Unambiguous assignment of the ground state of a nearly degenerate cluster

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A synergistic approach that combines first-principles theory and electron photodetachment experiment is shown to be able to uniquely identify the ground state of a nearly degenerate cluster in the gas phase. Additionally, this approach can complement the Stern-Gerlach technique in determining the magnetic moment of small clusters unambiguously. The method, applied to a Fe_3 cluster, reveals its ground state to have a magnetic moment of $10\mu_B$—in contrast with earlier predictions.

Although the ground states of atoms and dimers can be probed by spectroscopic techniques, their assignment in the gas-phase clusters containing as few as three atoms is a difficult, if not impossible, task. High level *ab initio* theories can, in principle, be used to determine the ground state of a cluster. However, a definitive identification of the ground state may be difficult even at the highest available level of theory if the cluster contains nearly degenerate (in total energy) states and the corresponding energy gaps are smaller than the accuracy of the calculations. Similarly, the ground states of clusters trapped in inert matrices can be probed by electron paramagnetic resonance (EPR), electron spin resonance (ESR), as well as Raman or infrared spectroscopies. Again, if the ground states of these clusters are plagued by near degeneracy, the effect of the matrix may be a significant factor and the ground state of the cluster in the gas phase cannot be inferred unambiguously.

In this paper we describe an approach that enables us to identify the ground state of nearly degenerate clusters. This approach is based on a combination of first-principle calculations and photoelectron spectroscopy. For illustration, we have chosen a Fe_3 cluster. Generally, transition metal clusters, due to narrowly spaced d levels, may possess a number of states with varying spin multiplicities that are energetically very close. For example, we will show that Fe_3 has three isomers with spin multiplicities $2S+1=9$, 11, and 13 with close total energies. Thus, these states have to be considered as nearly degenerate and definitive identification of the Fe_3 ground state is problematic. This near degeneracy is lifted as an electron is attached to form the Fe_3^- anion. We find Fe_3^- to have four states with spin multiplicities of 8, 10, 12, and 14 that are stable against autodetachment of the extra electron. The state with the spin multiplicity of 12 is the ground state of Fe_3^-. By comparing the calculated detachment energies from various isomers of Fe_3^- with experiment, we show that the ground state of neutral Fe_3 must have a spin multiplicity of 11 and thus a magnetic moment of $10\mu_B$.

We note that the conventional method of obtaining magnetic moments of clusters involves measuring the deflection of a cluster beam in a Stern-Gerlach field. In addition to the controversy that magnetic moments measured by this technique can be affected by the temperature of the cluster which is not known precisely, the method is not suitable for very small clusters or clusters with small magnetic moments. In this regard, the present approach can complement the Stern-Gerlach measurements, but without the associated ambiguity.

We first outline our theoretical procedure. We have used a linear combination of atomic orbitals (LCAO) method to construct cluster molecular orbitals. The atomic orbitals were represented by a contracted Gaussian basis $6\text{-}311+G^*$ $[10s7p4d1f]$ in the GAUSSIAN94 code.[1] The total energies were calculated using the density-functional theory and generalized gradient approximation (GGA) for the exchange functional due to Becke[2] and correlation functional due to Perdew and Wang.[3] (BPW91 in the GAUSSIAN94 software.) The BPW91/$6\text{-}311+G^*$ approach has previously been shown to reproduce binding energies of an extra electron in $3d$-metal oxide anions with an accuracy of 0.2 eV or better.[4–7] The cluster geometries for each spin multiplicity were optimized by using the method of steepest descent with a threshold of 10^{-4} a.u./Bohr for the gradient forces. Optimizations were performed within C_{2v} symmetry constraints (isosceles triangle). Harmonic vibrational frequencies were calculated for all the optimized configurations in order to confirm that they belong to stationary states.

Table I describes the electronic configurations, relative energies defined with respect to the total energy of the lowest energy state $^{11}A_1$ and bond lengths of neutral Fe_3 clusters corresponding to spin multiplicities $2S+1=7$, 9, 11, and 13. The $^{15}A_1$ state (i.e., the state corresponding to the spin multiplicity of 15) is unstable towards dissociation to Fe_2+Fe. The $^{11}A_1$ state has the largest difference between the bond lengths among all the isomers of Fe_3 considered. The $^9A_2$ state that lies closest to the $^{11}A_1$ state is an equilateral tri-

TABLE I. Relative energies (ΔE_{tot} in eV) of isomers of Fe_3 and Fe_3^- given with respect to the ground state $^{11}A_1$ of Fe_3. Bond lengths ($R_{1,2}$ and R_3 in Å) of the isomers of the neutral and anion clusters are also given.

	Fe_3				Fe_3^-		
State	ΔE_{tot}	$R_{1,2}$	R_3	State	ΔE_{tot}	$R_{1,2}$	R_3
$^7A_1$	+1.16	2.22	2.11	$^6A_2$	−0.04	2.11	2.11
$^9B_1$	+0.69	2.19	2.01	$^8A_2$	−0.35	2.14	2.15
$^9A_2$	+0.24	2.18	2.18	$^{10}A_2$	−0.81	2.25	2.09
$^{11}A_1$	0.0	2.33	2.09	$^{12}B_1$	−1.49	2.28	2.28
$^{13}A_1$	+0.34	2.28	2.43	$^{14}B_1$	−0.42	2.39	2.26

angle with a bond length of 2.18 Å. Castro and Salahub[9] have calculated this bond length to be 2.10 Å using both the local spin-density approximation (LSDA) and GGA theory, while Chen *et al.*[8] have given a value of 2.04 Å using the LSDA. Both groups have identified the state with a multiplicity of 9 to be the lowest-energy configuration.

In our calculations, the binding energy per atom, $E_b = -[E_{tot}(Fe_3) - 3E_{tot}(Fe)]/3$ of the $^{11}A_1$ and $^9A_2$ states are 1.51 and 1.43 eV, respectively. This energy difference is small, and it may be difficult to conclusively state that the ground state of Fe$_3$ has a magnetic moment $2S = 10\mu_B$ and not $8\mu_B$ as previous studies[8–10] have suggested. Thus, additional evidence is necessary in order to determine the correct magnetic moment of Fe$_3$ in its ground state.

This could be achieved by studying the energetics of Fe$_3^-$ and comparing it with that of Fe$_3$ and the results of photoelectron spectroscopy. We have, therefore, computed the total energies of several states of Fe$_3^-$ by optimizing configurations for spin multiplicities of 6, 8, 10, 12, 14, and 16. The bond lengths of the Fe$_3^-$ isomers which are stable towards autodetachment of an extra electron are given Table I. Also listed in the table are electronic terms and the energy differences with respect to the neutral Fe$_3$ cluster in its $^{11}A_1$ state. While three of these geometries corresponding to the spin multiplicities of 6, 8, and 12 are either equilateral or nearly equilateral triangles, those corresponding to $^{10}A_2$ and $^{14}B_1$ states are isosceles triangles. The most stable state, $^{12}B_1$, with a spin multiplicity of 12, has a bond length of 2.28 Å, which differs somewhat from the bond lengths of the lowest-energy state $^{11}A_1$ of the neutral Fe$_3$ cluster. The next lowest-energy anion state is $^{10}A_2$ which is higher in total energy than the $^{12}B_1$ state by 0.67 eV. This energy gap is much larger than that between the two nearly degenerate states $^9A_2$ and $^{11}A_1$ of the neutral cluster. Thus, we can confidently state that the ground state of Fe$_3^-$ is $^{12}B_1$. The spin multiplicity of 12 in the anion ground state can arise by a parallel (or antiparallel) attachment of the extra electron to neutral parent states with the spin multiplicity of 11 (or 13). This rules out the possibility that the Fe$_3$ cluster could possess the spin multiplicity of 9. Thus, the neutral ground-state Fe$_3$ cluster has a magnetic moment of $10\mu_B$, and not $8\mu_B$ as predicted by earlier studies.[8–10]

We further prove this statement by comparing our results with experimental data[11] obtained from laser photodetachment measurements. In the latter, negative ions are mass selected and crossed with a fixed frequency laser beam. By measuring the kinetic energy of photodetached electrons, their binding energies (or adiabatic electron affinities) can be derived. The adiabatic electron affinity (A_{ad}) measures the energy difference between the ground states of the anion and the corresponding neutral parent. Within the Born-Oppenheimer approximation applied in the present work, one may evaluate the A_{ad} of Fe$_3$ as

$$A_{ad} = E_{tot}(Fe_3) + Z(F_3) - E_{tot}(Fe_3^-) - Z(Fe_3^-). \quad (1)$$

The difference between zero-point vibration energies (Z) of Fe$_3(^{11}A_1)$ and Fe$_3^-(^{12}B_1)$ computed within the harmonic approximation equals -0.004 eV and is negligibly small. Our calculated A_{ad} value of 1.49 eV is in excellent agreement with the experimental value[11] of 1.47 ± 0.08 eV. This agree-

FIG. 1. Transition energies (ΔE_{tot} in eV) from Fe$_3^-$ with the spin multiplicities of $M = 2S + 1$ to neutral Fe$_3$ with the spin multiplicities of $M \pm 1$.

ment further validates our assignment of the ground states of Fe$_3$ and Fe$_3^-$. Note that at this level of theory we have computed the A_{ad} of Fe$_2$ to be 0.94 eV, which also agrees nicely with the experimental value of 0.902 ± 0.008 eV measured by Leopold and Lineberger.[12]

Detachment of an extra electron from the $^{12}B_1$ ground state of Fe$_3^-$ can also produce the neutral cluster in a $^{13}A_1$ excited state. This detachment energy occurs at 1.83 eV and is placed within the broadened lowest-energy experimental peak. To be confident that transitions from the $^{12}B_1$ state of the Fe$_3^-$ anion are the only ones seen in the experimental photoelectron spectra, we have computed the energies corresponding to all spin-allowed transitions from other stable states of Fe$_3^-$, namely, $^8A_2$, $^{10}A_2$, and $^{14}B_1$. Recall that these are stable against autodetachment of an extra electron. In Fig. 1 we list the energetics of these transitions. Note that the energy difference between the $^8A_2$ state of Fe$_3^-$ and the $^7A_1$ state of Fe$_3$ is very close to the experimental adiabatic electron affinity. However, not only the $^8A_2$ state of Fe$_3^-$ is 1.13 eV above the ground state of the anion, but an allowed transition to the $^9A_2$ state of the neutral should appear at 0.59 eV. Since there is no peak in this energy range in the experimental spectra, one should rule out the presence of the $^8A_2$ state of Fe$_3^-$ under the experimental conditions. Similarly, the transitions occurring from $^{10}A_2$ and $^{14}B_1$ states of Fe$_3^-$ are inconsistent with the experiment. If these states are present in the beam, they should produce features at 0.81 and 0.76 eV, which are again missing in the experimental spectrum. Thus, the photoelectron spectra[11] corresponds to detachment of an extra electron from the $^{12}B_1$ state of Fe$_3^-$ with a magnetic moment of $11\mu_B$. The corresponding neutral parent ground state is $^{11}A_1$, and the magnetic moment of Fe$_3$ in its ground state has to be $10\mu_B$.

We would like to add that the present way of determining the ground state of a neutral cluster using the negative ion spectroscopy and theoretical calculations rests upon the premise that the spin multiplicity of the neutral ground state differs from that of the anion by ± 1. This is reasonable since the removal of an extra electron from the anion is not likely to change the relative ordering of the remaining occupied majority and minority spin states. To the best of our knowl-

edge, all the available information on the structure of anions and their neutral parents confirms this premise.

In this context, we should mention that there has been a considerable amount of interest in understanding the magnetic moment of transition metal clusters. Due to their reduced size, low dimensionality, and coordination along with unique structure, clusters exhibit magnetic properties that sharply contrast with the bulk. For example, clusters of nonmagnetic elements become ferromagnetic, while those of antiferromagnetic elements become ferromagnetic or ferrimagnetic. There is even a suggestion that spins of clusters can be canted[13] as it has been found to be the case for some surfaces.[14] To prove these predictions, accurate and unambiguous experiments are necessary. The conventional experimental technique has employed a Stern-Gerlach field to measure the deflections of mass-selected clusters. The deflections are analyzed by using the super-paramagnetic model.[15] In this model, the measured magnetic moment μ_{eff} is related to the intrinsic magnetic moment μ through the equation:

$$\mu_{eff} = \mu \left[\coth\left(\frac{N\mu B}{k_B T} \right) - \frac{k_B T}{N\mu B} \right], \qquad (2)$$

where T is the temperature, k_B is the Boltzmann constant, N is the number of atoms, and B is the magnetic field. Thus, in order to evaluate μ_{eff}, one needs to know the cluster temperature precisely. Considerable controversy exists in assigning a value for T for a given cluster. Uncertainties in T have led the experimental estimates in the ''measured'' magnetic moments in Ni_n clusters to differ by as much as 50%.[16,17] In addition, μ_{eff} is determined by the deflection of the clusters as they go through the Stern-Gerlach magnets. These deflections depend on the total cluster magnetic moment and are extremely small for small clusters. The method has therefore been mostly applied to larger clusters. Our approach described here avoids this problem entirely. It certainly can be applied to very small clusters which are not amenable to Stern-Gerlach experiments and it does not rely on an explicit knowledge of the cluster temperature. High-level calculations and an analysis of photoelectron spectra for small clusters can be readily performed. Thus combining a high-level theory and laser photoelectron spectroscopy, one can answer such important questions about possible existence of canted spins, orbital magnetic moments, and the role of spin-orbit interactions on magnetic properties of transition metal clusters. It should be noted that for clusters containing more than 50 atoms, the photoelectron spectra are not very sensitive to the cluster size. Thus, the present approach can be useful to probe magnetic moments of small transition metal clusters containing less than 50 atoms. It is precisely the range of clusters that are difficult to study by Stern-Gerlach experiments and experimental error bars are rather large. It would be highly desirable to calculate the energetics of small anionic and neutral transition metal clusters for all possible multiplicities and compare them with the photoelectron spectra. The resulting magnetic moments, when compared with the results of Stern-Gerlach experiments, will undoubtedly yield a unique insight into magnetism at the atomic scale and its evolution from atoms to bulk.

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