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On the electron affinities of the Ca, Sc, Ti and Y atoms

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Abstract

For the Ca, Sc, Ti and Y atoms calculations are performed for the ground states of the neutrals and the ground and several low-lying excited states of the negative ions. Overall the computed electron affinities are in good accord with experiment. The calculations show the rapid stabilization of the $3d$ orbital relative to the $4p$ as the nuclear charge increases. The $^3F^o$ and $^3D^o$ terms are found to be close in energy in Sc^- and in Y^-. This confirms earlier speculation that some of the peaks in the photodetachment spectra of Y^- originate from the bound excited $^3F^o$ term of Y^-.

I. Introduction

In the past few years, advances have been made in determining the electron affinity (EA) of the transition metal atoms [1]. Interestingly, in the Sc^- and Y^- ions, as in the alkaline-earth negative ions, the extra electron occupies the p orbital, whereas in the remaining transition metal atoms it occupies the d orbital. Thus the order of filling of electron shells for the first-row transition series negative ions is found to be $3d^1 4s^2 4p^1$ (following Ca^- $4s^2 4p^1$) followed by $3d^k 4s^2 (k = 3, 4, \ldots, 10)$ [2]. This is consistent with the fact that the d orbitals are becoming increasingly stable with respect to the s and p orbitals as the nuclear charge increases for a given row of the periodic table. In addition to the accurate determination of the EA values, photodetachment spectroscopy is yielding information about the excited states of the negative ions. The ground electronic state of

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Sc$^-$ has been established experimentally [2] as $3d^1 4s^2 4p^1$, but it was not possible to distinguish which of the two terms, $^1D^o$ or $^3D^o$, is the ground state, and which is the excited state lying 0.15 eV higher. However, subsequent calculations by Jeung [3] have shown rather conclusively that the ground state is $(3d^1 4s^2 4p^1)^1D^o$.

The photoelectron spectrum of Y$^-$ has been interpreted [2] in terms of a $(4d^1 5s^2 5p^1)^1D^o$ ground state. Transitions to the $(4d^1 5s^2)^2D$ ground state of Y have been observed not only from the $^1D^o$ ground state of Y$^-$, but from the bound excited $^3D^o$ state of Y$^-$ as well. On the basis of the neutral energy-level spacings and the photelectron selection rules for s-electron detachment, it was possible to definitively assign the ground state of Y$^-$ as $^1D^o$, as well as to identify the bound state lying 0.14 eV higher as the $^3D^o$ term of the same electronic configuration. In addition to these two bound states of Y$^-$, the photelectron spectrum suggests the possibility of a third bound state, $(4d^1 5s^2 5p^1)^3F^o$, very close in energy to the $^3D^o$ term. This was based on the hypothesis that the feature near 0.5 eV in Fig. 3 of Ref. 2 was due to the $\mathrm{Y}^-(4d^1 5s^2 5p^1)^3F^o \rightarrow \mathrm{Y}(4d^1 5s^1 5p^1)^4F^o$ detachment.

In this work we consider the EA of the Ca, Sc, Ti, and Y atoms using large one-particle basis sets and an extensive treatment of valence correlation. The effect of core-valence correlation is minimized by referencing the calculations to a state of the neutral atom that has the same number of d electrons as the negative ion, and then adjusting to the ground state of the atom using the known atomic splittings [4]. We find that the $^3F^o$ term lies about 0.076 eV below the $^3D^o$ term in Y$^-$, thus supporting the proposed assignment [2] of the peak in the photoelectron spectrum of Y$^-$ near 0.5 eV as a $^3F^o \rightarrow ^4F^o$ detachment.

II. Methods

The Sc and Ti basis sets are derived from the (14s 9p 5d) primitive set of Wachters [5], and are contracted to [8s 4p 3d]. These sets are augmented with two diffuse p functions, a diffuse d function [6], and three f functions derived by fitting to a Slater 4f function with exponents of 1.6 and 2.0 for Sc and Ti, respectively. The basis sets are further augmented by adding a set of diffuse s, p, d and f functions to describe the negative ions. The exponents for the diffuse functions are taken to be a factor of 2.5 smaller than the smallest exponents in the valence basis. For Ca a similar procedure is followed, except that the six 3d functions are optimized [7] for the ^3D term, and all four f functions are even tempered with an exponent range from 0.716 to 0.046. Thus the Ca, Sc and Ti basis sets are all of the form $(15s\ 12p\ 7d\ 4f)/[9s\ 7p\ 5d\ 4f]$.

For yttrium we used the relativistic effective core potential (RECP) developed by Hay and Wadt [8]. Since this RECP does not include the $4s$ or $4p$ orbitals in the core potential, the $5s$ orbital has a node allowing us to correlate both the $4d$ and $5s$ electrons. The valence basis set is modified and supplemented as described in Ref. [9]. The three f functions from Ref. [9] are also included. As for Ca, Sc and Ti, this Y basis set is supplemented with a diffuse s, p, d and f function to provide an accurate description of Y^-. Thus the final valence basis set is of the form $(7s\ 7p\ 6d\ 4f)/[6s\ 5p\ 4d\ 4f]$. In all calculations only the pure spherical harmonic components of the basis functions are used.

At the SCF level, none of the atoms studied here have bound negative ions, i.e. the EA are negative. Thus for accurate results electron correlation must be included, at least for the valence electrons. It is possible to quantitatively account for the effects of valence correlation, at least on the left-hand side of the row, where the number of electrons correlated is relatively small. However, as core-valence correlation can significantly affect the atomic splittings, it is neccesary to adopt a computational strategy that minimizes this effect. Since the $(n+1)s$ and $(n+1)p$ orbitals are rather diffuse in both the neutral and ion, one expects a very small differential core-valence correlation effect when the extra electron is added to one of these orbitals. On the other hand, if an electron is attached into a compact nd orbital, a large differential core-valence correlation effect is expected. We avoid the need to calculate this effect by computing the EAs relative to the neutral atom with the same number of d electrons, and then adjusting the values relative to the ground state of the atom using known experimental atomic separations. In this way, it is possible to obtain computed EAs that are effectively corrected for core-valence correlation without having to perform the much larger (and often less reliable) calculations that arise when eight additional electrons are included in the correlation treatment.

Valence correlation is included using the complete-active-space-self-consistent-field (CASSCF) multireference configuration-interaction (MRCI) approach. The nd, $(n+1)s$ and $(n+1)p$ orbitals and electrons are included in the active space. For each state a separate CASSCF optimization is performed with full symmetry and equivalence restrictions imposed on the orbitals [10]. More extensive correlation is included using a second-order CI (SOCI) procedure: this consists of all configurations with up to two electrons in the secondary space and all distributions of the electrons in the active space.

The calculations were performed on the NASA Ames CRAY X-MP/48, and CRAY X-MP/14se computers using the MOLECULE-SWEDEN program system [11,12].

III. Results and Discussion

The computed EA values are summarized in Table I along with the available experimental results [2,13,14]. The Ca EA is in good agreement with experiment [13] and a previous theoretical value obtained using an extensive MCSCF wave function expanded in numerical orbitals [15]. Since the ^2D term lies 0.72 eV above the ground state, attachment of the electron into the $3d$ orbital is much less favorable. Note that the EA of the ^2D term of Ca is different by almost 0.3 eV, when computed directly with respect to the ^1S ground state of Ca, as opposed to first computing it with respect to the ^3D excited state of Ca, and then correcting to the ground state using the experimental energy separation [4]. The latter approach is significantly superior, as it avoids comparing states with a substantially different core-valence contribution. It is interesting to note that density functional theory (DFT) [15], which has the EA of the ^2P term too large, has the ^2D term unbound by 1.45 eV, or about twice as large as the CI approach. This illustrates the difficulty of describing the relative energies of the p and d orbitals from the density.

Our theoretical results, like those of Jeung [3] and Froese Fischer *et al.* [15] indicate that the ground state of Sc$^-$ is $(3d^1 4s^2 4p^1)^1D^o$. However, our SOCI results for the EA are in better agreement with experiment [2]. Further, our SOCI results indicate that the $(3d^1 4s^2 4p^1)^3D^o$ term of Sc$^-$ is bound, but our computed EA lies just outside the experimental error bars [2]. The $(3d^1 4s^2 4p^1)^3F^o$ term is found to be just slightly unbound at the SOCI level, but considering that our computed EA for the $^3D^o$ term is slightly too small, it is possible that this state is also weakly bound. In their analysis of the spectra, Feigerle *et al.* [2] assume the existence of only two ion states, and found that the $^1D^o$ and $^3D^o$ terms fit the data best. They therefore ruled out a bound $^3F^o$ term with 95% confidence. However, the calculations suggest the possibility that the $^3D^o$ and $^3F^o$ terms are both bound and so close in energy that detachment from both terms compose the peaks observed in the spectra. Unfortunately, the ${}^4F^o$ and ${}^4D^o$ terms of the neutral with the occupation $3d^1 4s^1 4p^1$ are probably too close in energy to be resolved with current technology. However, by using a higher photon energy it should be possible to observe detachment to the $(3d^1 4s^1 4p^1)^2F^o$ term at about 21 000 cm^{-1} above the ground state if the ${}^3F^o$ term is bound.

The $(3d^1 4s^2 4p^1)^1F^o$ and $(3d^2 4s^2)^3F$ terms of Sc^- are sufficiently high in energy that our calculations definitively determine them to be unbound. Again there is a large core-valence contribution to the EA as judged by the two EAs for the ${}^3F$ term tabulated in Table I. The first value, which is obtained by detaching to give the $(3d^2 4s^1)^4F$ term of Sc is the preferred EA value as it avoids problems with differential core-valence contributions. The second value, obtained by detaching to give the $(3d^1 4s^2)^2D$ ground state of Sc, results in this term being unbound by about 0.55 eV, which is in good agreement with the earlier theoretical calculations of Jeung [3]. As for Ca, adding an electron to the $3d$ orbital is found to be much less favorable with the DFT formalism [15]. Note that $3d$ attachment in Sc is much more favorable than in Ca, since the $3d$ orbital is becoming stabilized with respect to the 4p orbital as the atomic number increases across the row.

For Ti, the SOCI calculations are in agreement with experiment [14] in indicating that attachment of an electron into the $3d$ orbital is more favorable than attachment into the $4p$ orbital. The error in our computed result for Ti is larger than for Ca or Sc. Although this may be partly due to core-valence effects, it is more likely that the larger number of electrons correlated results in a larger error due to the neglect of higher excitations. In this regard we note that if we add the multireference analog of the Davidson correction [16], our computed EA for Ti is 0.105 eV, which is now just slightly larger than experiment. With the application of the Davidson correction, the ${}^4G^o$ term also becomes bound by 0.008 eV. As there is no experimental evidence that this term is bound, we suspect that the Davidson correction gives a slight overestimation for both the ${}^4F$ and ${}^4G^o$ terms.

Finally it is instructive to compare the results for Sc and Y summarized in Table I. The ground state of both negative ions is ${}^1D^o$, which is consistent with that deduced from the Y^- photodetachment spectra. The computed EA for Y is almost twice that for Sc and the computed value appears to have a larger error than for Sc. However, the experimental value [2] is for the lowest m_j component, while the computed value uses $L-S$ coupling and, therefore, corresponds to the weighted average. Using the weighted average reduces the error in Y so that it is only slightly larger than for Sc. All the states of Y^- are more stable than the corresponding states in Sc^-, and there are clearly three bound states of Y^- compared to two for Sc^-. However, the existence of a third bound state in Sc^- is not precluded by the present calculations. In our calculations the $^3D^o$ and $^3F^o$ terms of Y^- are reversed relative to Sc^-. However, they are sufficiently close in energy that with the inclusion of spin-orbit coupling the sublevels may actually overlap. This near degeneracy of the $^3D^o$ and $^3F^o$ terms is consistent with the speculation by Feigerle *et al.* [2] that these two terms are very close in energy. Therefore, the peaks at about 0.5 eV electron kinetic energy in their Y^- spectra probably correspond to detachment from the $^3F^o$ term, as they suggested.

IV. Conclusions

Overall the computed results are in good agreement with experiment. The rapid stabilization of the d orbital relative to the p orbital is quite apparent in the calculations. The $^3F^o$ term of Y^- is very close in energy to the $^3D^o$ term, being the more stable of the two in the present calculations. The near degeneracy of these two states shows that the peaks at about 0.5 eV in the Y^- photodetachment spectra of Feigerle *et al.* [2] are from the $^3F^o$ term, as they speculated.

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Table I. Summary of the electron affinities in eV.

Atom/Term	SOCI[a]	Previous Theoretical	Expt
$\mathrm{Ca}^-\ {}^2P^o(4s^24p^1)$	+0.022	0.045[b],0.171[c]	0.043±0.007[d]
$\mathrm{Ca}^-\ {}^2D(4s^23d^1)$	−0.720(−1.007)	−1.448[c]	
$\mathrm{Sc}^-\ {}^1D^o(3d^14s^24p^1)$	+0.195	0.152[b],0.452[c],0.14[e]	0.189±0.020[f]
$\mathrm{Sc}^-\ {}^3D^o(3d^14s^24p^1)$	+0.011	0.193[c],-0.02[e]	0.042±0.020[f]
$\mathrm{Sc}^-\ {}^3F^o(3d^14s^24p^1)$	−0.005		
$\mathrm{Sc}^-\ {}^1F^o(3d^14s^24p^1)$	−0.321		
$\mathrm{Sc}^-\ {}^3F(3d^24s^2)$	−0.343(−0.551)	−0.740[b],−0.601[c],−0.55[e]	
$\mathrm{Ti}^-\ {}^4F(3d^34s^2)$	+0.002(−0.147)		0.080±0.014[g]
$\mathrm{Ti}^-\ {}^4G^o(3d^24s^24p^1)$	−0.108		
$\mathrm{Ti}^-\ {}^2F^o(3d^24s^24p^1)$	−0.172		
$\mathrm{Y}^-\ {}^1D^o(4d^15s^25p^1)$	+0.398		0.308±0.012[f,h]
$\mathrm{Y}^-\ {}^3F^o(4d^15s^25p^1)$	+0.179		
$\mathrm{Y}^-\ {}^3D^o(4d^15s^25p^1)$	+0.103		0.165±0.025[f]
$\mathrm{Y}^-\ {}^1F^o(4d^15s^25p^1)$	−0.233		
$\mathrm{Y}^-\ {}^3F(4d^25s^2)$	−0.118(−0.193)		

[a] The SOCI value is computed as the EA relative to the neutral with the same number of *d* electrons, then corrected to the ground state of the neutral using the experimental separations. The value in parentheses is the computed EA directly to the ground state neutral for comparison.

[b] Multiconfigurational Hartree-Fock theory results from Ref. 15.

[c] Density-functional theory results from Ref. 15.

[d] Reference 13.

[e] CI results from Ref. 3.

[f] Reference 2.

[g] Reference 14.

[h] The EA for the weighted average of m_j components is 0.35 eV.