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Photoabsorption spectrum of small Ni_n (n=2-6, 13) clusters

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Abstract. Theoretical studies of the photoabsorption spectra of Ni_n clusters (n = 2-6, 13) have been carried out using a linear combination of atomic orbitals molecular-orbital approach within a density functional scheme and a first-order perturbation approach. An analysis of the electronic states based on an angular-momentum decomposition around the center of mass of the cluster has been used to label the various transitions. It is shown that the spectra change significantly with size and are sensitive to the geometrical arrangement. They can be used to identify the isomers.

PACS. 36.40.-c Atomic and molecules clusters – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 73.20.Dx Electron states in low-dimensional structures (superlattices, quantum well structures and multilayers)

The field of nanoscale materials is drawing considerable attention, since developments in experimental techniques now permit generation and characterization of size selected clusters of a single or a combination of elements [1]. These are important developments since the physical, electronic, magnetic, and chemical properties of clusters have been found to be different from bulk and change with size. While this progress continues to generate excitement, the basic problem of the direct determination of the geometrical arrangements at small size remains unsolved, since the clusters are small for microscopic determinations and large for conventional spectroscopic techniques. This is further compounded by the fact that the clusters are generated in beams. This has forced the development of indirect ways where one uses information on electronic structure or chemical behavior to access the geometry. For example, in a chemical approach [2] one absorbs weakly interacting gas and studies adsorption profiles as a function of pressure and temperature to obtain information on the number of distinct sites. This can be used to infer a possible geometry. The technique enters into difficulty when the cluster ground state has energetically close isomers, since the adsorption can lead to geometrical changes. On the electronic side, one of the successful methods is the negative ion photoelectron spectroscopy [3]. Here one starts with an anionic cluster and detaches the electron by transferring energy via high energy photons. A measurement of the energy of the ensuing electrons provides information on the ground and excited states of neutral clusters. In combination with first principle calculation [4], such a technique has been used to obtain geometries of simple metal clusters. Its application to transition metals, however, is not so trivial because of the presence of *d*-orbitals with a high density of electronic states. An alternative, which could be ideal for transition metals and would provide a direct fingerprint of the electronic structure, is to study the photoabsorption spectrum as in the case of solids. This would give the electronic distribution of states in the neutral cluster, which is sensitive to the geometrical arrangement of atoms [5] and thus could be compared with first principles calculations to obtain information on geometry. This technique has not been widely used partly because clusters in beams do not provide enough intensity. This problem is being overcome by developments in experimental techniques.

In this paper we present what we believe are the first theoretical photoabsorption spectra of Ni_n clusters containing 2-6, and 13 atoms. We also examine the sensitivity of photoabsorption spectrum to the geometry by theoretically calculating such spectrum on different geometries of a Ni_4 cluster. Our studies are carried out within a density functional formalism and use a perturbative approach to calculate the photoabsorption spectrum. To facilitate comparison with experiments and to allow a simple physical picture, we have carried out an angular-momentum decomposition of the electronic states with respect to center of mass of the cluster to characterize them by their overall symmetry. This is useful since the dipolar matrix elements entering the photoabsorption spectra are governed by the symmetry of the states. The transitions have therefore been labeled in terms of these symmetries.

In recent papers [6,7] we had presented theoretical studies of the ground state geometries, binding energies, spin S, and the magnetic moment of Ni_n (n = 2-6, 13)

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clusters using a linear combination of atomic orbitals-molecular orbital approach. The inner cores were replace by norm conserving non-local pseudopotentials [8] and the exchange correlation effects were incorporated via a local spin density functional using a form proposed by Ceperley and Adler [9]. To maintain consistency with pseudopotentials, which were developed by Bachelet *et al.* [8] using only local density, no gradient corrections were included. We had found that the magnetic moment per atom changes discontinuously with size and had predicted that a Ni_5 cluster would have an unusually high moment of 1.6 μB per atom. It is gratifying that following our prediction, experiments [10] on Ni_n clusters in beams did find Ni_5 to have an unusually high magnetic moment. Following our work, several theoretical papers [11–13] on the electronic structure of small Ni_n clusters have appeared. While some calculations [13] confirm our result on Ni_5, all electron density functional calculations [11,12] find a low moment for Ni_5 in disagreement with pseudopotential calculations and experiment. Since the pseudopotential calculations are in agreement with experiment, we believe that they provide a realistic description of electronic structure of small Ni_n clusters. We would like to add that we have just completed a study of the ground state geometries of Ni_7 and Ni_8 clusters [14] using pseudopotentials. The theoretical geometries agree with the experimental structures predicted using a chemical approach where adsorption profiles [15] of N_2 as a function of pressure and temperature were used.

Theoretical calculation of the photo-adsorption spectra within the framework of the density functional formalism is a difficult problem. The time-dependent density functional linear response theory [16] provides an accurate approach. However, actual calculations using this theory are difficult. A numerically feasible and sufficiently accurate approach is based on the first-order photo-adsorption processes but requires a calculation of the electronic excited states of the system. Note that the density functional method is ideally suited to ground state electronic densities and can have difficulties with excited states. However, in the absence of a better framework, we will assume that it provides a sufficiently accurate picture. The total photo-absorption cross-section, $\sigma(E)$, in the first-order perturbation approach within a framework of quantum electrodynamics, taking account of the dipolar electric approximation for the interaction between photons and the electrons in the cluster is given by

$$\sigma(E_p) = (4/3)\pi^2\alpha \sum_{i\neq j} \delta(E_p - E_{fi}) E_{fi} |\mathbf{X}_{fi}|^2 . \quad (1)$$

Here E_p is the photon energy, α is the fine structure constant, indices i and f denote the initial and final states, and $E_{fi} = E_f - E_i$ is the energy for the transition. Finally,

$$\mathbf{X}_{fi} = \langle fin|\mathbf{P}|in\rangle \quad (2)$$

is the matrix element of the n-electron electric dipole operator $\mathbf{P}$ between the initial and final states. It is important to point out that the cross-section σ in equation (1) is already averaged with respect to all orientations of the cluster and consequently with respect to polarizations of the incident photon.

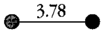
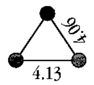
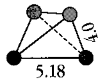
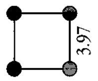
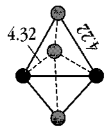
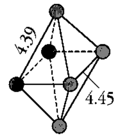
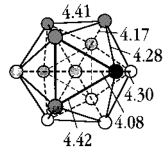
Size	Geometry	B.E.	S	μ
2		1.61	1	1.00
3		1.96	1	0.67
4		2.34	3	1.50
		2.34	3	1.50
5		2.83	4	1.60
6		3.27	4	1.33
13		4.24	4	0.61

Fig. 1. Ground state geometries, binding energy per atom (BE), total spin (S), and the moment per atom (μ) of Ni_n clusters. The bond lengths are in a.u., energies in eV, and μ in bohr magneton.

In order to calculate the photo-absorption coefficient using equation (1), one needs to calculate the matrix element $\mathbf{X}_{fi}$. We will assume that the ground state $|in\rangle$ and the excited state $|fin\rangle$ of the n electrons in the cluster can be described by the Slater determinant built from the n Kohn-Sham occupied and unoccupied orbitals. The ground state is associated with the Slater determinant built from occupied orbitals, while the excited state has determinants including unoccupied orbitals. Note that, while such an approximation may not be ideal for a detailed description of the electronic state, it is sufficiently accurate for calculation of the matrix element of the relevant electric-dipole moments since the matrix elements are governed by symmetry and are not very sensitive to the detailed spatial structure of the electronic states. Since $\mathbf{P}$ is a one-body operator, the relevant excited states are the ones, which conserve the spin. For these excited states obtained by moving an electron from an occupied orbital $\phi v(x)$ to an unoccupied orbital $\phi\mu(x)$ of the same spin, one obtains the following expression for the matrix elements:

$$\mathbf{X}_{fi} = \int \phi\mu^*(\mathbf{x})\mathbf{x}\phi v(\mathbf{x}) \mathrm{d}^3x . \quad (3)$$

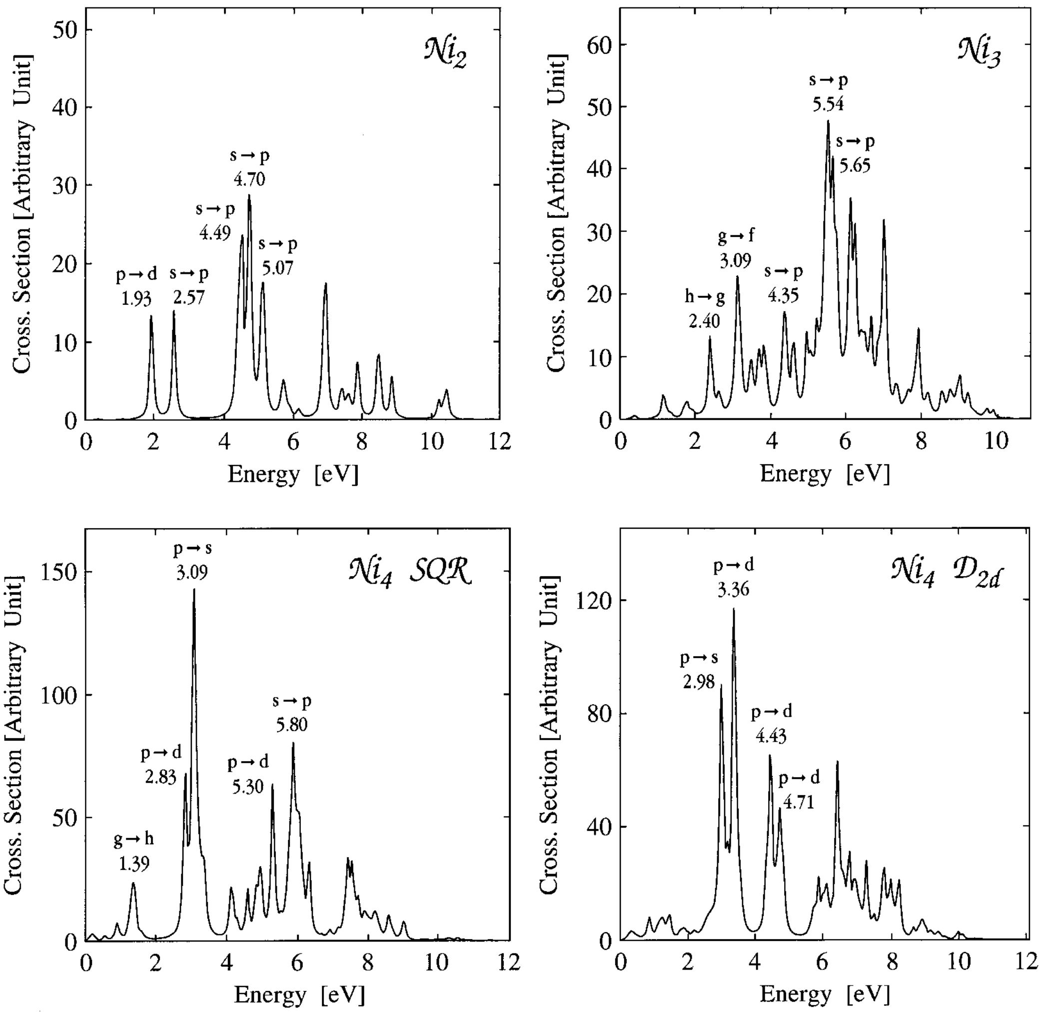


Fig. 2. Photoabsorption spectra of a Ni_2, Ni_3, and two isomers of Ni_4.

We further calculated the energy E_f of the excited states by transferring an electron from a ground state Kohn-Sham orbital to an initially unoccupied orbital and recalculating the energy of the system. The calculation therefore includes the final state effects. Finally, note that the spectra in equation (1) are line spectra. We broadened the lines using Lorenzians with a half width of 0.25 eV to make the trends of the spectrum more visible. It had no effect on the position of main peaks. The broadening, however, has the effect that the value of the cross-section depends on the width of the Lorenzians and the absolute values are no longer meaningful. All our curves are therefore marked in arbitrary units.

In Figure 1 we recall our earlier results [6,7] on the ground state geometries, binding energy, spin S and the magnetic moment of Ni_n clusters containing 2-6, and 13 atoms. Ni_3 has a C_{2V} ground state. For Ni_4, a D_{2d} geometry and a square are degenerate and have the same magnetic moment per atom. Ni_5 is a triangular bipyramid while Ni_6 is a square bipyramid. The ground state of a Ni_{13} is a D_{3d} distorted structure, which is a mild distortion of the perfect icosahedron [7]. For all the geometries, the photoabsorption spectra were calculated as outlined above. In Figures 2 and 3 we show the photoabsorption spectra of clusters containing 2,3,4,5,6, and 13 atoms. Figure 2 also shows the spectra for the two Ni_4 structures shown in Figure 1. As mentioned above, in order to simplify interpretation of the spectra, we carried out an angular-momentum decomposition of the electronic orbitals with respect to the center of mass of the cluster. This leads to a global labeling of symmetry of the electronic states. It is useful to point out that most states have components from several angular momentum states in such an analysis. In these cases, we have labeled the state by the strongest component. Since the ionization potential of Ni_n clusters is around 6 eV, only transitions below this limit are physically meaningful. We have therefore labeled only these peaks.

From Figures 2 and 3 we note that, as expected, the spectra become richer as the size is increased. Further, the position of the main and secondary peaks changes profoundly with size. For Ni_2 and Ni_3, the most intense transitions are from a global s to a p like state. The energy for these transitions changes from 4.70 in Ni_2 to 5.54 eV in

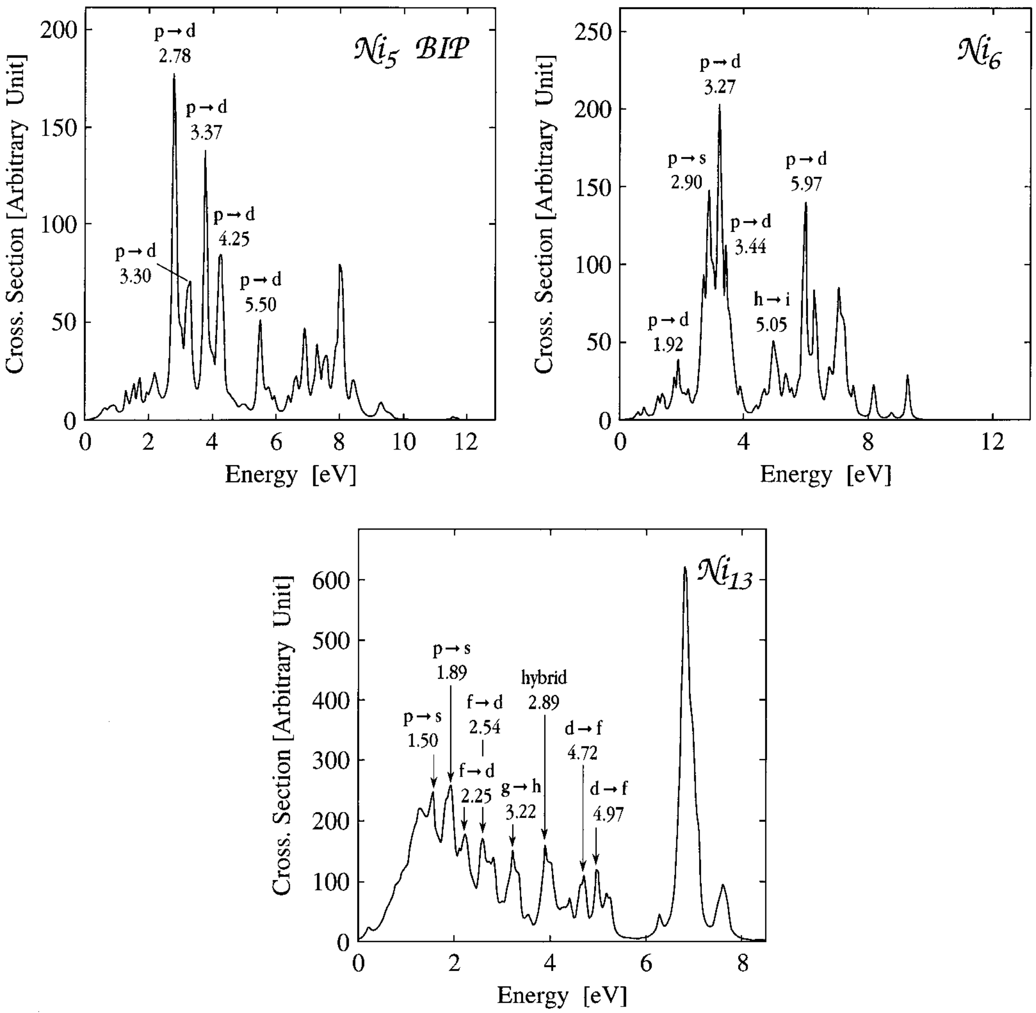


Fig. 3. Photoabsorption spectra of a Ni_5, Ni_6, and a Ni_{13} cluster.

Ni_3. In addition there are minor peaks at 1.93, 2.57, 4.49, and 5.07 eV in Ni_2, and at 2.40, 3.09, 4.35, and 5.65 in Ni_3. The case of Ni_4 is particularly interesting since the cluster has two isomers with the same magnetic moment per atom. The photoelectron spectra (Fig. 2) show that the isomers have peaks at different energies. For example, the lowest peak in a square Ni_4 is at 1.39 eV, while a D_{2d} structure has the first peak at 2.98 eV. The position of the most intense peaks is also very different. Whereas a square structure has a peak at 3.09 eV, the D_{2d} structure has a peak at 3.36 eV. Although not accessible experimentally, note that the global nature of states responsible for the main peak and the positions of sub-peaks are also different. All this shows that the photoabsorption spectra can provide a fingerprint of the geometry. For Ni_5 and Ni_6, main peaks at 2.78 and 3.27 eV mark the spectra in Figure 3, respectively. Finally, Ni_{13} presents very rich spectra with several peaks. This is expected because of the increase in the number of electronic levels. The states for the peak at 2.89 eV had mixture from several angular-momentum states and have been labeled as hybrid.

To summarize, we have presented what we believe are the first theoretical photoabsorption spectra for Ni_n clusters. The spectra not only change markedly with size, they depend sensitively on the geometry of the cluster. To this end, photoabsorption should be able to identify the isomers, which cannot be otherwise distinguished by their magnetic moment or other properties. As we mentioned in the beginning, there are currently no experimental spectra for Ni_n clusters and we hope that our work will stimulate these experiments.

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