PHYSICAL REVIEW B VOLUME 51, NUMBER 7 15 FEBRUARY 1995-I

Photoelectron spectroscopy of transition-metal clusters: Correlation of valence electronic structure to reactivity

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(Received 18 August 1994; revised manuscript received 18 October 1994)

The photoelectron spectra and the reactivity of H_2 with Fe, Co, and Ni clusters have been studied as a function of cluster size for clusters ranging from 5 to 26 atoms in size. It is shown that the variation of the reactivity correlates with the variation of the difference between the ionization potential and the electron affinity of the clusters. This finding is rationalized by using a simple model in which the probability of H_2 chemisorption on the cluster is proportional to the magnitude of an entrance channel barrier caused by Pauli repulsion between H_2 and the cluster. It is argued that the magnitude of this barrier is proportional to the promotion energy of an electron from the frontier orbital of the cluster to the lowest unoccupied *d* state of the cluster.

The microscopic understanding of the chemical reactivity of surfaces is of fundamental interest in chemical physics. Achieving this understanding will require close agreement between experimentally determined chemical trends and carefully constructed theoretical models.

Cluster science appears to be the natural field for the study of the microscopic mechanisms of surface reactivity. Surfaces of small clusters provide a very rich variation of chemisorption sites and are relatively simple to describe theoretically. Recently it has been shown that the reactivity of small clusters with simple molecules such as H_2 and NH_3 can vary dramatically with cluster size and form.[1–7] For H_2 chemisorption on small transition metal clusters, the reactivity was often found to change by several orders of magnitude as the size of the cluster was increased or decreased by a single atom. The origin of these dramatic reactivity oscillations with cluster size and form is not clear and represents a challenging problem in chemical physics.

Several attempts have been made to link the reactivity of clusters to features in their electronic structure. The reactivities of neutral niobium and iron clusters with hydrogen were reported to correlate with their ionization potential.[8,9] The proposed mechanism involves the promotion of an electron from the cluster into the antibonding $2\sigma^*$ state of the hydrogen molecule.[10,11] This model fails to explain the reactivity patterns of other clusters, and also fails to explain the fact that the reactivity pattern of ionized clusters is typically relatively similar to that of the neutral clusters. Alternative models for the reactivity patterns of transition metal clusters with small molecules have emphasized the details of the electronic structure of the cluster.[12,13] While such models will undoubtedly be successful in certain cases, their specificity prevents general conclusions about cluster reactivity to be drawn.

In this paper we demonstrate a strong correlation between the experimentally observed reactivity of various transition-metal clusters with H_2 and the difference between the experimentally determined electron affinities and the ionization potentials of the clusters. It will be argued that this correlation can be understood via a simple mechanism where the reactivity of the cluster is determined by the height of an entrance channel barrier due to the Pauli repulsion between H_2 and the cluster. The magnitude of this barrier is proportional to the promotion energy of an electron from the frontier orbital of the cluster to one of the more localized unoccupied states of the cluster. This mechanism is a generalization of a model originally proposed for the reactivity of transition-metal surfaces.[14]

The supersonic negative-ion laser vaporization source used in the production of clusters of iron, cobalt, and nickel clusters has been described elsewhere.[15] Clusters were produced by laser vaporization of a target disk (of iron, cobalt, or nickel) in the presence of a pulse of helium at about 300 Torr. The clusters of interest were selected by using a simple three-grid mass gate and then decelerated and crossed by a 3.5-eV detachment laser. The photoelectrons were collected by means of a recently developed magnetic time-of-flight photoelectron spectrometer.[16] Typical spectra consist of 5000–10 000 counts. Each spectrum was done three times to ensure reproducibility. The photoelectron spectra of iron, cobalt, and nickel clusters in the size ranges of 8–20, 5–26, and 7–20, respectively, were measured. The observed photodetachment thresholds of these spectra provide a measure of the vertical electron affinities. These values are only estimates because of the lack of any knowledge of (i) the Frank-Condon factors involved in the photodetachment process and (ii) the internal temperature of these species that may lead to hot bands. The electron affinities (EA's) presented in this study are obtained by drawing a straight line down the steepest slope of the first major peak in the spectra. The intersection of this line with the binding-energy axis is taken to be the EA. The estimated error is on the order of 35–40 meV. The ionization potentials (IP's) used in this study are those reported by Yang and Knickelbein.[17] Estimated errors in their values are reported to be 40 meV.

Figure 1 shows the variations of the IP as a function of cluster size for the elements iron, cobalt, and nickel. Also plotted in these graphs are the variations in the relative reactivity of the respective neutral cluster species with

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H_2. The relative reactivity is defined as

$$\kappa(N) = \ln\left[\frac{k(N)}{k(\mathrm{min})}\right], \qquad (1)$$

where $k(N)$ is the absolute rate constant of the cluster with N atoms. The constant $k(\mathrm{min})$ is the absolute rate constant of the least reactive cluster.

In Fig. 2 the electron affinity and relative reactivity are plotted as a function of cluster size. These plots are direct reflections of the variations in the valence electronic structure of these clusters. Since the reactivity of any system is a direct consequence of the valence electronic structure, these data on the EA and the IP should allow for a more in-depth investigation of the variations of the chemical reactivity of the clusters. The model that lends itself best to this analysis is the charge transfer model.[10] In this model, two crucial steps are involved: (i) charge transfer from the highest occupied molecular orbital (HOMO) of the metal to the antibonding orbital of H_2, followed by (ii) retro-electron donation from the hydrogen bonding orbital to a vacant orbital in the cluster. These charge transfer processes will be facilitated by a low IP and a large EA. Thus we expect the reactivity to correlate with the EA and anticorrelate with the IP. It can clearly be seen from these figures that neither the ionization potential nor the electron affinity correlates well with the observed reactivity.

In order to develop a more microscopic understanding of the variations of the reactivity with cluster size, the various contributions to the potential energy surface of a H_2 molecule outside a cluster will now be discussed. At large separations, the interaction between a H_2 molecule and a small cluster is characterized by a van der Waals force which is determined by the polarizability of the cluster. As the separation becomes smaller, the Pauli principle results in a repulsive force between H_2 and the cluster.[10] If no electronic rearrangement of the cluster can occur, this repulsion creates a significant entrance channel barrier for chemisorption of H_2 on the surface.[18] For chemisorption to occur, this barrier must be overcome. While the depth of the physisorption well is directly proportional to the polarizability of the cluster,[18] the height of the entrance channel barrier is proportional to the energy of orthogonalizing the frontier orbitals of the cluster to the $H_2(1\sigma)$ orbital. The barrier can be lowered by the promotion of electrons from the frontier orbitals of the cluster into states which mediate less Pauli repulsion.[18,19] Examples of such inert states are the d states, which are localized around the metal cores, or states with a symmetry different from the $H_2(1\sigma)$ orbital.

The promotion of an electron from an occupied state to

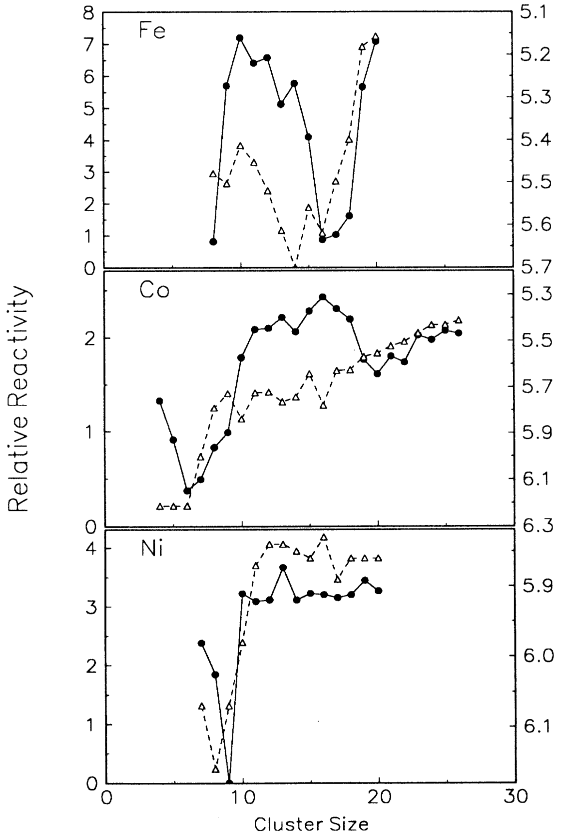

FIG. 1. Plot of the relative reactivity Eq. (1) (solid line) and ionization potential I_P (dashed line) as a function of cluster size. The upper figure is for iron, the middle figure is for cobalt, and the lower figure is for nickel clusters.

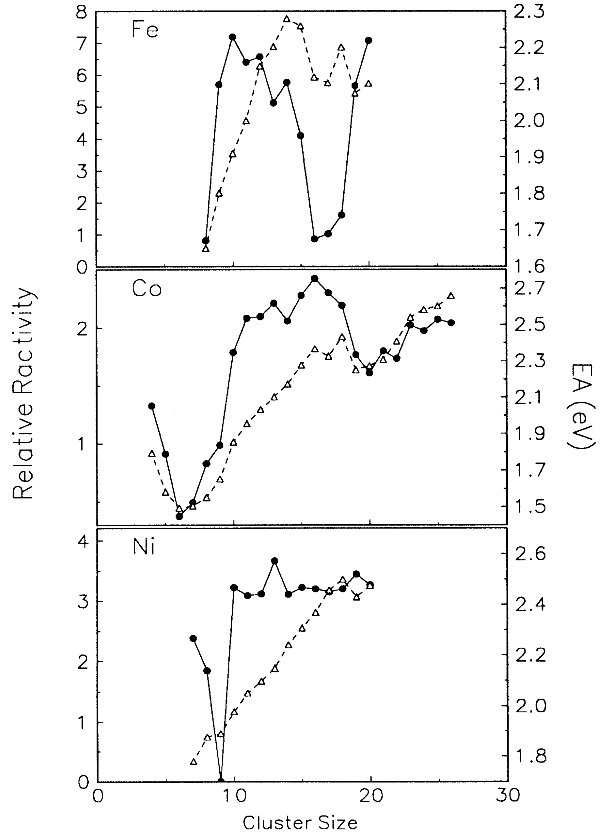

FIG. 2. Plot of the relative reactivity Eq. (1) (solid line) and electron affinity E_A (dashed line) as a function of cluster size. The upper figure is for iron, the middle figure is for cobalt, and the lower figure is for nickel clusters.

an unoccupied state will require a finite energy. Within a one-electron picture, the lowest excitation energy of the cluster is given by the difference between the HOMO and the lowest unoccupied molecular-orbital levels. A lower bound for the entrance channel barrier is thus provided by this energy difference, which can be obtained from the experimentally measured electron affinity and ionization potential of the cluster using[20]

$$E_P(N) = I_P(N) - E_A(N) - \frac{e^2}{R(N)}. \tag{2}$$

In this equation, the Coulomb energy between the electron and the positively charged cluster has been subtracted. For simplicity, this energy is calculated assuming that the clusters are spherical with a radius

$$R(N) = d_b N^{\frac{1}{3}} + r_0, \tag{3}$$

where d_b is taken to be 90% of the interatomic distance of the corresponding bulk crystal. N is the number of atoms in the cluster and r_0 is the effective image plane of the cluster. Typical values for r_0 on surfaces range from 0.6 to 1.5 Å.[21] Since the purpose of the present paper is to investigate the general trends of the reactivity, a fixed value of r_0=1.3 Å was used in Eq. (3) for all clusters. The Coulomb corrections performed are thus monotonic and do not influence the detailed variations of E_P with N.

In Fig. 3 the variation of the relative reactivity of H_2 and E_P is plotted as a function of cluster size. For Fe and Co, the correlation is clearly better than that shown in Figs. 1 and 2. For Ni, the quality of the correlation between the reactivity and E_P is similar to the correlation between the reactivity and I_p shown in Fig. 1. Since the experimental errors on E_A and I_p are estimated to be around 50 meV, variations of E_p of that order may be due to experimental uncertainties. The small variations in E_p between adjacent clusters are therefore not significant. For the Ni_{19-20} clusters, a relatively large discrepancy between the reactivity and E_P can be seen. The magnitude of this discrepancy is 0.1 eV. A possible reason for the discrepancy could be the experimental uncertainties in I_p and E_A. However, we cannot exclude the possibility that specific features in the electronic structure of the Ni_{19-20} clusters may influence their reactivity.[12,13] Another possibility may be structural changes of these clusters. Although a quantitative agreement between E_P and the reactivity for certain clusters such as Fe_8, Fe_{14}, Fe_{18-20}, Co_{10-17}, Ni_{13}, and Ni_{19-20} is lacking, the overall variation of the cluster reactivity as a function of cluster size is followed by a similar variation in $E_P(N)$.

It is important to note that a one-electron picture does not provide an accurate description of the ionization and affinity energies of the cluster. A characteristic feature of transition metal clusters is the near degeneracy of the s and d states. Thus both the ionization level and the affinity levels will to some extent contain both s and d states. The frontier orbitals of the cluster are predominantly composed of s states since the d states are localized around the metallic cores. The experimentally determined ionization potential measures the binding energy of the frontier orbitals since the cross sections for photoexcitation of s states are larger than the cross section for excitation of the d states.[22] The negative-ion state, on the other hand, contains a relatively large admixture of d states. This is due to the fact that the d electrons are particularly efficient in screening the Coulomb repulsion in a small negatively charged cluster.[23] The energy of the negative-ion state therefore correlates with the energy of the lowest unoccupied d states. For these reasons, E_P will correlate with the energy difference between the frontier orbitals and the lowest unoccupied d states.

As the size of the cluster becomes larger, the screening of the negative-ion state is efficiently mediated by the delocalized valence electrons rather than the localized d states. In this limit, $E_P(N)$ does not correlate with the promotion energy between the frontier orbital and the localized d states, but is determined only by the size of the cluster. As in the case of H_2 on the transition metal surface,[14] the magnitude of the entrance barrier is now determined simply by the energy difference between the lowest unoccupied d state and the frontier orbital.

Clusters that exhibit shell closing will remain unreactive due to the relatively large energy required to open the shell and promote an electron into an excited d state.

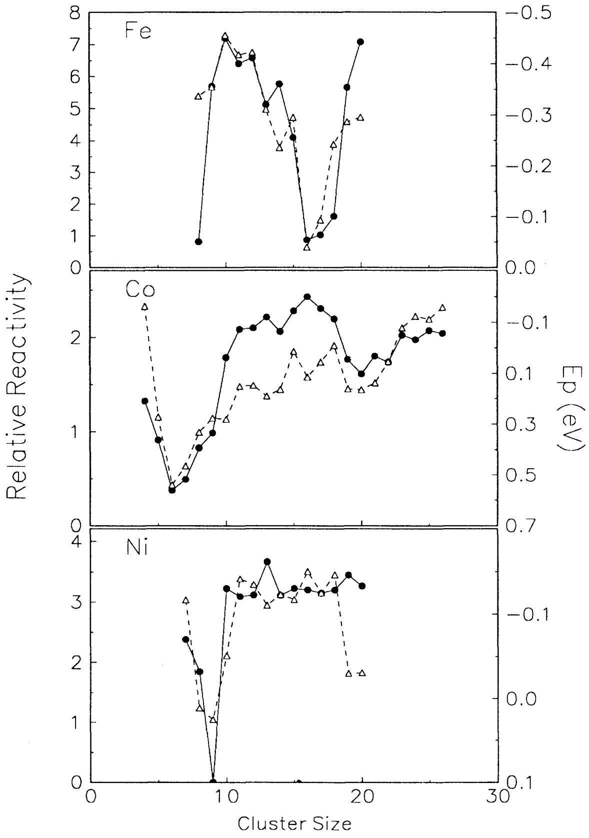

FIG. 3. Plot of the relative reactivity Eq. (1) (solid line) and the promotion energy E_P Eq. (2) (dashed line) as a function of cluster size. The upper figure is for iron, the middle figure is for cobalt, and the lower figure is for nickel clusters. The axis for E_p is reversed, i.e., E_p becomes increasingly negative toward the top of the figures.

For such clusters, we therefore expect very large variations in the reactivity. Such variations have been observed in experiments on V, Nb, and Ta clusters.[4]

It is interesting to note that the polarizability of the clusters also correlates with E_P. The polarizability of a species can be written as a sum of virtual electronic excitations in the cluster. A small value of E_P therefore results in a large polarizability. Since the van der Waals force is proportional to the polarizability, the depth of the H_2 physisorption well will correlate with E_P. This fact enhances the dependence of the reactivity on E_P. Large E_P results in a shallow physisorption well with a large barrier, while a cluster with small E_P is characterized by a deep physisorption well and a small barrier. Recent studies of the reactivity of metal clusters with inert gases such as argon and krypton have shown that the reactivity patterns are very similar to those of hydrogen.[24] This finding gives strong support for our idea that the reactivity of H_2 molecules with small metal clusters is determined by an entrance channel barrier in the physisorption regime.

Finally, we would like to discuss the concept of hardness and softness of molecules. These terms were introduced in inorganic chemistry to understand the stability and chemical reactivity of acids and bases and aromatic species.[25] The chemical hardness of a molecule is defined as the difference between the ionization potential and the electron affinity and is similar to our quantity $E_P(N)$.[26] While the common rule for determining the stability of molecules, the principle of maximum hardness, seems to apply for small metallic clusters,[26] the rule for determining the trends in reactivity between species fails. Since H_2 is a hard molecule, the principle[26] "hard likes hard and soft likes soft" would predict an increased reactivity with clusters characterized by large E_P. The current finding is the opposite trend.

In conclusion, we have shown that the experimentally determined reactivity of small transition-metal clusters with H_2 molecules correlates well with the difference between the ionization potential and the electron affinity of the clusters. A microscopic justification for this correlation has been presented. In this model, the chemical reactivity of the cluster is determined by the magnitude of an entrance channel barrier due to the Pauli repulsion between the molecule and the cluster. The height of this barrier is equal to the promotion energy of an electron from the frontier orbital to the lowest unoccupied d state. This model is likely to apply to the interaction between any closed-shell molecule with metallic clusters.

We would like to thank Professor Per Siegbahn and Dr. Mark Knickelbein for fruitful discussions and communications. This research was supported by the U.S. Department of Energy, Division of Chemical Sciences, and the Robert A. Welch Foundation.

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