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Relationship between photoelectron spectroscopy and the magnetic moment of Ni_7 clusters

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We show that total-energy calculations based on the density-functional theory and the generalized-gradient approximation can account for the observed photodetachment peaks in the Ni_7 cluster completely and quantitatively. Such an understanding, however, cannot be obtained by analyzing the electron density of states deduced from single-particle energy levels. We further show that a comparison between the calculated and experimental photodetachment peaks sheds light on the spin multiplicity, and hence the magnetic moment, of neutral Ni_7 clusters.

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Photodetachment spectroscopy experiment[1] is known to provide accurate information on the electronic structure of mass-selected negative cluster ions. Here, one starts with an anionic cluster and analyzes the energy of the photodetached electron with a fixed-frequency laser. Assuming that $E(X_n^-)$ and $E(X_n)$ are, respectively, the total energies of the anionic cluster, X_n^-, and neutral cluster, X_n, the following equation must hold:

$$E(X_n^-)+h\nu=E(X_n)+E_k, \tag{1}$$

where $h\nu$ is the energy of the photon and E_k is the kinetic energy of the ejected electron. The peaks in the photoemission spectra then correspond to the various transitions from the ground state of the anion to the neutral cluster at the ground-state energy. If the ground-state geometries of the anion and neutral cluster do not differ much from each other, the transition peaks are narrow. Thus the broadening of the peaks provides a measure of how different the geometries of the anion and neural cluster could be. In addition, the photoemission peaks also carry information about the vibrational and electronic excitations.

Conventionally,[2] one assumes that the photoemission peaks provide information on the electron density of states of neutral clusters as one considers transitions from the highest occupied molecular orbitals and those lying below. The validity of such an analysis relies on Koopmans's theorem. Within the Hartree-Fock approximation, Koopmans's theorem[3] provides a physical interpretation of the energy bands of solids that distinguish between metals, semiconductors, and insulators. It states that the energy difference between two systems containing N and $N-1$ electrons is equal to the energy required to remove the electron from the state, say, j while leaving the other electrons of the system undisturbed. Consequently, the energy, ΔE needed to remove an electron from "j" and place it in state "i" is given by

$$\Delta E=\varepsilon_i-\varepsilon_j. \tag{2}$$

where ε_i (ε_j) is the energy of the electron in state i (j). The validity of the Koopmans's theorem requires that the one-electron wave functions remain unchanged during this process. This approximation should be reasonably valid in a solid where electrons are delocalized, nearly free, and the energy bands are wide.

Clearly, Koopmans's theorem does not hold for atoms. The reason is that one-electron wave functions of an atom are altered as an electron is added or removed. The question is whether Koopmans's theorem is valid in atomic clusters, which constitute a new phase of matter intermediate between atoms and solids? It should be noted that until now the validity of the Koopmans's theorem for clusters is implicitly assumed[2] and photodetachment spectra[1] are believed to provide electronic structure of neutral clusters. To our knowledge, no critical analysis of its validity in clusters has been performed. In this paper we provide such an analysis.

A priori there are many reasons why Koopmans's theorem should not hold for clusters.

(1) Atomic clusters have finite size and hence finite number of electrons. Unlike solids where electrons belong to bands, electrons in clusters belong to discrete energy levels. Note that even if Koopmans's theorem is valid, $\Delta E=h\nu-E_k$ would measure the energy levels of the anion since electrons are removed starting from the highest occupied molecular orbital (HOMO) of the anion. Thus, the photodetachment spectra would not reveal the electronic structure of the neutral cluster since the HOMO's of the anion and neutral clusters are expected to be different.

(2) An atomic cluster would generally possess a net spin, and in transition-metal clusters, this is particularly expected to be high. Consider an anionic cluster to have N number of unpaired electrons and, hence, a multiplicity of $M=2S+1=N+1$. As an electron is photodetached from the anionic cluster, the spin multiplicity of the corresponding neutral cluster could be either $M+1$ or $M-1$ depending on whether the highest occupied molecular orbital is characterized with a minority-spin $\downarrow$ or a majority-spin $\uparrow$ electron. The electronic wave functions of a cluster with $N-1$ electrons must, therefore, depend upon the spin configuration of the ejected electron.

(3) Unlike solids, a cluster is expected to relax structurally following the ejection of the electron, and hence vibrational excitations would play an important role in the interpretation of the photodetachment spectra.

(4) Clusters could possess energetically degenerate isomers.[4] The photodetachment spectra and hence the validity of Koopmans's theorem cannot be understood unless all of the above factors are independently explored for the ground state of the anion as well as its nearly degenerate isomer.

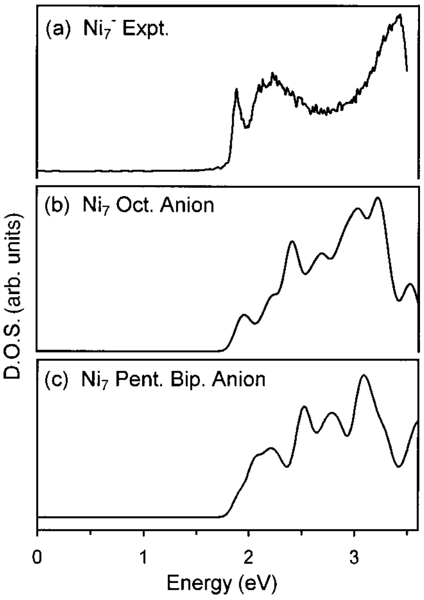

FIG. 1. (a) Experimental photodetachment spectra of Ni$_7$ anion compared with the density of states of its two isomers, (b) capped octahedron, (c) pentagonal bipyramid.

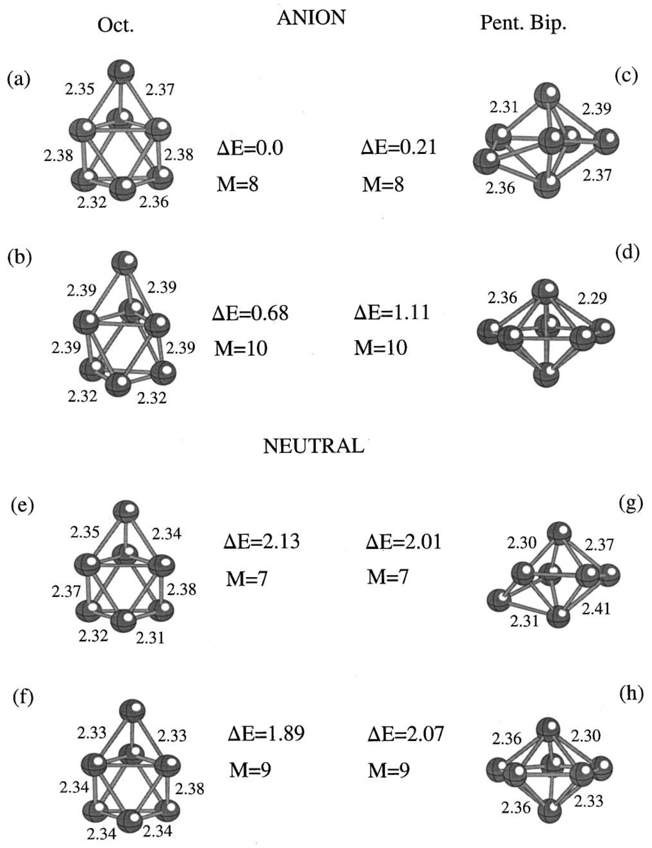

FIG. 2. Geometries of Ni$_7$ anion and neutral isomers corresponding to different spin multiplicities. The relative energies measured with respect to the ground state in (a) are given for all structures.

We should reemphasize that the Koopmans's theorem is valid in the Hartree-Fock approximation. Janak[3] had derived a similar expression for the density-functional theory. He had shown that the energy of the lowest unoccupied molecular orbital (LUMO) is equal to the negative of the electron affinity and that of HOMO equals the negative of the ionization potential provided the exchange-correlation energy functional in the density-functional theory is known exactly.

To achieve an understanding of how well the HOMO and LUMO account for the electron affinity and ionization potential, we have considered the Ni$_7$ cluster as a test system. This choice was made as a large number of experiments have already been performed. For example, (1) photodetachment spectra of Ni$_7$ anion is available using two different photon energies,[1] (2) magnetic moment of Ni$_7$ has been measured using the Stern-Gerlach experiment,[5] (3) the reactivity of Ni$_7$ with molecular nitrogen has been studied experimentally[6] and information on the likely geometry of Ni$_7$ has been obtained, (4) the ionization potential,[7] that is, the energy needed to remove an electron, of Ni$_7$ has also been measured.

In Fig. 1(a) we show the experimental photodetachment spectra of Ni$_7$ taken at 3.49 eV photon energy by Wang and collaborators.[1] We note a sharp peak at 1.91 eV and a broad peak at 2.23 eV electron binding energy. The experiment does not reveal the origin of these two peaks nor why one is narrow while the other is broad. According to Koopmans's theorem, these peaks should bear a signature of the energy levels near the HOMO of the anion, and a broad spectrum could arise if the energy levels are very closely spaced. However, there are other factors, which also could give rise to a broad transition. For example, if the ground-state geometry of the anion is very different from that of the neutral, vibrational progression following electron detachment could lead to a broad transition. The two peaks could also correspond to transition from the anion with spin multiplicity M to a neutral cluster of spin multiplicities $M \pm 1$. It is also possible that the ground state of the anion and neutral cluster could possess energetically nearly degenerate isomers, and the transition energies could be too close to form a broadened spectra. While previous theoretical calculations have indicated the existence of isomers of neutral Ni$_7$,[4] it is not known if Ni$_7^-$ also possesses nearly degenerate isomers.

We have, therefore, carried out a comprehensive calculation of total energies and equilibrium geometries of neutral and anionic Ni$_7$ clusters and their isomers for various spin multiplicities using the density-functional theory in the generalized-gradient approximation[8] for exchange and correlation potential. The actual calculations were carried out using the NRLMOL code developed by Pederson and co-workers.[9,10] Here, the molecular orbitals are formed from a linear combination of atomic orbitals centered at atomic sites. Further, the atomic orbitals are composed of large Gaussian basis sets and consisted of $7s$, $5p$, and $5d$ functions.[10] For details, the reader is referred to earlier papers.[9] The geometries were optimized by calculating the force and relaxing the structure until the forces reached a threshold value of 10^{-4} a.u./Bohr

In Fig. 2 we show the geometries of isomers of Ni$_7$ anions for spin multiplicities of 8 and 10. The isomers either have a capped-octahedron or a pentagonal-bipyramid structure, and

TABLE I. Vertical and adiabatic electron affinities of Ni_7^0; isomers [Figs. 2(a) and 2(c)].

Isomers	Capped octahedron [Fig. 2(a)]		Pentagonal bipyramid [Fig. 2(c)]	
Transitions	$8\rightarrow 9$	$8\rightarrow 7$	$8\rightarrow 9$	$8\rightarrow 7$
Vertical electron affinity	1.89	2.19	1.93	2.01
Adiabatic electron affinity	1.89	2.13	1.86	1.80

the degree of their distortion varies from one multiplicity to another. The geometries corresponding to the capped octahedron and pentagonal bipyramid were first optimized assuming a C_{3v} and C_{2v} symmetry, respectively, and further allowed to relax without any symmetry constraint. The final structures, therefore, correspond to complete relaxation without symmetry. The relative energies measured with respect to the total energy of the ground state of the anion of the isomers are also given in Fig. 2. Note that all these isomers have nearly the same interatomic distance, namely, 2.35 ± 0.05 Å. The ground state of the Ni_7 anion is a capped octahedron [Fig. 2(a)] with a spin multiplicity of 8 (magnetic moment of $7\mu_B$). The next higher-energy isomer that too has a spin multiplicity of 8 but the structure of a pentagonal bipyramid [Fig. 2(c)], lies only 0.21 eV above the ground state. This energy difference is very small and at the present level of theory we can only conclude that both structures are energetically nearly degenerate.

As pointed out in Eq. (2), an understanding of the photodetachment spectra requires calculations of the total energies of neutral Ni_7 isomers for spin multiplicities of 9 and 7. We have calculated the total energies of neutral Ni_7 having the anion geometries of Figs. 2(a) and 2(c). The energy difference, $\Delta E = E(Ni_7^-) - E(Ni_7)$ for these two isomers yield vertical electron affinities. These are compared with experimental results in Table I. Note that the vertical transitions from the capped-octahedron anion to the corresponding neutral cluster with spin multiplicity of 9 and 7 are at 1.89 and 2.19 eV, respectively while those from the pentagonal-bipyramid anion isomer are at 1.93 and 2.01 eV, respectively. Recall that the experimental peaks in Fig. 1 are at 1.91 and 2.23 eV. We clearly see that the experimental 1.91-eV peak results from transition from $M=8$ of both anion isomers to $M=9$ of the corresponding neutrals. The peak at 2.23 eV can only arise if one considers transition from $M=8$ of the anion to $M=7$ of the neutral, and this can only happen by photodetaching an electron from the majority (↑) spin state—something, as we will see later, forbidden if one assumes the validity of the Koopmans's theorem. The vertical transitions to the $M=7$ configuration of the neutral isomers occur at 2.19 and 2.01 eV for the capped octahedron and pentagonal bipyramid, respectively. Note that the corresponding experimental peak at 2.23 eV is broad and both of these transitions are within this peak.

To understand why one peak in Fig. 1 is narrow while the other is broad, we have to consider the possible relaxations in the anion geometry following electron detachment. As mentioned earlier, broadening of the spectra could also have vibrational origin if the ground-state geometry of the neutral cluster is very different from that of the anion. To study this possibility, we have optimized the geometry of the neutral isomers of Ni_7 using the procedure mentioned before. The corresponding results for spin multiplicities $M=7$ and 9 are plotted in Fig. 2. We again see that the neutral isomers have either a capped-octahedron or a pentagonal-bipyramid structure. The degree of distortions of these structures again varies from one multiplicity to another, but the interatomic distances remain fairly insensitive, namely, 2.35 ± 0.05 Å. The ground state of the neutral is again a capped octahedron. However, the next higher-energy isomer, which has a pentagonal-bipyramid structure lies only 0.12 eV above the ground state. Again, at the present level of theory, these two states can only be said to be energetically nearly degenerate.

Unlike the anion isomers, which had the same spin multiplicity of 8, the neutral isomers have different spin multiplicities. The capped octahedron [Fig. 2(f)] has a multiplicity of 9 while the pentagonal bipyramid [Fig. 2(g)] has a spin multiplicity of 7. The neutral Ni_7 cluster with a spin multiplicity of 9 lies only 0.12 eV above the $M=7$ state. The adiabatic electron affinity, defined as the energy difference between the ground states of the anion and neutral cluster, are given in Table I for both the isomers. The difference between vertical and adiabatic electron affinities provides a measure of structural relaxation. Note that the adiabatic and vertical electron affinities of the capped-octahedron isomer are virtually the same. This means that the geometry of the capped-octahedron anion isomer does not change following photodetachment. Thus, there cannot be any vibrational progression of this isomer and the origin of the broadening at 2.23 eV has to be sought elsewhere. The situation is different for the pentagonal-bipyramid isomer. Here the adiabatic and vertical electron affinities corresponding to the transition from $M=8$ of the anion to $M=9$ of the neutral cluster are nearly the same. That means the transition at the 1.89-eV peak must remain narrow. However, the adiabatic electron affinity corresponding to the $M=8$ to $M=7$ transition of the pentagonal bipyramid is 0.2 eV lower than the corresponding vertical electron affinity. This is due to structural relaxation. Hence, the experimental broadening at the 2.23-eV peak arises due to the presence of pentagonal bipyramid. This agreement not only proves the existence of the isomers, but also provides a definitive signature that electrons are removed from the majority-spin orbitals of the anion. We would like to emphasize that the total-energy calculations account for all the features in the photodetachment spectra quantitatively.

We now want to see if the electron density of states of any or both of these anion isomers can explain the experimental spectra in Fig. 1(a). We first examine the energy levels for the majority and minority electrons near the HOMO-LUMO gap of the two isomers [Fig. 2(b) and Fig. 2(f)]. We find that the HOMO's of both the isomers are characterized by the minority (↓) spin electrons. The HOMO of spin-down electron lies 0.52 and 0.29 eV above those of the spin-up electrons in capped-octahedron and pentagonal-bipyramid isomers, respectively. Thus, the spectra in Fig. 1(a) can only arise from the photodetachment of the minority electrons. In other words, the spin multiplicity of the corresponding neutrals following photodetachment must be 9. As we have already shown, based on total-energy calculations, this is not the case. Furthermore, transition from $M=8$ of the anion to $M=7$ of the neutral cluster is essential to explain the broad peak at 2.23 eV.

The total electron density of states (DOS) for the two-anion isomer are calculated by broadening each energy level with a Gaussian function of width 0.1 eV. The results are plotted in Figs. 1(b) and 1(c). To compare these densities of states with experiment in Fig. 1(a), we have aligned the first peak (corresponding to HOMO) of the DOS of both isomers with the experiment. The second peak in the density of states corresponds to the energy level just below the HOMO (i.e., HOMO-1). Note that the DOS of the pentagonal-bipyramid isomer in Fig. 2(f) does not agree with experiment while that of the ground state in Fig. 2(b) has some features seen in Fig. 1(a). In particular, the energy difference between HOMO and HOMO-1 levels of the isomers in Figs. 2(a) and 2(c) are, respectively, 0.08 and 0.13 eV. The corresponding experimental value is 0.32 eV. Thus, while Koopmans' theorem applied to the isomer in Fig. 2(a) does somewhat explain the separation between the experimental photo-detachment peaks, it fails for the other isomer. More importantly, it does not explain the broadness of the second peak observed experimentally.

We will now demonstrate that the synergy between total-energy calculations and photodetachment spectra also enables us to derive reliable information on the magnetic moment. Judging from the quantitative accuracy of the current theory, we can conclude that the magnetic moment per atom of neutral Ni_7 cluster could be either $1.1\mu_B$ or $0.9\mu_B$ [see Figs. 2(f) and 2(g)]. The experimental value obtained by Bloomfield and co-workers is $1.5\mu_B$. This disagreement between theory and experiment is much larger than what we witnessed for the electron affinities. This could arise from many factors: (1) There could be additional contributions coming from the orbital moment, (2) another possibility may be the inherent inaccuracies in the experiment itself. The work of Khanna and Linderoth uses the superparamagnetic model[11] that requires a precise knowledge of the temperature of the cluster—a quantity whose experimental determination has been controversial.[12] In this context it is worth pointing out that the magnetic moment of large Ni clusters obtained by Ref. 11 differs from the experiment of de Heer and co-workers[12] by 50%.

Our studies also shed some light on the early experimental data on the reactivity of Ni_7 with N_2. Riley and co-workers[6] have found the N_2 uptake of Ni_7 to exhibit several plateaus indicating that Ni_7 adsorbs one N_2 molecule initially and seven N_2 molecules when the N_2 pressure is increased. They suggested that Ni_7 is most likely a capped octahedron since the atom with the smallest coordination can be reactive. However, our findings are not inconsistent with their measurements since both isomers can absorb seven N_2 molecules under high N_2 pressure while the capped octahedron can absorb one N_2 under low-N_2-pressure condition. To quantify the relative reactivity of two isomers, we have calculated the hardness parameter η, which measures the difference between the vertical ionization potential (I_P) and adiabatic electron affinity (AE_A). The I_P was 6.49 eV for the capped octahedron [Fig. 2(f)] and 6.14 eV for the pentagonal bipyramid [Fig. 2(g)]. The experimental I_P is 6.07 eV. For the capped octahedron, $\eta = I_P - E_A = 4.60\,\text{eV}$ while that for the pentagonal bipyramid, $\eta = I_P - E_A = 4.28\,\text{eV}$. These two values are very similar indicating that their reactivity toward N_2 may not be significantly different.

In conclusion, we have carried out a comprehensive study of the energetics, electronic structure, and magnetic properties of Ni_7 isomers in both neutral and charged forms. We find that both Ni_7^- and Ni_7 neutral clusters possess nearly degenerate isomers. The total energy calculations quantitatively account for the photodetachment spectra and validate the existence of isomers. The electron density of states, on the other hand, is at odds with the photodetachment spectra casting a doubt on the validity of the Koopmans's theorem. We are also able to derive, from the synergy between photodetachment spectra and calculations, that the spin magnetic moment of Ni_7 is between $0.9\mu_B$ and $1.1\mu_B$. This value, which is significantly smaller than the experimental value of $1.5\mu_B$, makes a strong case for revisiting the experiment. Calculations of the hardness parameter suggests that both isomers have similar reactive properties, and that their simultaneous existence is consistent with the reactivity measurements.

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