



Probing the electronic structure of small iron clusters

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Abstract

The electronic structure of small iron clusters is probed with size-selected anion photoelectron spectroscopy. The photoelectron spectra for Fe_9^- to Fe_{16}^- exhibit consistently sharp features near the threshold and their spectral changes correlate well with changes of their chemical reactivity. Extended Hückel calculations, based on body centered cubic structures for Fe_9 to Fe_{16} , provide a reasonable explanation of the experiment. These calculations also yield insights into the cluster magnetism and allow an interpretation of the cluster chemical reactivity based on their electronic structure.

1. Introduction

The study of metal clusters has attracted broad attention over the past decade. One of the central questions concerns how the properties of an isolated atom are transformed to that of clusters and, ultimately, to that of the bulk (see for example Ref. [1]). Transition metal clusters are especially interesting due to their diverse physical and chemical properties that may be harnessed for practical applications (e.g., as catalysts). Unusual magnetic properties are expected for clusters of the transition elements and have been studied intensively [2–10]. Extensive chemical reactivity studies have also been carried out for these clusters and have been found to be strongly size dependent [11–15]. However, understanding the electronic structure of these clusters has presented a

considerable challenge, both theoretically and experimentally.

In this Letter, we present an experimental study of the electronic structure on small iron clusters through photoelectron spectroscopy (PES). We have obtained the PES spectra of Fe_n^- ($n = 3$ to 24) at 3.49 eV photon energy. Sharp features in the spectra are consistently observed in this size range. Spectral variations, as a function of size, are found to correlate well with the changes in their chemical reactivity. Extended Hückel molecular orbital (EHMO) calculations are performed systematically for all the clusters as a first step to understand their electronic structure and aid the interpretation of the PES spectra. Consistent qualitative agreement is found for Fe_9 to Fe_{16} on several properties between the EHMO predictions and the available experimental results, namely, their energy levels near the threshold region, their magnetic property, and their chemical reactivity. We believe these agreements reflect the validity of the key underlying structural assumption: bcc-type

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(body centered cubic) structures for Fe_9 to Fe_{15} [16,17], and a similarly more closely packed Fe_{16} . In this Letter, we focus our discussions on the size range from $n=9$ to 16. Full discussions on the whole size range from 3 to 24 will be published in detail elsewhere [18].

Small iron clusters have been most extensively studied in comparison with other transition metal clusters [2–4,6–19]. Their chemical reactivity with H_2 exhibits striking size effect with orders of magnitude variation from sizes 15 to 16, 18 to 19, and, to a less extent, from 22 to 23 [14,15]. Various interpretations have been proposed to account for this strong size effect [15,20,21], but it has not been well understood. All iron clusters are found to be magnetic with high spin-multiplicity [2–4]. Ionization potentials (IPs) [22,23] and dissociation energies of the positive clusters [24] have also been measured. The only previous PES study of the iron clusters is on Fe_2^- [19]. Several theoretical studies have been carried out to understand the electronic structure of the iron clusters [6–10,17,25]. Particularly, the IPs of Fe_n ($n=3$ –25) have been calculated systematically with a tight-binding method and found good agreement with measured IPs by assuming a bcc-type structure for $n \geq 9$ [17].

2. Experimental

Our experiments are performed with a high resolution magnetic bottle time-of-flight (MTOF) photoelectron spectrometer [18], which is a modified version of the one described in the literature [26,27]. A laser vaporization cluster source is used to generate the Fe_n^- clusters. Two pulsed molecular beam valves are employed to deliver a short and intense helium carrier gas pulse which mixes with and cools the laser-induced plasma to produce the clusters. The cluster/gas mixture undergoes a supersonic expansion and forms a cold and collimated beam by two skimmers. The negative clusters are extracted perpendicularly from the beam and subjected to a time-of-flight (TOF) mass analysis. A three-grid mass gate selects a desired cluster to enter the interaction zone of the MTOF electron analyzer. The mass-selected cluster beam is then decelerated by a momentum decelerator [18] before it interacts with the

detachment laser beam (the third harmonic of a Q-switched Nd:YAG laser). This deceleration is essential for obtaining high resolution PES spectra with the MTOF. The measured TOF spectra, typically averaged over between 10000 to 30000 laser shots at 10 Hz repetition rate, are converted to electron kinetic energy distributions, calibrated with the known spectrum of the Cu^- ion. The kinetic energy is subtracted from the photon energy to obtain the binding energy spectra presented. The spectrometer has an energy resolution of about 30 meV at 1 eV electron kinetic energy.

3. Results and extended Hückel molecular orbital calculations

Fig. 1 displays the spectra for Fe_9^- to Fe_{12}^- and Fig. 2 shows those for Fe_{13}^- to Fe_{16}^- . The small tails, present in all the spectra at low binding energies, are due to a combination of thermal excitations of the anionic clusters and, possibly, a small fraction of isomers that have low electron affinities, since their intensity depends on the cluster source conditions. There is a sharp and intense feature near the threshold for n up to 15. At $n=16$, this feature seems to become the second band, and a new weak feature appears at the threshold. This PES spectral change from Fe_{15} to Fe_{16} correlates remarkably with the chemical reactivity change, suggesting that not only may there be a geometrical change [10], but also a significant accompanying electronic structure change. There are also apparent PES spectral changes from Fe_{18}^- to Fe_{19}^- and from Fe_{22}^- to Fe_{23}^- , correlating with the chemical reactivity changes occurring in the same sizes [18].

Photoelectron spectroscopy probes the electronic structure of matter. PES spectrum has usually been interpreted based on the single electron approximation, where single electron removals from individual molecular orbitals (MOs) yield the spectral features. Although this approximation ignores relaxation effects and electron correlations, it still provides a useful means to interpret the main PES spectral features. Due to its high number of unpaired d electrons, iron clusters have been very difficult to handle theoretically. Several theoretical studies have been performed on the electronic structure of a few

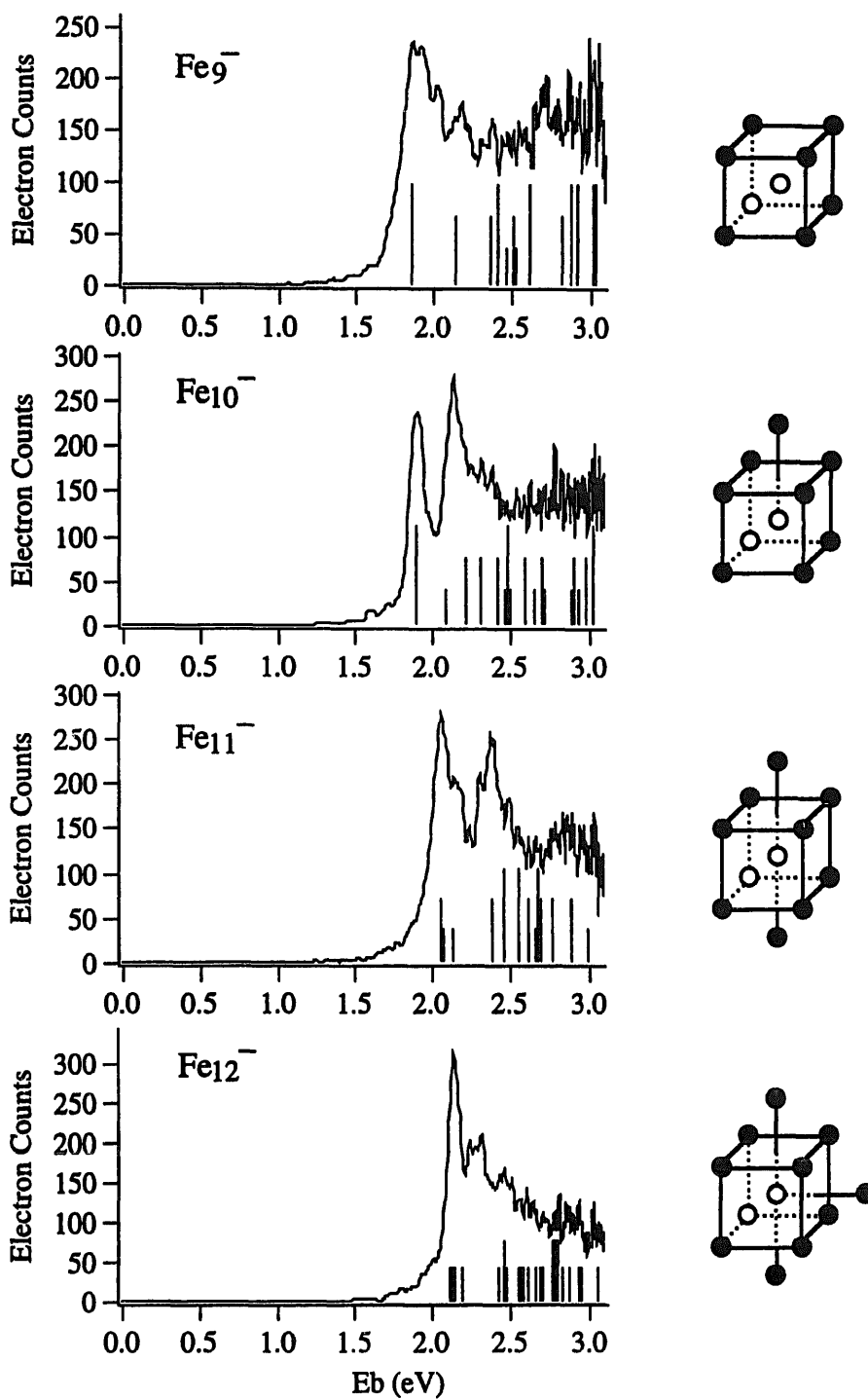


Fig. 1. Photoelectron spectra of Fe_9^- to Fe_{12}^- at 3.49 eV photon energy. The stick spectra are the extended Hückel occupied energy levels by aligning the HOMO level with the threshold feature. The stick height is proportional to the orbital degeneracy and electron occupancy. The assumed structures in the calculations are also shown.

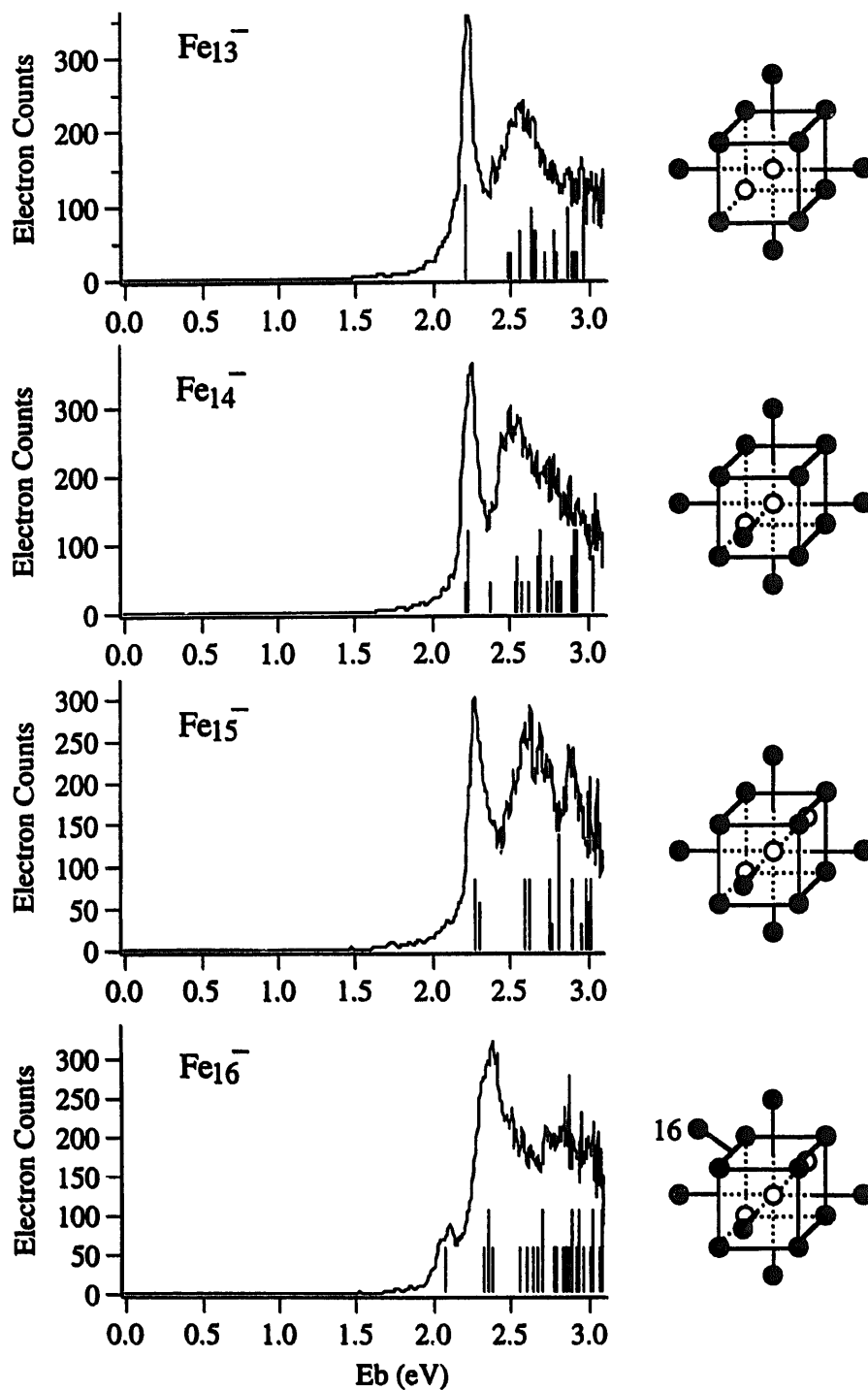


Fig. 2. Photoelectron spectra of Fe_{13}^- to Fe_{16}^- at 3.49 eV photon energy. The stick spectra are the extended Hückel occupied energy levels by aligning the HOMO level with the threshold feature. The stick height is proportional to the orbital degeneracy and electron occupancy. The assumed structures in the calculations are also shown.

larger Fe clusters [6,7,25]. However, consistent interpretations of the PES spectra based on these calculations are not possible. As a first step to systematically understand the PES spectra and gain better insight into their electronic structure, we have carried out EHMO calculations for these iron clusters.

The EHMO theory is a semi-empirical quantum mechanical method [28] which has considerable success in studying chemisorption phenomena on surfaces and a variety of solid state chemistry and physics problems by Hoffmann and co-workers [29–31]. It provides a simple and heuristic view on many physical and chemical processes in the condensed phase, despite its admitted lack of numerical accuracy. For the Fe cluster calculations, the 3d, 4s, and 4p are taken as valence orbitals, of which the 4s and 4p are represented with a set of single zeta basis functions and the 3d with double zeta basis functions. For each cluster, we obtain a set of electronic energy levels and the corresponding MOs with a given structure. Previous chemisorption studies [16] indicate that a bcc close-packed structure is a very likely candidate for Fe₁₅. IP calculations based on bcc-type structures for Fe_n ($n \geq 9$) also yield impressive agreement with the measured IPs [17]. We assume similar structures for the iron clusters in the EHMO calculations: bcc for Fe_n ($n = 9–15$) and a more closely packed Fe₁₆ with atom-16 capping a cube edge, as shown in Figs. 1 and 2. The nearest neighbor distance used throughout the calculations is 2.43 Å.

A central issue is the assignment of the electron occupancy in the EHMO electronic energy levels. While the lower levels are doubly occupied, the occupancy in the upper levels may be singlet, depending on the specific energy level structures. For the iron clusters, the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) would be nearly degenerate if all electrons were paired in the occupied orbitals. Therefore, according to Hund's rule [32], the electron pairs in the upper levels are broken into singly occupied levels; the excess electrons are then transferred into the higher energy levels until an apparent energy gap (0.5 eV or larger) is encountered. This is natural to do since it lowers the electron–electron repulsion due to the exchange energy [32]. In so doing consistently, one obtains a set of occupied energy levels for each cluster with

Table 1

The numbers of unpaired electrons in the iron clusters obtained from the EHMO calculations. The average magnetic moment (μ_B) is given in the parentheses

n	Present work	Ref. [7]	Ref. [25]	Ref. [6]
Fe ₉	20 (2.22)	21 (2.33)	26 (2.89)	26 (2.89)
Fe ₁₀	22 (2.20)			
Fe ₁₁	24 (2.18)	33 (3.0)		
Fe ₁₂	26 (2.17)			
Fe ₁₃	28 (2.15)	33 (2.54)		
Fe ₁₄	30 (2.14)			
Fe ₁₅	32 (2.13)	39 (2.60)	44 (2.93)	40 (2.67)
Fe ₁₆	36 (2.25)			

numerous unpaired electrons – thus, the magnetism in these clusters is ‘naturally’ revealed. The same effect, i.e. the exchange interaction, produces magnetism in bulk metals [32]. The numbers of unpaired electrons from the EHMO calculations for Fe₉–Fe₁₆ are listed in Table 1, together with available values obtained from previous calculations. The average magnetic moment ranges from 2.13 μ_B to 2.25 μ_B , very close to the bulk value of iron, 2.12 μ_B . Other theoretical methods seem to give much higher values for the magnetic moments of small Fe clusters. Considering the simplicity of the EHMO calculations, this is a remarkable result.

4. Discussion and interpretation of size-dependent cluster reactivity

The occupied energy levels are plotted as stick spectra in Figs. 1 and 2¹. The agreement between the experiment and the EHMO predictions is impressive, especially near the threshold regions. The sharp features are well accounted for, being caused by orbital degeneracy and high density of levels. It is particularly gratifying to see that the threshold feature in the spectrum of Fe₁₆⁻ is reproduced very well. Calculations by assuming two other structures, a true bcc fragment and one with atom-16 capping a cube corner, give quite different energy level structures.

¹ In the extended Hückel theory, the extra electron in the anion does not alter the energy level structure of the cluster; it enters the lowest energy, singly occupied level.

The calculations also indicate that the density of states increases significantly at higher binding energies. This agrees qualitatively with the experiments that show continuous signals up to the cutoff energy at 3.2 eV binding energy.

Upon inspecting the wavefunctions, we find that all the orbitals are fairly delocalized. Interestingly, the HOMO levels, including all those responsible for the sharp features in the spectra of Fe_9^- – Fe_{15}^- , and those MOs responsible for the second band in Fe_{16}^- , are mainly of 3d-characters with considerable contributions from the central atom. This explains nicely the apparent similarities of the characteristic sharp features in the Fe_9^- to Fe_{15}^- spectra, as well as the second band in Fe_{16}^- . The origin is due to the closely similar bcc-type structures and the high symmetry it imparts onto the clusters. If proven to be true, this will be highly unusual since clusters at these small sizes ($n = 9$ – 15) already have a similar structure to that of the bulk. This structural feature may also be coincidental because the bcc structures for the small clusters are also rather closely-packed, something the transition metals prefer. Larger iron clusters have been suggested to adopt close-packed polyicosahedral structures when saturated with ammonia [33]. Our result suggests that Fe_{16} begins to deviate from the bcc structure to a more closely packed one as shown in Fig. 2.

The MO corresponding to the threshold feature in Fe_{16}^- is distinctly different: it mainly has 4s characters with minor 3d contributions. We believe this provides the key insight into the dramatically different reactivity toward H_2 from Fe_{15} to Fe_{16} . First, the orbital delocalization shows why the primarily local structure change from Fe_{15} to Fe_{16} can result in a dramatic change of reactivity. Furthermore, when H_2 approaches a cluster, the effective orbital overlap between the $\text{H}_2 \sigma^*$ and the HOMO of the cluster is critical in determining the reactivity. Two factors will affect this orbital interaction, the energy of the HOMO and, more importantly, the symmetry of the HOMO. Thus, it is not surprising to find a somewhat correlation between the IP and the reactivity [15,20,21]. But that is only a minor effect since the HOMO level changes, as revealed by their IPs [22], are rather small. The dominating factor should be the orbital symmetry. Only the correct types of symmetries will result in effective interaction between the

$\text{H}_2 \sigma^*$ orbital and the HOMO of the clusters. For Fe_{15} , as well as Fe_9 to Fe_{14} , the HOMO is composed mostly of d orbitals, and is symmetry-matched with the $\text{H}_2 \sigma^*$ orbital, leading to high reactivity. However, the HOMO of Fe_{16} is mainly of 4s characters and is not symmetry-matched with the $\text{H}_2 \sigma^*$ orbital, hence an extremely low reactivity. The s-type HOMO of Fe_{16} effectively provides a 'shielding effect' to protect the cluster from being attacked by the incoming H_2 molecule despite the presence of the nearby symmetry-matched d-type orbitals corresponding to the second band in the PES spectrum. There is a factor of about 20 difference between the reactivities of Fe_{15} and Fe_{16} with H_2 [14].

5. Conclusions

In summary, we have studied the electronic structure of small iron clusters through anion photoelectron spectroscopy. The results are interpreted with EHMO calculations, which also yield insights into the cluster reactivity and magnetism. This is the first attempt to systematically understand the electronic structure of the small iron clusters. From Fe_9 to Fe_{15} , the clusters seem to grow according to the bcc structure. At Fe_{16} , the cluster begins to adopt a more closely packed structure other than bcc. The sharp PES features near the threshold, and the similarity of this feature among these clusters, are due to the high symmetry of the bcc structure. It would be highly desirable to test these conclusions by high level theories that, thus far, have been elusive with respect to these complicated systems.

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