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Spectroscopy of transition metal clusters: Correlation of electronic structure to reactivity

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Rice University, 1992
RICE UNIVERSITY

SPECTROSCOPY OF TRANSITION METAL CLUSTERS:
CORRELATION OF ELECTRONIC STRUCTURE TO REACTIVITY

by

JOSE J.B. CONCEICAO

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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April, 1992
ABSTRACT

Spectroscopy of Transition Metal Clusters:
Correlation of Electronic Structure to Reactivity

by

Jose J.B. Conceicao

Photoelectron spectra of negatively charged iron, cobalt and nickel clusters in the size range of 5 to 20 (4 to 26) and 5 to 20 atoms respectively have been obtained. The electron affinity (E.A.) values along with the reported ionization potential (I.P.) have been used as a probe of the valence electronic structure of these clusters. This information is further used to understand the reactivity of the neutrally charged counterpart clusters of iron, cobalt and nickel with dihydrogen. An excellent anticorrelation between an empirically determined quantity called Ep, defined as $IP - EA - e^2/r$, and the reactivity of these clusters is observed. Ep is a direct measure of the polarizability of the clusters; The excellent anticorrelation is consistent with the Pauli Repulsion mechanism and is found to be a significant factor in controlling the reactivity of these clusters.
Acknowledgment

I would like to thank my advisor Dr. R.E. Smalley for his patience and guidance during my graduate career at Rice University. He has been an inspiration to me and a model of what a good scientist ought to be like. "Be quantitative, but know when to say when" is a thought that constantly rings through my mind and an excellent example of the detailed but yet practical nature of Dr. Smalley’s methods.

In addition to my advisor, I had have the opportunity to meet many graduate students, a few of whom I have become very good friends with. They have provided me with very insightful and helpful discussions as well as support in both good and bad times. I wish to thank Dr. Kelly Taylor, my second mentor and very good friend, Dr. Claire Pettiette for her understanding and patience, Dr. Shihe Yang, Dr. Changming Jin for his friendship, insightful comments and "tennis", Dr. Ting Guo for his friendship and the many long hours of discussions, Dr. T. Laaksonen, Dr. Yan Chai, Dr. Bob Hauffman; My thesis committee consisting of Dr. G.P.Glass and Dr. P. Nordlander another second mentor, and finally the "mother hen" of our group, Mrs. JoAnn Timmins.

I would also like to thank my undergraduate advisor Dr. M.P. Doyle for his many years of guidance, without which I would surely not have made it through graduate school.

Last but not least, I wish to thank my family and to my dear friend Afo for their support in all matters, their patience and kindness and for being the "Wind beneath my wings".
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Introduction

The study of the reactivity of small transition metal clusters has seen a tremendous growth over the past ten years. The technical advances made in the past few years caused an explosive growth in the various methods of cluster production and probing\(^1\). The invention of the laser vaporization method followed by the incorporation of the fast flow reactor ushered in the early days of cluster reactivity research. In recent years, ICR mass spectrometers were successfully adapted to the laser vaporization and supersonic nozzle sources to generate and study the reactivity behavior of clusters. It is a general belief of many researchers that these small cluster species are directly responsible for many industrially important processes and as a result of the technological advancements, various fundamental questions regarding catalysis, vapor deposition and microelectronics can now being address\(^3\).

Over the past five years, intense efforts have been made to understand the observed reactivity pattern of clusters formed from the first and second row transition metals. In particular, the reactivity with molecular hydrogen and nitrogen respectively has been by far the most interesting. These systems show large variations in the reactivity of clusters in the size range of 3 - 25 atoms\(^4,5,6\). Examples of such variations are shown in Figure 1.
Figure 1. Representative plots of the reactivity of iron, cobalt and nickel neutral cluster reactivity with H\textsubscript{2} as a function of cluster size.
To date, clusters of iron, cobalt, nickel, copper, rhodium, palladium, and platinum, to name a few, have been generated and studied. Despite these efforts, our understanding of cluster reactivity is still in the stages of infancy. By far the most controversial explanation given, regarding cluster reactivity, is that proposed by Whetten et.al.\(^7\). These workers observed a good anticorrelation between the Ionization Potential (IP) and the reactivity of neutrally charged iron clusters with molecular hydrogen. (In other words, the most reactive clusters had the lowest IPs.) This observation was rationalized by supposing that the key step in dihydrogen dissociative chemisorption on a cluster was the donation of electron(s) from the cluster into the antibonding orbital of dihydrogen. If a cluster had a low IP, electron donation would be facile and thus reactivity is enhanced. This type of correlation was apparently quite wide spread and similar behaviors were observed for other transition metal clusters as well.\(^8\)

Although this explanation seemed reasonable then, four main questions remained unanswered. Firstly, the involvement or role of the 3d orbitals was unclear - Consider the question of the difference in reactivity of copper vs. iron, cobalt and nickel clusters. The former are totally unreactive while the latter show large variation in reactivity as a function of size. The most obvious reason for this difference is that copper has filled d orbitals and the latter metals have partially filled ones. What then is the role played by these d orbitals?

Secondly, this simple charge transfer model didn't explain why the observed reactivity behavior of the positively and negatively charged species were near identical to those of the neutrals. If indeed charge transfer was an essential step, the positive ions should be much less reactive while the negative ions would be much more reactive.

Thirdly, no physical reason was given why there should be such strong variations in the IP to begin with, i.e. what is the underlying physical factor that controls the electronic structure of these clusters.
Lastly, this simple charge transfer hypothesis doesn’t address the question of geometric structure and whether these have any effect on the valence electronic structure and thus the observed reactivity.

More accurate studies of the rates of reaction and measurements of IPs have surfaced in recent years. These findings indicate that there was never a very good anticorrelation between the observed rates and IPs of the respective clusters. In actuality, this anticorrelation is quite bad. Figure 2. shows a plot of the IP and reactivity of neutrally charged iron clusters. Values used are from the work of the Argonne group.

![Image of a graph showing the relationship between cluster size, ln(k), and IP (eV).](image)

**Figure 2.** Plot of the reactivity of neutral iron clusters (with H2) vs. the IP of the respective clusters as a function of cluster size. IP in solid line, reactivity in dashed line.

This thesis presents new and very striking findings regarding the reactivity of transition metal clusters of iron, cobalt, and nickel respectively. The photoelectron spectra of iron cobalt and nickel anionic clusters have been measured. These results, coupled with the reported values of IP for the respective clusters provide us with a direct probe of the
valence electronic structure of these systems. We have used these two measurements to obtain a quantity called $E_p$. When $E_p$ is plotted against the reactivity of the respective neutral clusters of iron, cobalt and nickel, a near perfect anticorrelation is observed. $E_p$ is experimentally determined and defined as follow,

$$E_p = IP - EA - e^2/r$$

where $r$ is the radius of the cluster. Details of this expression are described in the latter sections. Figure 3. shows a representative plot of the reactivity vs. $E_p$ as a function of size.

![Plot of reactivity vs. cluster size](image)

**Figure 3.** Plot of the reactivity of neutrally charged iron clusters (with $H_2$) vs. the $E_p$ of these respective clusters. Reactivity in dashed line, $E_p$ in solid line.

As the above plot shows, an excellent anti correlation exists between the reactivity and $E_p$ for iron clusters. Similar results are also observed for niobium, cobalt and nickel clusters. This striking correlation is consistent with the Pauli Repulsion model proposed by Harris et. al\textsuperscript{10}. These findings, coupled with the jellium calculations of Yamaguchi
et.al\textsuperscript{11}, along with the additional reactivity findings of this work, indicate that \textit{hydrogen chemisorption on transition metal clusters of Group VIII elements occurs only if a Pauli Repulsive entrance barrier can be overcome}. The nature of this barrier lies in the overlap of the valence orbital of H\textsubscript{2} and the spilled out exponential tail of the s-like orbitals of the cluster. Both of these orbitals are filled and the resultant effect is the formation of a Pauli Repulsive Potential between the incoming H\textsubscript{2} and the cluster. To reduce this barrier, the cluster electrons residing in the s-like orbitals must be promoted or polarized into smaller d orbitals. The ease of this promotion is substantially influenced by the availability of close lying vacant or partially filled d orbitals at the valence level and by jellium shell closing in these clusters.
Experimental

Iron, Cobalt, and Nickel clusters are generated by the laser vaporization technique. The output of a Nd-YAG laser is focused onto a very pure cobalt disc. This vaporizes a small quantity of material that is then swept up and entrained in a pulse of helium gas directed over this target. The helium gas, along with the seeded component, undergoes a supersonic expansion out of the vaporization region and into a vacuum chamber; before the completion of the process an excimer laser intersects the expanding gas to generate the negative ions. A collimated molecular beam is formed from the expanding jet by means of a skimmer. Clusters of various sizes are extracted from this molecular beam by means of a Wiley-McLaren type time of flight mass spectrometer. The ions of different masses are separated from each other in time. The cluster of interest is selected by means of a device called the mass gate. The cluster is then slowed down and interrogated by a laser. The photoelectrons thus produced are collected and analyzed by a magnetic time of flight energy analyzer. The details of the apparatus will now be described in details below.

Vaporization and clusters formation.

Figure E1 shows a schematic drawing of the nozzle/vaporization region used to generate the clusters.

The experimental cycle begins when a pulse of helium carrier gas is emitted from each of the two pulsed valves (V1, V2). These valves are available commercially.(From R.M. Jordan Co.\textsuperscript{12} Rise time of 20μsecs, pulse duration of 120μsecs and a throughput of 0.06sccm/pulse giving a peak operating pressure of 300 torr.) and were chosen because
they provide fast gas delivery, a characteristic found to be important in controlling the growth and cooling of the clusters.

![Diagram of nozzle region](image)

*Figure E1. Drawing of the nozzle region in which the clusters are produced.*

A precisely timed interval (one that varies from 20 to 140 μsecs) after the gas pulse, a Q-switched Nd-YAG (the 2nd harmonic at 532nm) laser fires and the output is focused onto the sample (S). In this particular instance, the sample is either an iron, cobalt, or nickel disc (Aldrich Chemical Co. 99.999% pure.)

Irradiation of the target material by this focused (0.6mm², duration of 9ns and 20mJ per pulse) laser beam vaporizes the exposed surface area and generate an intense plasma that consists mainly of positively and negatively charged cobalt atoms. To avoid burning deep
holes into the sample by the laser pulse, the target is made to rotate (1 rpm) and translate (1/2 rph) there by creating a motion that is similar to a phonograph record.

**Clustering Mechanism.**

Clustering of these atomic species occurs during the time interval they reside in the vaporization region before the expansion. This process is very much dependent upon the pressure of the carrier gas, a parameter controlled directly by the timing delay between the helium and the YAG laser pulse.

The majority of particles in the plasma are ionic atoms (of both charge states) as well as electrons; cluster formation$^{13}$ occurs when these species collide to form highly excited dimers. The latter species are quickly stabilized by collisions with the surrounding buffer gas. Further collisions of these dimers with other atomic or dimeric species lead to larger cluster formation. These undergo consequent collisions with helium to produce stable clusters that are long lived enough for analysis.

Depending on the buffer gas density, the clustering process could be precisely controlled. The pressure in the vaporization zone when the plasma is formed, is directly controlled by the delay time between the initiation of the helium pulse and the firing of the vaporization laser. The helium pulse has a duration of 120usec and peak pressure is achieved in the nozzle at this time; thus, by firing the vaporization laser at some timed interval after the helium pulse is initiated, it is possible to create the plasma at differing instances of pressure in the nozzle. In general, at peak gas density large neutral clusters (10 - 30 atoms) are formed while at a lower gas density, smaller charged clusters (4 -9 atoms) are observed.

To effect rapid thermalization and stabilization of these newly formed clusters, this experiment was performed, in most instances, under conditions whereby the highest
possible pressures or even peak gas pressure existed over the target when the YAG laser fired. This allows the clusters to experience the maximum number of collisions. By operating the source in this mode, neutrally charged clusters of size ranging from 4 to 30 atoms were observed.

The negatively charged cluster ions were produced by electron attachment to the neutrals. To generate a cloud of free electrons, the output of an ArF excimer was directed down the throat of the nozzle (vaporization region) as the gas pulse begins to exit the cone (to be described shortly). Electrons that are photoemitted from the surface of the nozzle as well as neutral cobalt clusters attach to some of the other neutral cluster species. To remove the energy from this electron capture process (an amount of energy that is equal to the electron affinity of the cluster), a 6 cm cone (15° internal angle) was attached to the nozzle. This confined the gas pulse and prevented it from expanding for at least 60 usecs. The effect of this is to allow the "hot" cluster radical anions to re-thermalize before the expansion.

At the end of the 6 cm cone (Figure E2), the seeded gas is allowed to expand freely into a vacuum. (10^{-6} torr).

The physical dimension of the cone is such that the gas would expand out of it under conditions termed a supersonic expansion^{14}. This expansion has the property of converting the enthalpy of the gas (the random thermal energy) into directed kinetic energy. The flow of the gas under such conditions is hydro-dynamic and a large number of collisions occur. This process redirects the random motion of the gas into directed flow out of the nozzle. Under such conditions, the internal degrees of freedom of the gas communicate with the translational degrees of freedom, thus converting thermal energy into directed kinetic energy. This decreases the internal temperature of the gas, a well sought after property in any type of spectroscopic work.
Figure E2. Drawing representing the three main chambers of cluster production, and extraction.

Mass analysis and detection.

The gas pulse on exiting the nozzle region and into the main vacuum chamber (base pressure of $1 \times 10^{-6}$ torr, $5 \times 10^{-5}$ torr during operations) travels a distance of 15 cm before it is collimated into a beam by means of a skimmer (Beam Dynamics, 5mm orifice) that is mounted co-axially along the molecular beam axis. This skimmer also serves to provide differential pumping of the extraction chamber in which the cluster ions are mass analyzed.
This extraction chamber is maintained at a pressure of $5 \times 10^{-7}$ torr and houses a Wiley-McLauren type\textsuperscript{15} time of flight mass spectrometer. This set-up consists of 5 plates: repeller, D.O.G., two D.O.G. "guard" and the ground plate. A high voltage pulse (-1000V) is applied across the plates. The timing of this pulse is set to fire at some delay after the vaporization laser pulse. Thus at some optimum time that corresponds to the arrival of the cluster ion packet at the center of this stack, the pulse fires and the ions are repelled down a time of flight tube. The stacks are arranged so that the cluster ions would travel in a direction orthogonal to their initial flight path.

The idea behind the Wiley-McLauren mass spectrometer is that all clusters are given the same initial amount of energy by the electric field in the stack, since there are clusters of various masses, they will have different velocities and thus take different amounts of time to travel the fixed distance down the flight tube from the repeller to the detector. The mass analysis comes about when the different clusters arrive at the detector at different times.

The time of flight tube is 1.25m in length, and mounted at the front of this tube, close to the repeller, is a pair of vertical plates (deflector plates). A dc. voltage is applied across these plates and they serve the function of removing the velocity component the clusters have along the original molecular beam direction. As the clusters travel down this tube, they pass through an einzel lens. This focuses the ion packet and prevents them from dispersing as they travel towards the detector. The detector consists of 2 micro-channel plates (Galileo Channel Plates) and are mounted inside a third chamber called the electron detachment chamber (Figure E3).
Figure E3. Drawing of the E-Chamber where mass selection, deceleration and photo detachment take place.

**Mass separation and Photoelectron spectroscopy of metal clusters.**

Along with the detector, a number of other devices are mounted inside the electron chamber. These include the mass gate (M.G.), the decelerator (D.C.) and a pulsed solenoid, all of which serve respectively to select the cluster of interest, decelerate it, and eventually collect the photo detached electrons for analysis. These various devices are now described.
Before the ions reach the detector, they travel through a set of parallel plates, the MG/DC that are mounted orthogonal to the direction of flight of the ions. These form the mass selection and deceleration devises. The first plate is kept at ground potential and a negative high voltage (-1100V) is applied onto the second plate. This creates a repulsive field to the on coming clusters. At a predetermined time, a positive high voltage pulse (of the same magnitude as the dc. negative voltage) is applied onto the second plate. This effectively pulls the voltage on this plate to ground and removes the repulsive field. Since mass analysis is done on the basis of arrival time at the detector, clusters of each mass will arrive at the mass gate with some characteristic time. The positive pulse to the mass gate corresponds to such a characteristic time; thus when the positive pulse is applied, the repulsive field is removed only for the cluster ions of a particular mass.

A second pair of plates is mounted behind the mass gate. These plates serve as the decelerator. This device slows the parent ions down before they are crossed by the detachment laser. The decelerator consists of two plates, the second one has a 5cm long, 2cm diameter cylinder mounted on it coaxial to the ions' flight path. As the ions leave the first two plates (the mass gate) and enters into the decelerator, a negative high voltage pulse (700-900V) is applied to the forth plate. The third plate is kept at ground. This creates a repulsive field for the ions as they enter into the region between these last two plates. As the ions travel through this region, they have to climb a potential hill and this loses some of their kinetic energy in the process. This effectively slows the ions down, a factor that is very important in reducing the Doppler Effect that is known to destroy the resolution of our electron energy analyzer\textsuperscript{16}. As the ions exit the last plate, they have to travel through the 5cm tube. At this instant, the negative voltage is removed. Since the ions are inside this hollow cylinder, the effect of removing the negative voltage is not felt and thus the ions would not be perturbed by this voltage change.
As the mass selected ions drift towards the detector, they are crossed by the detachment laser (3rd Harmonic of a Nd:YAG for iron and nickel, XeF excimer laser for cobalt clusters respectively) to produce photoelectrons. Again the timing of the detachment laser is set to occur when the ions arrive at the center of the chamber.

The photoelectrons are collected and energy analyzed by means of a Magnetic Time of Flight Energy analyzer\(^{17}\). This analyzer consists of a solenoid mounted orthogonal to the direction of flight of the ions and along the center line of the chamber. This solenoid produces a strong magnetic field (5000G) that is cylindrically symmetrical and highly divergent. Photodetachment occurs in the center of this field. The detached electrons are of low enough energy that they would be trapped by the field lines and directed to move along them in a helical path. This divergent field has the property of rapidly redirecting all the photoelectrons and points them down towards the low field region where a 3.34m flight tube is mounted co-axially to the solenoid. Since the kinetic energies of the photoelectrons are different, they will travel down the fixed length of the flight tube with different velocities and thus arrive at the detector at different times. This forms the basis of the MTOF analyzer. To prevent any perturbation by stray magnetic or electric fields on the flight time of these electrons as they travel down the flight tube, the latter is surrounded by a 2G solenoid that runs the length of the tube. A triple micro channel plate assembly is mounted at the end of the flight tube. The time of flight is recorded by means of a transient digitizer with a resolution of 10nsec. On the basis of the known flight times of photoelectrons from copper atom detached by the 3rd Harmonic/XeF laser, one could readily calibrate the instrument to convert from time into kinetic energy and thus binding energy.

\[
M^{-} + h\nu \rightarrow M + e^{-} \quad \text{(K.E.)}
\]

\[
\text{Binding Energy} = h\nu - \text{K.E.(electron)}
\]
This calibration is then used to convert the flight times of the photoelectrons of cobalt clusters into to their respective energy spectra. The spectra are smooth with a 30meV window and are shown in Figures 4, 5 and 6. All the spectra presented were done in triplicates and the estimated errors of the electron affinities were taken as the deviation from the average value.
RESULTS

The PES of iron, cobalt and nickel clusters in the size ranges of 8-20, 5-20 and 7-20 respectively are presented in figures 4, 5 and 6. Photon energy of 3.5 eV was used for the detachment process. The observed photodetachment onsets for these PES spectra from the negative clusters provide an estimate of the vertical electron affinity. These values are only estimates because of the lack of any precise knowledge of the internal temperature of the clusters as well as the Frank-Condon factors involved in the photodetachment process. In this particular study, no attempt has been made to compensate for instrumental errors as has been the case in previous studies.

Various methods are currently used in determining the EA value from the photoelectron spectra. These include the Watanabe method\textsuperscript{18}, linear extrapolation\textsuperscript{19} and the method of Lineberger et.al\textsuperscript{20}. The electron affinities (EA) reported in this study are measured by drawing the best straight line down the steepest slope of the first major peak in the spectra. The extrapolated intersection of this line with the x-axis (Binding Energy axis) is taken to be the EA. This method is most similar to the linear extrapolation method and is used in our case for the sake of consistency with previously reported works. This simple rule is applied to all the clusters uniformly. The EA picked this way is identical in value to the method of picking the EA at the position in the spectra that shows a 10% intensity of the maximum peak height. The horizontal bars in the cobalt cluster spectra represent the position where the EAs are picked and allow for the reader to independently judge the reasonableness of each choice. The estimate error in the EAs is about 35-40 meV.
Figure 4. Photoelectron spectra of anionic iron clusters in the size range of 3 to 8 atoms with photo energy of 3.5 eV. x-axis is in units of eV.
Figure 4 (cont'd). Photoelectron spectra of anionic iron clusters in the size range of 9 to 14 atoms. x-axis is in units of eV.
Figure 4 (cont'd) Photoelectron spectra of anionic iron clusters in the size range of 15 to 20 atoms. x-axis is in units of eV.
Figure 5. Photoelectron spectra of cobalt clusters in the size range of 7 to 10 atoms. 3.5 eV photodetachment energy used.
Figure 5. (cont'd) Photoelectron spectra of cobalt clusters in the size range of 11 to 16 atoms.
Figure 5. (cont'd) Photoelectron spectra of cobalt clusters in the size range of 17 to 20 atoms.
Figure 5. (cont'd) Photoelectron spectra of cobalt clusters in the size range of 21 to 26 atoms. Photon energy of 6.4 eV was used.
Figure 6. Photoelectron spectra of nickel clusters in the size range of 7 to 12 atoms.
Figure 6 (cont'd) Photoelectron spectra of nickel clusters in the size range of 13 to 18 atoms.
Figure 6 (cont'd) Photoelectron spectra of nickel clusters in the size range of 19 to 20 atoms.
The presence of oxides (roughly 10% of the parent) did not interfere with the PES measurements up to cluster size 20, after which there was some overlap between the oxide peak and the parent peak. In these cases the PES spectra were measured at the leading edge of the cluster mass peak where the concentration of oxide was low. Spectral results.

Iron

This is the first report of the photoelectron spectra of anionic iron clusters to date. These clusters show highly structured spectra even for those with as many as 15 atoms. It is noteworthy that groups of spectra can be identified showing very similar spectral features. This is especially noticeable in the range of 12-15 atoms and then from 16-20 atoms.

Cobalt and Nickel

Like iron, this is the first report of the photoelectron spectra of cobalt clusters. Nickel clusters on the other hand have been studied by Meiwes-Boer et al. All spectral features observed in the previous report are reproduced but with higher resolution. This may be due to the colder clusters produced in our source. The photoelectron spectra of clusters of cobalt and nickel are less structured that those of iron, structure is observed only for the smaller clusters n<10. Beyond that, the density of states is sufficiently large to wash out any resolvable feature(s).

Tables 1, 2 and 3 gives the EA values in eV as measured from this study, also listed are the IP from Knickelbein et al and the Ep values evaluated from these IP and EA respectively.
<table>
<thead>
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<th>Iron Clusters</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>Ep (eV)</th>
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<td>5.48</td>
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<td>9</td>
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<td>5.16</td>
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Table 1. EA of iron clusters in the size range of 8 to 20 atoms. Also listed are IP values from Argonne and Ep values evaluated from the listed EA and IP.
<table>
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Table 2. EA of cobalt clusters in the size range of 8 to 20 atoms. Also listed are IP values from Argonne and Ep values evaluated from the listed EA and IP.
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Table 3. EA of nickel clusters in the size range of 8 to 20 atoms. Also listed are IP values from Argonne and Ep values evaluated from the listed EA and IP.
Figure 7 plot the reactivity (of the various charged states) of iron, cobalt and nickel clusters towards molecular hydrogen\textsuperscript{23}. These measurements were made in an ICR mass spectrometer, details of this experiment can be found in reference 1. Local minima (dips) in reactivity are observed for all three elements in the cluster size ranges of 8 and 20 atoms. The reactivity patterns of the various charged states show strong similarities to each other as well as to the neutral counterpart. The relative size of the dip at 20 (compared to that at 8) becomes less pronounced as one goes from iron to cobalt to nickel. In general the positive clusters are more reactive than the negative ones. A simple pseudo-first order kinetics rate law was used to evaluate the initial uptake of hydrogen. Since an exact value of the pressure of hydrogen in the cell is not known, only relative rate constants are reported. The estimated error in the reported relative rate constants based on multiple runs is about 15-20%.

Figure 8 plots the Ep vs. reactivity of iron, cobalt and nickel clusters. The estimate errors in Ep are about +/- 60 meV for all three elements. As can be observed, an excellent anticorrelation exist between Ep and the reactivity of these clusters with H\textsubscript{2}. 
Figure 7. Plot of the reactivity of iron, cobalt and nickel clusters (with $\text{H}_2$) as a function of size and in the various charged states of negative, neutral and positive.
Figure 8. Plots of the Ep vs reactivity of iron, cobalt and nickel clusters.
DISCUSSION

Deficiency of the Charge transfer mechanism.

Since the initial report of Whetten et. al regarding their apparent excellent anti correlation between the reactivity of neutral iron clusters (with hydrogen) and the IP of the respective clusters, much attention has been given to this charge transfer model. This model is based on the well-known theoretical conclusion\textsuperscript{24} of Hoffmann et.al regarding the factors responsible for H\textsubscript{2} chemisorption on transition metal surfaces, atoms and clusters. Two main factors were deemed the most important:

1) The overcome of a repulsive barrier between the incoming H\textsubscript{2} and the frontier orbitals of the surface.

2) The donation of the $\sigma$ bonding electrons into an empty valence orbital of the metal followed by back donation from the filled valence orbital of the metal into the $\sigma^*$ antibonding orbital of H\textsubscript{2}. The combined effect is the weakening of the H-H bond and the formation of the M-H bond (Where M stands for metal).

Figure 9 gives a schematic representation of these interactions: Interaction 1 is the donation of electron from the metal to the antibonding orbital of H\textsubscript{2}, interaction 2 is the
back donation of electron from H₂ to the metal and interaction 3 is a 2 orbital, 4 electrons interaction and is repulsive.

![Diagram showing interactions in H₂ chemisorption on metal surfaces]

Figure 9. Schematic representation of the interactions that take place in H₂ chemisorption on metal surfaces.

It is important to note that there are two parts to this mechanism: an initial approach of the H₂ towards the cluster in which an entrance channel barrier has to overcome, and then and only then is there the possibility of orbital overlap which may lead to subsequent reaction. Unfortunately, the charge transfer model focuses only on the latter part of this mechanism and totally ignores the more important part, namely the initial entrance channel barrier. As would be shown in a later section, data from this study
indicate that the dominant effect for H₂ chemisorption is indeed dependent upon the ability to overcome the initial entrance channel barrier.

In order to show the significant role of the entrance channel effect, an analysis similar to that of Whetten et. al is performed to see the affect, or lack thereof, of charge transfer. The plots of IP and EA vs reactivity would then be contrasted to that for Ep. This parameter is believed to be a direct measure of the entrance barrier height.

Figure 10. is a plot of EA and reactivity as a function of size for iron, cobalt and nickel clusters respectively. Figure 11. is a similar plot but with the IP and reactivity plotted instead.
Figure 10. Plot of the reactivity (solid lines) vs. the EA of iron, cobalt and nickel clusters respectively.
Figure 11. Plot of the reactivity (solid lines) vs. the IP of iron, cobalt and nickel clusters.
A careful inspection of these plots quickly reveals little indication of a charge transfer mechanism at work in the reactivity of these clusters. This mechanism, as proposed by Whetten et al., states that two factors are involved in the dissociative chemisorption of molecular hydrogen on metal clusters. Firstly, charge transfer from the metal to the antibonding orbital of hydrogen occurs, followed by reverse charge transfer from the sigma bonding orbital of hydrogen into the LUMO of the metal to complete the process. The relative importance of each donation step could readily be monitored by measuring the IP and the EA of the clusters. If a cluster had a low IP, it should be reactive since charge transfer to the hydrogen would be facile, the EA would in this case be high since it should be close in energy to the hydrogen bonding sigma orbital. An inspection of Figure 6 should quickly reveal the lack of any anticorrelation between the IP and the reactivity. This may mean, with the charge transfer model, that the initial transfer of electron(s) from metal to hydrogen is less important than the reverse charge transfer from hydrogen back to the metal, the ease of the latter process should reflect itself in the EAs of these clusters. If this step is indeed the dominant factor, a strong correlation between the EA and the reactivity should be observed. Figure 6 shows that this is not the case though. Besides these observations reactivity studies have also cleared up the weakness of the Whetten mechanism, studies of the reaction of negatively and positively charged clusters of iron, cobalt and nickel show trends that are very similar to their neutral counterparts (Figure 1). If a charge transfer mechanism was at work, the charged clusters should show a different behavior.

On the other hand, if $E_p$ is plotted against the reactivity of these metal clusters, an excellent anticorrelation is observed. Figure 12 is a plot of these anticorrelations. As the following discussion will show, $E_p$ is believed to be a direct measure of the entrance channel barrier height.
Figure 12. Plots of Ep vs reactivity of iron, cobalt and nickel clusters.

The excellent correlation between Ep and the reactivity of iron as well as other transition metal clusters indicate that we have discovered a fundamentally important quantity that maps out the important factor(s) controlling the reactivity of these clusters. To understand what this factor(s) may be, we need to understand Ep and the underlying
physical processes in which it describes. Ep is simply taken as the difference between the IP, EA and a correction term. It is defined as,

\[ Ep = IP - EA - \frac{e^2}{r} \]  

(1)

With a simple MO Theory picture, IP - EA, in essence, describe the energy difference between the HOMO and the LUMO levels. This can be represented schematically in Figure 13.

![Figure 13. Schematic representation of the orbital energies measured by IP and EA.](image)

Simplistically, Ep may thus be viewed as the energy difference between two orbitals, the HOMO and the LUMO. This being the case, what then is the excellent anticorrelation of Ep to reactivity telling us? Looking closely at the plots of Figure 12., one can see that a low reactivity correlates to a large Ep and vice versa. This excellent anticorrelation of
reactivity to Ep would seem to indicate that the cluster needed to undergo an electronic transition from the ground state to an excited state before reaction can occur.

Before going into the physical reasons behind this transition, it is important to consider the experimental implication of the above definition of Ep as it relates to a HOMO-LUMO gap.

HOMO-LUMO gaps are easily identified; If indeed a HOMO-LUMO gap was present, certain characteristics features should be readily observed in the PES of the anionic clusters. For example, consider the case of anionic copper clusters where HOMO-LUMO gaps are observed in their photoelectron spectra. In these spectra, a distinctive small initial feature followed by a larger band is always seen. The initial feature comes from the detachment of the lone electron residing in the LUMO while the larger band comes from electrons detached from the HOMO of the neutral cluster. From the spectra in Figures 4 to 6, it is obvious that certain inconsistencies exist between the experimental data and the HOMO-LUMO theory, in particular, no HOMO-LUMO gaps similar to those of the copper system are observed.

Consider each element individually; For iron, a distinct initial feature separated from a larger band (as in the case of copper anionic clusters) is indeed observed for some of the clusters. The problem with this observation though is two folds:

1) The intensity of this initial feature is too large for photodetaching just one electron. The observed photoelectron signal is proportional to the number of occupied orbitals in which the photoelectrons are coming form. For transition metals, one would expect to have a very dense and degenerate valence level. If indeed the extra electron in the anion is sitting alone in the LUMO, one would expect to see a much weaker initial feature, as compared to the photoelectron signal coming from the dense valence band, in the PES.
An easy solution to this question is that the orbital at the valence level is degenerate and partially filled, thus on photodetachment, the electron signal coming from that orbital is greater.

2) One would expect a HOMO-LUMO gap only for unreactive clusters. As is obvious in the PES of iron clusters, such "gaps", if indeed these are the ones of interests, are present in both the unreactive and reactive ones as well, Fe₉ is a good example. In the case of cobalt and nickel, such gaps are not observed except for a few of the smaller clusters as Co₆.

The absence of distinctive photodetachment features in the PES is not always indicative of the absence of a HOMO-LUMO energy difference. One possible explanation for not seeing a gap is the limited resolution of the spectrometer. Under the current experimental conditions, the resolution of the spectrometer is about 120 meV. This resolution is purely instrumental and doesn't take into account any of the internal properties of the cluster. Temperature effects for one has been shown to dramatically decrease the resolution. Clusters of a particular size but generated under different thermalizing conditions (one is hotter, the other is colder) have produced spectra differing by 50% in spectral resolution. For open shell system, the statistical weight of the final product states is another factor and can contribute to the overall congestion of the spectra. If numerous final states are accessible as may well be the case for transition metals, then one would anticipate seeing a very complicated and congested spectrum. It is important to note that even in copper clusters where distinct gaps are predicted, only those gaps with an energy width of 300 meV or more were just discernible. Thus, a more realistic limit of the actual resolution for this experiment should be twice as much as the calculated instrumental value. If the band gaps of these species are less than this working resolution, it would not be possible to resolve the peaks and see a gap. Thus, interpretation of the photoelectron
spectra for HOMO-LUMO gaps should be done with caution. Equal care should be taken in using theoretical calculations to evaluate the energetic of the orbitals at the valence level, especially the HOMO and the LUMO. Numerous calculations on transition metal clusters have surfaced over the past ten years\(^{27}\). The general conclusion is that transition metal clusters have highly degenerate and densely spaced valence levels with little energy difference between the HOMO and the LUMO. These results should be interpreted with one very important point in mind: Namely, the energy levels calculated are based on the electronic structure of the ground state (GS) of these species. To properly evaluate the energy needed to promote an electron from the HOMO level to the LUMO level, one needs to calculate the energetics of the first excited state of these clusters and compare it to the GS energy. If indeed the difference is zero, then and only then can one say that there is no difference between these two states. This is an important point to remember because the energetics of an excited state species involves other terms in addition to that contained in a 1 electron Hamiltonian description of the energies of molecules. As will be discussed in the following paragraphs, clusters of iron, cobalt and nickel do indeed have a "gap" between the GS and the first excited state. If this was indeed evaluated computationally, one would find that this gap involves energy contributions from electron-electron interaction terms in addition to that of the 1 electron Hamiltonians.

A more subtle reason exists for the "lack of a gap" than just the lack of instrumental resolution. As was stated in the above discussion, \(E_p\) is a measure of the transition energy needed to go from the GS to the first excited state of the cluster. There is a tremendous difference between this statement and simply saying that \(E_p\) is a measure of the energy difference between the HOMO and LUMO orbitals. In a transition, various other factors come into play and the energetics involved are more complicated than just taking the
difference in energy between the orbitals as described by 1 electron Hamiltonians. In order to evaluate the energy needed for this transition, one can in principle measure the UV/VIS spectrum of the cluster. This proves to be experimentally impossibility due to the low concentrations of these cluster species. Alternatively, one may resort to another method and the one that would map out the orbital diagram of a molecule would be photoelectron spectroscopy. At this stage it is informative to mention some of the assumptions inherent in the interpretation methods used in photoelectron spectroscopy. Photoelectrons emitted from a molecule are assumed to occur via a one electron process, in other words, it is assumed that the removal of an electron from the molecule would not disturb the other electrons in any way. This is a natural consequence of the 1 electron approximation regarding orbitals. Under such an assumption, the removal or addition of an electron to the molecule would not perturb the energy levels at all. However in transition metal clusters, discrete electron electron interactions cannot be discounted in these clusters and an understanding of what Ep is actually describing really requires a careful analysis of the meaning of IP and EA in terms of the intricate details of going from one state to another rather than just the energy difference between two orbitals.

This will be done in the following section.

This analysis not only brings out some of the more subtle points about Ep but also shed light on the mechanism that would be necessary for H₂ chemisorption on transition metal clusters.

Koopman's theorem²⁸ is by far the most commonly used approximation linking the observed features in the photoelectron energy spectra to the orbitals of the system under study. This theorem states that the IP can be directly related to the orbital energy as follow,
IP = - $\epsilon_{\text{homo}}$

where $\epsilon_{\text{homo}}$ is the orbital energy of the highest occupied level of the cluster calculated at the Hartree-Fock SCF level. Energies calculated are based on a 1 electron Hamiltonian and corrected by assuming some averaged electron-electron repulsive potential. What is overlooked in such calculations is the electronic and nuclei rearrangements that occur during ionization. To more accurately represent IP the following correction should be made.

IP is the ionization potential of the cluster and is the energy needed to remove an electron from the neutral to form the positively charged species. Energetically, this can be expressed as,

$$IP = \epsilon_{\text{homo}} - \epsilon_{\text{relax}} - \epsilon_{\text{corr}} \quad (2)$$

where $\epsilon_{\text{homo}}$ is the energy of the highest occupied cluster orbital as defined above. One extra term needed is $\epsilon_{\text{relax}}$, the reorganization or relaxation energy associated with the electronic reorganization that takes place when one forms the positively charged cluster from the neutral.\textsuperscript{29} This is an important term since Koopman's theorem assumes a "frozen orbital" configuration in which the electronic orbitals are treated as though they are unchanged or "frozen" during ionization. $\epsilon_{\text{corr}}$ is the correlation energy, a necessary correction for orbital energies calculated in the Hartree Fock formalism.

EA, electron affinity, is defined here as the amount of energy needed to remove an electron from the valence orbital of the anionic cluster species. Similarly, the EA can be expressed as,

$$EA = \epsilon_{\text{lumo}} - J_{\infty} + \Sigma K_{no} \quad (3)$$
where $\epsilon_{\text{lumo}}$ is the energy of the lowest unoccupied cluster orbital as evaluated under the assumptions of Koopman's method for the neutral. For the sake of argument, let's assume that the cluster had a doublet neutral ground state in which only orbital "o" is singly occupied. One then needs to include $J_{oo}$ the Coulombic interaction integral between the two electrons of orbital "o" (self energy) in the anion. i.e. The extra electron in orbital "o" interacting with the electron that was already residing in that orbital. If the system now have $m$ singly occupied orbitals in the system as is the case for most transition metal clusters, a second term, $\Sigma K_{no}$, is needed. These are the exchange integrals and are summed over all $m$ orbitals. This term is small compared to $J_{oo}$ and is usually neglected.

The last term of equation (1) is simply a correction term. It is a smooth and continuously varying function of cluster size and takes into account the electrostatic interaction between the leaving electron and the positively charged cluster when the neutral was ionized. $r$ is the radius of the cluster and is evaluated using the method described by Lineberger et. al. Briefly, $r$ is defined as,

$$ r = r_s n^{1/3} + r_0 $$

(4)

where $r_s$ is the taken to be 90% of the bulk metal inter atomic distance, $n$ is the number of atoms in the cluster and $r_0$ is the spill out radius that is taken to be 1.1 Angstroms for all three elements. Details of these parameters can be obtained from the referenced literature.$^{30}$

Substituting equations (2) and (3) for IP and EA respectively into equation (1), one obtains the following expression for $E_p$,

$$ E_p = (\epsilon_{\text{homo}} - \epsilon_{\text{lumo}}) \cdot (\epsilon_{\text{relax}} - J_{oo} + \Sigma K_{no}) - \frac{e^2}{r} $$

(5)
Equation (5) is grouped into two main terms, the terms in the first set of brackets are the 1 electron cluster orbital energies of the HOMO and the LUMO, it is important for the reader to note that this term is a measure of the interaction energy between the electron and the nuclei of the cluster framework under some averaged electron-electron repulsive potential and, as we have noted above, treats the electron as if though it was the only one in the system. Energies calculated in such a way are also unaffected in the attachment and/or removal of an electron. Indeed there are numerous molecular systems whereby their main electronic orbital energy differences do lie in the first term of equation (5), i.e. the energies are well defined by 1 electron Hamiltonians and for such systems, the main difference in IP - EA is dominated by the energy difference of the HOMO and LUMO levels with only a small contribution from the second term. It is for systems as such that MO Theory is so appropriately applicable to Photoelectron Spectroscopy.

But what of those systems that apparently have degenerate or near degenerate valence levels? By this, it is understood that \( E_{\text{homo}} \equiv E_{\text{lumo}} \) (i.e. as calculated at the HF-SCF level). Under these conditions, the second term in equation (5) takes over. There are three parts to this second term, the first one relates to the energy of reorganization of the system when a hole is generated in the HOMO level, the second one relates to the repulsive interaction between the resident electron in an orbital and when an extra electron is placed into this same orbital, while the third one relates the exchange energy between the extra electron and any other electron of the same spin residing in degenerate orbitals. In terms of an electronic promotion, the energy difference represented by these terms can be expressed as follow,

\[
s^\text{n+1}d^\text{m} \rightarrow s^\text{n}d^\text{m+1}
\]
and shows the intricate and subtle electron - electron relaxation and repulsive interactions that takes place in an electronic excitation from the ground state electron configuration, $s^n d^m$, to an excited state configuration, $s^{n-1} d^{m+1}$. The labels "s" and "d" simply designate the orbitals with "n" and "m" are the number of electrons in them. It is exactly these terms that describes the detail energetics of an electronic transition, in terms of hole formation, electron electron repulsion and exchange in the excited state, beyond the simple orbital picture. These intricate electron-electron interactions are believed to be the major players in controlling the magnitude of $E_p$ in transition metal clusters of iron, cobalt and nickel.

This interpretation of IP - EA is not a novel one and has been used extensively in solid state physics to describe electron motion is transition metal oxides. Briefly, the conduction of electrons in a transition metal may be represented by the following

$$d^n d^m \rightarrow d^{n-1} d^{m+1}$$

whereby an electron has been transferred from one atom to another. This ease of this process is measured by how easy it is to remove an electron from one atom and then to place it into another. One can readily see that this difference is measured by IP of the one atom and the EA of the other, where IP - EA would give the transition energy. The IP and EA are of course that of the bulk materials. This is called the Hubbard U in solid state terms. In effect, it is a measure of the ease of the electron transfer.

To summarize, $E_p$ is a measure of the transition or promotion energy in going from the GS to the first excited state of the cluster. For systems whose energies are readily defined by 1 electron Hamiltonians, $E_p$ is simply the energy difference between the HOMO and LUMO levels. For other systems whose energies cannot be readily defined by 1 electron
Hamiltonians, and in which discrete electron interactions have to be accounted for, $E_p$ reflects the energy changes in these latter processes.

With this in mind, it is now possible to explore the various models available in explaining the chemisorption of dihydrogen onto transition metal clusters. Before getting to the main mechanism of interest, it is informative to discuss the theory of Hard Soft Acid Base Theory. Much physical insight can be gained from this.

**Hard - Soft Acid - Base Theory.**

The concept of IP - EA in chemical reactivity is not a novel one; As early as the 1960s, various chemical reactions have been described by the "Hard Soft Acid Base Theory"$^{32}$. This theory relates the reactivity of certain inorganic ions to their polarizability. The polarizability of a species can be shown quantum mechanically to be expressed as,

$$
\alpha = \sum \frac{|\langle 0 | \mu | n \rangle|^2}{(E_n - E_0)}
$$

where $\alpha$ is the polarizability with the numerator being proportional to the probability of a transition from the GS to the "n" excited state, and the numerator is the difference in energy between the GS and the "n" excited state.

If the first excited state is the only one of concern, the above equation in essence states that the polarizability of a molecule is inversely proportional to the energy difference between the GS and first excited state. This inverse relationship is exactly what is observed for the reactivity vs. $E_p$ in iron, cobalt and nickel clusters. Thus, as an alternative point of view regarding transition metal activation, one may similarly conclude that for $H_2$ chemisorption on metal clusters to occur, some form of polarization of the clusters is required. This is a most significant observation since it lends strong
support to the idea of an entrance channel barrier to dihydrogen chemisorption onto transition metal clusters. Polarization of an electron cloud in essence is a distortion of the cloud. This distortion may be a shift in the electron density from some symmetrical form to an asymmetric one, or it may be a shift in electron density from a delocalized and diffused orbital into a more localized one, all of which would depend on the degree of mixing (as the numerator of the polarizability equation indicates) and the spatial nature of the excited state. The polarization of the cluster’s electron cloud may occur in such a way such that the electron density repulsive towards the incoming H₂ is diverted away and thus reducing the electron-electron repulsive barrier. Despite the qualitative consistency of Hoffmann’s model and the polarization effect, various details of the chemisorption process are still missing. For example, the role of d- orbitals is unknown nor has the structural aspects of these clusters and their influence of the reactivity been addressed.

Polarizability of the cluster is not the only aspect one needs to consider in the chemisorption process. Another point one needs to consider is the involvement of the d-orbitals. The most obvious place to start is to contrast the difference between the reactivity of copper vs iron (or for that matter cobalt, and nickel) clusters towards H₂. Copper clusters are totally inert towards H₂ while iron clusters shows large variations in their reactivity. Similar behavior is also observed for cobalt and nickel. The most obvious difference between copper and iron, cobalt and nickel is that copper has totally filled d orbitals while the latter three elements have vacant ones. In other words, vacant d orbitals are important for H₂ chemisorption.
Pauli Repulsion Model

In theoretical papers by Harris et.al\(^{33}\) and Norlander et.al\(^{34}\) respectively, the mechanisms of H\(_2\) chemisorption on some transition metal surfaces were studied. These authors note the importance of the two factors mentioned by Hoffmann et.al but also found that the second factor mentioned at the beginning of this discussion, that of Pauli Repulsion played a very important role as an activation barrier in the chemisorption process.

Pauli Repulsion can be understood by considering the physical processes that take place when an H\(_2\) molecule approaches the surface of a metal. For transition metals, the valence band consists of both s and d electrons residing in orbitals of s and d parentage respectively. The s electrons are heavily delocalized while the d electrons are more localized. As the H\(_2\) approaches the surface, the electron cloud that extends out from the surface begins to feel the attractive potential of the H\(_2\) molecular nuclei. This would provide for a stabilizing interaction if not for the fact that a couple of bonding electrons are already residing in the potential well of H\(_2\). Since the Pauli Exclusion principle prohibits the occupation of any orbital by more than two electrons, the overall effect is an increase in the kinetic energy of the electrons which causes the energy of the system as a whole to increase and thus a non favorable interaction occurs.
Figure 13. Schematic representation of the interaction of an incoming hydrogen with a generic transition metal dimer. One without and one with a vacant d orbital.

The above interactions are schematically represented in Figure 13. The spilled out electrons are mainly the highly diffuse s electrons. To reduce this repulsion, some mechanism must exist to reduce the size of the electron cloud. This is readily solved if the system of interest has vacant d orbitals that are energetically close to the diffused s orbitals. Most transition metals do fulfill this requirement and the mechanism at work in lowering the activation barrier of Pauli Repulsion involves the transfer (promotion) of s electrons into the vacant d band. Since d orbitals are known to be localized near the atom cores\(^{35,36}\), electrons residing in these orbitals would have a much smaller spatial extent that those residing in the cluster orbitals of s parentage. More importantly, the symmetries of these d orbitals are different enough that they would have minimum
overlap with the bonding orbital of the approaching H₂. These two ideas can be schematically represented in Figure 14.

Figure 14. Schematic representation of the transition from an s-like orbital to a d-like orbital.

How then does this mechanism relate to the excellent anticorrelation of Ep to the reactivity and the physical process that Ep describes as discussed in the previous sections? Recapping the major conclusions from the previous section, Ep is a measure of the transition energy needed to promote an electron from the ground state to the first excited state. Physically this is equivalent to a shift in the electron cloud in the cluster.
This polarization is exactly what is required in the Pauli Repulsion mechanism. In this case, it is from one that is repulsive towards the incoming hydrogen to one that is not. Although there is no concrete evidence that this mechanism indeed is occurring, the need for the polarization step and the excellent correlation of Ep strongly indicates that such a mechanism is most consistent with the experimental observations. This mechanism also clarifies the role of the d orbitals and is consistent with the observation of the lack of reactivity in copper clusters.

To summarize, in order for H₂ chemisorption to occur on transition metal surfaces, the criterion that would reduce Pauli Repulsion would be the existence of low lying d like cluster orbitals that would easily act as a sink for the spilled out s electrons thus reducing their interaction with the bonding electrons of H₂. The key idea here is the requirement of promoting an electron from the HOMO of the cluster to the next level up. This promotion energy is what Ep measures. Intuitively, these ideas seem to make sense, but there are two questions that need to be addressed before one can truly say that Ep is measuring the energetics of this process in the Pauli Repulsion mechanism. The two questions are as follows:

1) What is the nature of the orbital that IP is measuring? Is it really the s like orbitals with the large spatial extent? Here, one has to be aware of the fact that the valence band is a mix of both s and d orbitals.

2) What is the nature of the orbital the extra electron resides in the anion? Is it really an orbital of d parentage?

In order to answer these questions, one has to analyse the ionization and detachment process in order to elucidate the nature of the orbital the electron is coming from during the ionization (IP) as well as the electron detachment process (EA). As has been stated
earlier, the valence level of the cluster is highly degenerate consisting of a mix of orbitals of both d and s parentage. The ionization of the neutral by removal of an electron from this level would most likely be of s character. These orbitals are known to exhibit detachment cross-sections that are an order of magnitude greater\textsuperscript{37} than those of d orbitals. It is therefore safe to say that the IP is a measure of the energy required to remove a valence electron of s parentage. The EA on the other hand is a measure of the detachment of an electron from the valence level of the anion. We believe that this extra electron resides in an orbital of d character. Evidence in support of this statement is found in the reactivity of these clusters, in particular, the reactivity of the negative vs. the neutrals where a similar pattern is observed in both. This would indicate that this extra electron is in an orbital that is non Pauli active. This would have to be a d orbital.

Up to this point, we have tried to explain the excellent correlation of \( E_p \) to the reactivity of neutrally charged with the Pauli Repulsion mechanism. If \( E_p \) is indeed a measure of the rearrangement energy, an alternative mechanism may also be invoked to explain this correlation. This mechanism also relies on a reorganization or promotion.

Sieghbahn et.al have recently published various papers addressing the mechanism of molecular hydrogen chemisorption on transition metal clusters. In their model, the important step in molecular hydrogen chemisorption on metals is the bonding preparedness of the metal valence orbital. In other words, before bonding can occur, the orbitals on the metal must possess the proper symmetry and energy to interact with the incoming hydrogen. In many instances, the ground state of the metal may not be the appropriate one for bonding; To get to a state that is more appropriate, excitation to higher states is necessary and is the process of hybridization. Under these conditions, the \( E_p \) value measured in our experiment may just as well reflect the excitation or promotion energy necessary for the mechanism described by Sieghbahn et.al.
**Geometric structures**

The above discussions have centered around the variations in the valence electronic structure of the clusters that lead to different chemisorption behavior. A more fundamental question that one may ask is: What is the underlying physics that controls the observed electronic structure of these clusters? Conventional wisdom supports the importance of geometric structure as the eventual cause of the observed electronic properties. This has remained unchallenged because of the difficulty in approaching this problem both theoretically and experimentally. With the advent of more powerful computers this is beginning to change, recent theoretical works by Yamaguchi et al.\(^3\) indicate the applicability of the jellium model\(^3\) to transition metal clusters. These workers found that the valence electronic structure consists of a 3d band and a shell-structure like 4s band overlapped onto the former. The 3d electrons are localized near the atoms while the 4s electrons are delocalized throughout the cluster. In addition to this, transition metal surfaces of iron, cobalt and nickel, have predominantly \(d^{n+1}s^1\) atomic occupation. This leaves one electron in the conduction band or in the case of clusters, each atom contributes only one electron to the 4s band. These two findings would indicate that clusters of iron, cobalt and nickel may well behave like those of the noble metals. In the classical jellium model for coinage metal clusters, local energy minima occur at 8 and 20 atom clusters. If indeed the clusters of iron, cobalt and nickel did exhibit jellium behavior, would any special behavior be seen for clusters in the size range of 8 and 20 atoms? An inspection of the reactivity data of iron, cobalt and nickel clusters in all three charge states show some very interesting findings. A minima in the reactivity is observed for these clusters in the range of 8 and 20 atoms. More importantly and most obvious in the case of cobalt is the observation that for the negative ion, \(\text{Co}_{19}\) is the least reactive in this size range, while \(\text{Co}_{20}\) of the neutral and \(\text{Co}_{21}\) of the positive show a
similar reactivity behavior. If these clusters did indeed have 1 electron per s orbital, then the above unreactive species of all three charged states have 20 valence electrons. This so happens to be the second shell closing point for jellium systems. It seems too coincidental and indeed, aspects of jellium behavior may be at work in these clusters. Even if this were true, how then does this shell closing behavior affect the observed reactivity and the Pauli Repulsion model proposed earlier. Recalling the P.R. mechanism, one needs to promote an electron from an s-like orbital into one that is d-like. If the jellium behavior is at work, shell closing would occur at 8 and 20 atom clusters. At a shell closing, the energies of the s orbitals are dramatically lowered. This creates a larger difference between the s and d states and thus makes it less likely for a promotion to occur. This behavior becomes less prominent as one goes to iron and nickel. It can be see quite readily that the minima are not exactly at 8 and 20 for iron and nickel. It is important to remember that transition metal clusters are not metal surfaces and that the exact atomic occupancy may not be $d^{n+1}$ s, thus the exact position of shell closing may not be at 8 or 20 but would depend on the exact hybridization of each atom in the cluster. Another point to note is the gradual decrease in prominence of the dip in the 20 atom range as one goes from iron to cobalt to nickel. Density of state calculations shows that the d band shifts toward lower energy in going from iron to cobalt to nickel. This would mean a gradual coming together of the s and d bands as one moves from left to right and leads to an overall and rapid loss of distinction between the s and d bands with the result of washing out the jellium effect in the 20 atom size range.

Conclusion and future work.

The reactivity of transition metal clusters of iron, cobalt and nickel as well as preliminary studies on niobium indicate that the difference between their IP and EA respectively is an excellent indicator of the reactivity of these clusters. A large difference can be correlated
to a low reactivity and vice versa. This correlation of Ep to the reactivity suggests the need for an electronic promotion process before reaction can occur. This is consistent with the Pauli repulsion model put forth by Harris et al and indicates that d electrons play a crucial role in reducing the entrance channel barrier to chemisorption of molecular hydrogen onto these clusters. Although there is no direct proof at this point of the promotion mechanism, future studies may shed some light in this area. A noteworthy study of this mechanism is to prepare the clusters in the excited state and monitor their reactivity behavior. This could be done by continuously irradiating the clusters with a laser of appropriate energy as they undergo reaction in a fast flow reactor tube. If indeed the chemisorption is an activated process, at some appropriate frequency of excitation, certain size clusters would undergo a transition from a non reactive form into the reactive one. Alternatively, one may prepare a beam of mass selected cluster ions of well defined velocities and subject them to collisional induced reactions by crashing them into a cell of molecular hydrogen. If the interconversion of translational energy to electronic energy were efficient, one may monitor the onset of reaction as a function of translational energy of the clusters. By doing this for the various clusters, a plot similar to Ep vs size should be obtained. Another point that needs to be addressed is the affect of d orbitals on the reactivity of these clusters. At this stage of our investigations, all that is known about the d orbitals is that they're needed for chemisorption. An interesting question to ask is, does the number of these orbitals matter. This brings us to the point of mixed clusters; a cluster of copper is totally unreactive toward dihydrogen, would the inclusion of an atom of iron, or cobalt or nickel change this behavior, would this mix system behave like a single atom or iron, cobalt or nickel, or would it be totally different? Lastly, the most direct way to probe the existence of a promotion gap is to investigate the reactivity behavior of clusters with isomeric forms of a particular cluster, this can readily be done for niobium with 10 atoms. Two isomeric forms are known, one is reactive while the
other is not. If indeed a gap were present, this gap should be larger for the unreactive form. The IP and EA of this form can be readily obtained if the reactive form is first titrated away with molecular hydrogen in a fast flow reactor before spectroscopic measurements of IP and EA are done.
Appendices

Supersonic Expansions and Cluster cooling.

The technique used in these experiments utilize sudden and extreme heating of a metal surface to generate a very hot plasma of the material of interest. The species in this plasma are usually charged atoms and electrons. To affect clustering, a third body is required to remove the energy release in bond formation in the cluster. This third body is provided by the bath of inert helium gas and thermalization usually occur within microseconds after the plasma is formed. In addition to assist in cluster formation, another aspect that relates to spectroscopy, is the desirable to generate the species of interest in their lowest energy (vibrational, rotational and electronic) state. By producing molecules in such a state, spectra congestion is reduced and spectral assignments can be done more readily. To produce this type of additional cooling beyond thermalization, the technique of a seeded supersonic expansion is utilized. In this technique, the molecule of interest is seeded in an inert carrier gas as helium and this is allowed to expand from a region of high pressure into a region of much lower pressure. More importantly, the orifice in which the expansion takes place must have a diameter, D, whereby \( D >> \lambda \), where \( \lambda \) is the mean free path of the gas in the high pressure side. Under these conditions, the gas atoms and the seeded material undergo a tremendous number of collisions. In the process, slower travelling atoms collide with faster ones, the more collision suffered by the gas, the more uniform will be the distribution and the overall effect is a conversion of the random motion into directed mass flow. If a seeded molecule is present in the beam, the internal degrees of freedom of the molecule (in addition to its translational degree of freedom) will also equilibrate with the translational degree of freedom of the cold carrier gas. Under such conditions, the internal energy of the
molecule is converted into directed kinetic energy of the gas. This is where the cooling comes from in a supersonic expansion.

**Collision frequency in the nozzle and during the supersonic expansion.**

The number of collisions a single particle makes during the duration of time it spends in the nozzle region can readily be calculated by classical hard sphere gas dynamics methods. Although a knowledge of the collision frequency is not sufficient to allow us to evaluate the internal temperature of the particles in the gas, nonetheless, it gives us a relative gauge of the degree of cooling of these particles. The collision frequency of a single particle in a gas can readily be calculate via the following equation,

\[ z = \left(\sqrt{2} \sigma \nu \rho / (kT) \right) \]

where \( \sigma \) is the cross section of collision and is taken to be 0.3 nm\(^2\), \( \nu \) is the velocity of particles in the gas and \( \rho \) is the pressure of the gas. \( k \) is the Boltzmann constant and \( T \) is the temperature and is taken to be 350K. Based on arrival time estimates, the residence time of the gas in the nozzle region is estimated to be 60 \( \mu \)sec. The total number of collisions a single particle would suffer under such conditions in estimated to be 7500. This estimate is of course based on fairly crude approximation of the number density of the gas and should be taken as only an approximate value. The number of collisions suffered by the gas during the supersonic expansion can also be evaluated. The collision frequency of a single particle exiting the nozzle of orifice diameter of 15 mm can be estimated by the following equation:

\[ z_{\text{jet}} = \sqrt{2} n \sigma \nu \left[ 1 + \frac{1}{2}(\gamma - 1) M^2 \right]^{-1/2} \]

Where \( n \) is the gas density at the point of interest, \( \gamma \) is the ratio of the heat capacities, \( C_p/C_v \). \( M \) is the local Mach number and is given by,
\[ M = 3.26 \times (x/D - 0.075)^{0.67} - 0.61 \times (x/D - 0.075)^{-0.67} \]

where \( x \) is the distance from the orifice and \( D \) is the diameter of the orifice. \( x \) is taken to be 8 mm and \( D \) is 15 mm. The calculated collision frequency for particles under such conditions of pressure is 1000 if they exist in this environment for 10 \( \mu \)sec.

The effects of the number of collisions can be readily seen in the following two spectra. Figure A1, and A2 are the PES spectra of Fe_{10} taken under two different conditions of pressure in the vaporization region. The first spectra was taken under "cold conditions" where by the pressure in the vaporization region is roughly 75\% of peak value while the second spectra was taken under "hot conditions" where the pressure in the vaporization region was roughly 50\% of peak value. A dramatic difference in spectral resolution can be observed. Although the exact temperature of the clusters are unknown, such results give us a relative feel for the degree of cooling in these nozzle systems. The resolution of the first major peak increased by 40\% due to insufficient cooling of this cluster. All other conditions were identical in these two runs.
Figure A1 and A2. Plot of the PES of Fe$_{10}$ taken under two different clustering conditions. A1 is the cool spectrum while A2 is the hot spectrum.

The electron energy analyser used in this experiment utilizes an intense and highly divergent magnetic field to collect the photoelectrons emitted from the clusters. This energy analyser is based on the original design of Kruit and Read with some significant modifications. The field is produced by a pulsed solenoid and photodetachment occurs at the front face of this solenoid rather than inside of it. There are two reasons for this design: (a) In the photoelectron experiments of current interest to us, high energy photons (6.4, 7.9 eV) are commonly used. These energies are above the work function of the stainless steel parts in the photodetachment chamber and even with precise control of the path of the laser beam, some stray light will induce photoemission from the surfaces of the chamber producing background photoelectrons. With the current design of photodetaching the clusters at a position in front of and on axis to the pulsed solenoid, stray electrons from the surfaces are strongly suppressed and the majority of the photoelectrons detached from the clusters are directed straight to the detector. (b) As one can see from Figure 13, the center of the pulsed solenoid is hollow. This is a deliberate design to reduce the number of stray background photoelectrons that may be mapped directly onto the cluster photoelectrons signal and to the detector. The collection efficiency of this magnetic photoelectron spectrometer is on the order of 98% efficient, in other words, 98% of all photodetached electrons are collected. This is very important when the parent signal is low as is the case in most of cluster research.

Figure A4a shows the magnetic field lines and the trajectory of an electron along one of these lines. Notice the gradual tightening of the helical motion as the electron travels from the region of high field to the low field region. The amount of time it takes to convert any non axial velocity into axial velocity is the parallelization time.
Figure A4a. Magnetic field in the detachment region. Any electrons detached outside of this region would not be guided towards the detector.

In addition to the above modifications to optimize the performance of the spectrometer, by far the most important factor to consider is the resolution. Three factors are directly responsible for this. 1) Parent ion velocity, 2) Photon energy used in the photodetachment, 3) Rate of electron velocity parallelization (This is the amount of time it takes for the magnetic field to convert the velocity components of the electron that are not parallel to the field lines into the velocity component that is parallel to the field lines). The overall resolution of the spectrometer can be subdivided into contributions from each of the above factors as follow,
\[ dE = 4 \times [(m_e/m_\lambda) \times (E_e \times E_\lambda)]^{0.5} + E_e \times (B_f/B_i) + 45 \times E_e^{-0.5} \]

where \( m_e \) is the mass of the electron, \( m_\lambda \) is the mass of the parent ion, \( E_e \) is the kinetic energy of the electron and \( E_\lambda \) is the parent ion's velocity. \( B_f \) is the magnetic field in the flight tube and \( B_i \) is the magnetic field at the detachment point. The last term corrects for the turn around time of photoelectrons that were ejected directly back towards the solenoid. Of the various terms, the parent ion velocity and the electron's kinetic energy (and thus indirectly the detachment laser energy) is the major cause of energy spread in this spectrometer\(^{42} \).

**Conversion of Time of Flight Photoelectron signal into an Energy spectrum.**

The photoelectron signals arrive at the detector at differing times depending on their kinetic energy. This signal is converted into a voltage which is then digitized by a Transiac 2001 Transient Digitizer with a time resolution of 5 nsec and an 8 bit intensity resolution. Figure A3 is a plot of this raw data before energy conversion. Figure A4 is a plot after energy conversion and smoothing.
Figure A3 and A4. Plots of: fig. A3 the raw time of flight data (x axis is time in micro seconds, a total of 20) as collected by the digitizer and fig A4, a plot of the spectra after conversion to energy (x axis is in energy over the range of 0 to 3.4 eV).
The conversion from time to energy is done readily by the following equations,

\[ BE = E_{\text{laser}} - A - B/(t-C)^2 \]

where \( BE \) is the binding energy, \( E_{\text{laser}} \) is the energy of the detachment laser, \( A, B, \) and \( C \) are fitting parameters to adjust for shifts in energy, length of the flight tube and time respectively. The causes for these shifts may be due to stray fields, inaccurate measurements of the exact length of the flight tube and timing variations in the timing circuits used in controlling the experiment, e.g. firing time of the laser, triggering of the photodiode etc. Values of \( A, B, \) and \( C \) are obtained from an optimization programme using the simplex method\(^{43} \). In this programme, the time of arrival for photoelectrons detached from a standard, in our case, the \( \text{Cu}^+ \), and the known binding energies of these electrons are used to evaluate the parameters of \( A, B \) and \( C \). Those values that gives the best fit are then used in the conversion of the raw time of flight data into an energy spectrum. Since the conversion from time to energy is a nonlinear process, the observed photoelectron intensities need to be converted from \( I/dt \) bin into \( I/dE \) bin in a nonlinear fashion as well, this is done as follow,

\[ I_E = I_t \times (0.01 \times t - B)^3/(2 \times A \times 0.01) \]

All the spectra shown are converted by such a scheme. Figure A5 shows the photoelectron spectrum of \( \text{Cu}^+ \) used in the calibration.
Figure A5. Photoelectron spectrum of Cu⁺ detached with the XeF laser. The time of arrival and the known binding energies were used to calculate A, B, and C for calibration.

**Photoelectron Spectroscopy.**

The interaction of short wavelength light with a free molecule can cause the ejection of electrons from the occupied molecular orbitals. Photoelectron spectroscopy is the study of these electrons. The energies and abundance are characteristic of the individual molecular orbitals from which they originate. Consider the interaction of light, $h\nu$, with
a molecule to generate photoelectrons, part of the photon energy is used up in overcoming the binding energy of the electron to the molecule (the electron's orbital energy) and if any energy remains, it manifests itself as kinetic energy in the electron. Different photoelectrons ejected from different orbitals will thus have different kinetic energies. These electrons are separated according to their kinetic energy and subsequently detected. Thus by knowing the wavelength of the photon used for the detachment process and the kinetic energies of the emitted photoelectrons, one can readily evaluate the energies of the orbitals of the molecule. Energetically, this can be expressed as,

\[ KE = h\nu - I_k - E_{\text{vib, rot}} \]

where \( I_k \) is the orbital energy of orbital "k" and \( E_{\text{vib, rot}} \) is the energy of vibrational and rotational transitions that accompanied the photoemission. This can be represented by the processes depicted in Figure A6.

![Figure A6](image.png)

*Figure A6. Schematic representation of the observed photoelectron peaks and their relationship to the molecular orbitals of the system.*
The intensities in a photoelectron spectrum can also provide information regarding the occupancy of the orbitals. Two approximate rules govern the interpretation of intensities:

1. The relative probability of ionization (also called the partial cross sections) are proportional to the area of the photoelectron bands. The observed intensity for a given orbital is proportional to the number of equivalent electrons that are available to be ionized. This rule applies to the ionization from the closed shells of an open or closed shelled molecule.

2. For open shelled molecules, the relative probability of ionization is proportional to the statistical weight (or probability) of the final state produced. In other words, if two final states can be produced in a photodetachment process, the intensities of the photoelectron peaks will depend on the statistical weight of these two final states.

In order to properly assign the various orbitals in a molecular system via photoelectron spectroscopy, one final aspect needs to be addressed. This is the selection rules. The most important point to remember in this type of spectroscopy is that it is a one electron process. In other words, the removal of an electron from the molecule occurs without affecting the behavior of any of the other electrons. (This is a natural consequence of the one electron orbital model). If indeed this rule is followed in the photodetachment process, then any transition is allowed because the emitted photoelectron can carry any unit of angular momentum to satisfy the selection rules.
References

8 See reference 5.
12 R.M. Jordan Co., CA.
13 S. O'Brien, Ph.D Thesis, Rice University, Houston, TX.
17 M.J. Craycraft, M.S. Thesis, Rice University, Houston, TX.
22 IP of Knickelbein at Argonne, see reference 19.
23 Preliminary results to be published.
26 See Appendix and spectra of Fe10 taken under two different F 1 conditions.
30 See reference 14.
36 Theory of chemisorption.
38 Yamaguchi et.al see reference 11.
42 M.J. Craycraft, M.S. Thesis, Rice University, Houston, TX.
43 Changming Jin, PhD. Thesis, Rice University, Houston, TX.