ + T\Delta S^\circ$, variations in K_{eq} reflect variations in

$-\Delta H^\circ$, the cluster-adsorbate binding energy. Often such variations with cluster size provide important information on cluster structure.

3. Results and Discussion

3.1 Binding rules

Before structural information can be derived from an identification of the number and nature of adsorbate binding sites, it is necessary to determine the binding rules for the molecules of interest. The rules that we have developed derive from both our observations and those of surface science and theoretical studies of molecular binding to metal surfaces. For water, the rules are [10, 7a-c] 1) water binds to atop (single atom) sites, and 2) the lower the metal-metal coordination of the atom, the more strongly it binds water. Water thus identifies clusters that have unique, low-coordinate metal atoms on their surfaces. Ammonia also binds to atop sites, and also prefers atoms of lowest coordination [7a-c]. Saturation with ammonia thus can count the number of "apex" or "corner" atoms a cluster has. Molecular nitrogen has a somewhat more complex set of binding rules [11, 7d]. With a few exceptions, *all* of the metal atoms on the surface of a cluster can bind a nitrogen molecule, and some can bind two. The binding rules are: 1) N_2 binds to atop sites in the end-on configuration; 2) metal atoms that are four- or less coordinate can bind two molecules, although the second molecule is generally more weakly bound than the first; 3) metal atoms that are five- to eight-coordinate will readily bind one molecule at saturation; 4) metal atoms with nine and higher coordination will bind N_2 weakly if at all; and 5) the lower the metal-metal coordination

of a binding site, the higher the binding energy. With these rules, it is now possible to go from experimentally measured saturation levels and/or binding energies to propose possible cluster structures.

3.2 *Examples for small clusters*

As described above, the saturation of clusters with ammonia serves to count the number of "apex" atoms. This is illustrated in Fig. 2, which shows ammonia uptake plots for Ni₁₉ and Co₁₉ [12]. There is an extensive plateau at $\bar{m} = 6$ for Co₁₉. In fact, over a broad pressure range there is a single Co₁₉(NH₃)₆⁺ peak in the mass spectra. Ni₁₉ shows a smaller plateau at $\bar{m} = 12$ at substantially higher ammonia pressures, but again there is a single Ni₁₉(NH₃)₁₂⁺ peak in the mass spectra in this pressure range. The obvious conclusion from these results is that Co₁₉ has six apex or relatively low-coordinate atoms and Ni₁₉ has twelve. While there are many possible geometrical configurations for 19-atom clusters, three provide clear choices as to the number of apex atoms. These are shown in Fig. 3. The fcc octahedron and the hcp structure have six apex atoms (shown shaded in the figure) which have only four nearest neighbor metal atoms, while the remaining atoms on the clusters' surface have seven. These are obvious possibilities for the structure of Co₁₉. As it turns out, additional information suggests that the hcp structure is the most likely one for Co₁₉. The double icosahedron, also shown in Fig. 3, has 12 atoms on its caps that have six nearest neighbors, and five "waist" atoms that have eight. This cluster is a good candidate for Ni₁₉. Notice, however, that the 12 cap atoms are quite close together. The dipole-dipole repulsion forces between

adjacent bound ammonia molecules will require higher ammonia pressures to achieve saturation than for Co_{19} , as is seen in Fig. 3.

This suggestion that Ni_{19} is the double icosahedron is beautifully supported by the nitrogen uptake behavior for this cluster. The N_2 uptake plot for Ni_{19} is shown in Fig. 4 [13]. Clearly the highest saturation level for this cluster is at $\bar{m} = 17$, and the double icosahedron has 17 atoms on its surface. (The fcc and hcp structures have 18.) According to the nitrogen binding rules, all of these atoms should bind one molecule at saturation. However, at -40°C the uptake data show a short plateau at $\bar{m} = 12$, implying that 12 of the sites bind N_2 more strongly than the final five. This is entirely consistent with the double icosahedron and the fifth N_2 binding rule: the 12 sites that are initially occupied are just the 12 six-coordinate cap atoms, and the last five sites are on the five eight-coordinate waist atoms.

The data in Fig. 4 illustrate the importance of being able to measure adsorbate uptake over a wide range of temperatures. Only at -40°C is the plateau at $\bar{m} = 12$ evident. Similar uptake data have been collected at several temperatures for nickel and cobalt clusters in the 3- to 19-atom size range[7d, 14], and in most cases structures can be proposed. Figure 5 summarizes the results. As is evident, for clusters with more than seven atoms nickel and cobalt generally have different structures, with nickel tending to adopt structures based on pentagonal packing while cobalt is more likely to show packing characteristic of the bulk.

3.3 Examples for large (50 to 150 atoms) clusters

The chemical probes experiments have shown that both cobalt and nickel clusters in the 50- to 150-atom size range tend to adopt structures based on icosahedral packing [7a, 7c]. This is illustrated in Fig. 6 for the reaction of cobalt clusters with ammonia. Shown is $\bar{m}$ for two different ammonia pressures in the FTR plotted versus n , the number of cobalt atoms. It is evident that for certain cluster sizes there is a minimum in $\bar{m}$, often near $\bar{m} = 12$. The specific cluster sizes that show this minimum, at one pressure or another, include $n = 55, 71, 80, 92, 101$, and 116 . These are among the numbers of atoms that form closed shells or subshells for icosahedral packing [2]. An inspection of models of these particular clusters shows that they indeed tend to have twelve "apex" or corner atoms that should provide primary ammonia binding sites [7b]. It should be noted that the appearance of "magic behavior" for $n = 55$ is no proof that this cluster is the closed shell icosahedron. Face-centered cubic packing also produces a closed shell 55-atom cluster, the cubo octahedron, which likewise has 12 apex atoms. However, the sequence of closed subshells seen in Fig. 6 is characteristic of icosahedral packing only.

It might well be asked if saturating a cluster with adsorbate molecules could change cluster structure. This is where the equilibrium reaction with water becomes useful, since the (rather weak) interaction of a single water molecule with a cluster of tens of atoms is unlikely to alter cluster structure. As discussed above, ideally we would determine the equilibrium constant K_{eq} for the reaction of a cluster M_n :

where $K_{eq} = [M_nH_2O]/[M_n][H_2O]$, $[x]$ being the concentration of species x in the FTR. Unfortunately, it is not always possible to measure the water pressure accurately (there is often considerable background water in the

FTR) but it is usually easy to keep the water pressure constant. Also, to a good approximation the $[M_nH_2O]/[M_n]$ ratio is given by $I(M_nH_2O^+)/I(M_n^+)$, the ratio of peak heights in the mass spectra. Hence we can plot $Y = kT \ln\{I(M_nH_2O^+)/I(M_n^+)\} = -\Delta G^\circ + kT \ln[H_2O]$ vs n , and changes in Y values will reflect changes in cluster-water binding energies. Such a plot is shown for nickel clusters in the 50- to 150-atom size range in Fig. 7.

It is evident from the data in Fig. 7 that there is indeed substantial variation in cluster-water binding energies, with certain clusters showing an enhancement as a local maximum in Y . The significance lies in the sequence of cluster sizes *one atom smaller* than those clusters with enhanced water binding. This sequence includes $n = 55, 71, 80, 92$, and 101 , among others, just what is expected for icosahedral packing. The conclusion is that clusters having one metal atom more than a closed (sub)shell show enhanced water binding. This is perfectly consistent with the water binding rules outlined above, since in every case the extra atom has lower metal-metal bonds than the atoms in the closed shell or subshell. These results, and similar ones for cobalt clusters, indicate that usually saturation with ammonia does not alter the structure of these clusters.

4. Conclusions

The results presented here suggest that small cobalt and nickel clusters tend to adopt different packing schemes, while for larger clusters they more often show the same structure. These observations have important relevance to model potentials that attempt to describe the local properties of transition metal systems. It may be that the smallest clusters tend to be more molecular in behavior, and their structure will be

sensitively dependent on the d-orbital occupancy, while for larger clusters the drive to maximize the binding of surface atoms, which pentagonal symmetry does, dominates. Eventually, of course, clusters will adopt the packing of the bulk metal, but at what cluster size this occurs is not yet known.

Another feature that emphasizes the importance of d-electron binding is that our chemical probe studies generally provide little if any structural information for iron clusters, and substantial indications of icosahedral structure for copper clusters [15]. This trend is not too surprising: as the d-orbitals become progressively more filled the atoms behave more like closed shell systems such as the rare gases. Nevertheless, the variety to be found in clusters of the transition metal series offers many insights into and challenges for theoretical treatments of the origins and effects of short-range interactions in metal systems.

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FIGURE CAPTIONS

- Fig. 1 Mass spectrum of nickel clusters Ni_n . The additional peaks for $n < 25$ are due to reactions with background nitrogen. Other minor peaks are due to cluster monoxides.
- Fig. 2 Uptake plots for ammonia reacting with Ni_{19} and Co_{19} . From Ref. 12.
- Fig. 3 Models for three 19-atom clusters. Atoms that provide the primary ammonia binding sites are shown in grey.
- Fig. 4 Nitrogen uptake plots for Ni_{19} at several FTR temperatures. Adapted from Ref. 13.
- Fig. 5 A comparison of the structures of many 3- to 19-atom nickel and cobalt clusters. For Co_{15} , Ni_{16} , and Co_{16} two views of the clusters are shown.
- Fig. 6 A plot of $\bar{m}$ vs n for the reaction of ammonia with cobalt clusters in the 50- to 150-atom size region. Two ammonia partial pressures in the FTR are shown. Values of n having special significance are indicated. Adapted from Ref. 7c.
- Fig. 7 Cluster size dependence of $Y = RT \ln([\text{Ni}_n\text{H}_2\text{O}]/[\text{Ni}_n])$. Significant values of n are indicated. Adapted from Ref. 7a.

fcc

hcp

icos

Same structures:

n	Ni _n , Co _n
3	triangle
4	tetrahedron, square
5	trigonal bipyramid
6	octahedron
7	capped octahedron

Transition region:

n	Ni _n	Co _n
8	bisdisphenoid	bicapped octahedron
9	tricapped trigonal prism	tricapped trigonal prism or tricapped octahedron
10	tricapped pentagonal bipyramid

Different structures:

n	Ni _n	Co _n
12	icosahedron minus one atom	fcc/hcp minus one atom
13	icosahedron	fcc/hcp
14	bicapped hexagonal antiprism	twinned tetrahedron
15	bicapped icosahedron	centered hexagonal antiprism
16	tricapped icosahedron	C _{2v}
19	double icosahedron	hcp