Binding energies and structure of transition metal negative ions

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The photoelectron spectra of 11 transition metal negative ions have been obtained in a crossed beam experiment using a sputter type ion source and a fixed frequency ArF laser (488 nm). The electron affinities (E.A.'s) are measured to be E.A.(Ti) = 0.080 ± 0.014 eV, E.A.(V) = 0.526 ± 0.002 eV, E.A.(Cr) = 0.667 ± 0.010 eV, E.A.(Zr) = 0.427 ± 0.014 eV, E.A.(Nb) = 0.894 ± 0.025 eV, E.A.(Mo) = 0.747 ± 0.010 eV, E.A.(Rh) = 1.138 ± 0.008 eV, E.A.(Pd) = 0.558 ± 0.028 eV, E.A.(Ta) = 0.323 ± 0.012 eV, E.A.(W) = 0.816 ± 0.008 eV, and E.A.(Ir) = 1.566 ± 0.008 eV. The ground states of the negative ions of these elements are determined from analysis of the photoelectron spectra and all are found to be of a $d^{s-1}$ configuration with the exception of Pd$^{-}$ of $d^{s-2}$ s. Excited electronic states of Pd$^{-}$ ($4d^{s}5s^{2}$) $2D_{15}$ and Ta$^{-}$ ($5d^{s}6s^{2}$) $1P_{1}$ are identified. Calculation of relative intensities of photoelectron transitions is used extensively in the analysis of the spectra and is compared with experiment for a number of cases. The spin–orbit separations for Rh $^1P$ and Ta $^1D$ are measured and compared with values obtained from ratio isoelectronic extrapolation. The accuracy of this extrapolation technique is discussed and an extensive table of extrapolated splittings for transition metal negative ions is given. Plots of the $s$-electron binding energies of the transition metal negative ions versus the number of $d$ electrons exhibit smooth trends and striking similarities for each of the three transition series.

I. INTRODUCTION

The electron affinity (E. A.) of atoms is an important quantity for a variety of reasons. In the appropriate thermodynamic cycle E. A.'s provide one of the numbers necessary for the determination of gas phase acidities or homolytic bond dissociation energies. Experimental electron affinities, when coupled with converged Hartree–Fock energies for the neutral and negative ion, give "experimental" correlation energy differences between the two species. The methods of threshold photodetachment and laser photoelectron spectroscopy have provided us with most of the accurately measured atomic electron affinities. The state of these measurements has been recently reviewed. We report in this paper the laser photoelectron spectra of 11 transition metal negative ions; analysis of these data increases by nearly one third the number of accurately known atomic electron affinities.

Investigations of the periodic nature of atomic properties has made a substantial contribution to our understanding of atomic structure and structure-reactivity relationships. Electron affinities are one such property for which lack of experimental data has slowed such studies. There have been especially few accurate measurements of electron affinities for the transition metals. Previous measurements are limited to E. A.'s of Cr, Fe, Ni, Cu, Ag, Pt, and Au. The basic technological problem that has restricted the number of these measurements is the availability of suitable ion sources to make atomic metal negative ion beams. While there has been some progress by the use of volatile organometallic complexes in a gas discharge ion source, no completely general prescription for making metal negative ions in this fashion has yet emerged. The development of a sputter type ion source has made the production of modest negative ion beams of these elements comparatively simple.

Through the use of such a source, we report in this paper the measurement of the electron affinities of 11 transition metals: Ti, V, Cr, Zr, Nb, Mo, Rh, Pd, Ta, W, and Ir. The ground state designations of negative ions of these elements are inferred from the photoelectron spectra. The ground electronic configuration of each of these negative ions, with the exception of Pd$^{-}$ is found to be $d^{s-2}$. In addition to the electron affinity measurements we have also determined the positions of excited fine structure states of Rh$^{-}$ and Ta$^{-}$, and of excited electronic states of Ta$^{-}$ and Pd$^{-}$. The details of the individual photoelectron spectra of these ions are presented in the section on experimental results. In particular, the results of angular momentum analysis of relative intensities are used extensively and compared with experiment for a number of cases.

Owing to the lack of accurate experimental values for the electron affinities of many of the transition metals, the previous best estimates of these numbers have come from extrapolation techniques. One of the most successful of these techniques (horizontal analysis) is based on an extrapolated series trend in the $s$-electron binding energy for the transition metal negative ions. The measurements in this paper, together with some earlier measurements, provide a sufficient subset so that we can now begin to look at series trends in the binding energies of transition metal negative ions, with accurate experimental data as a basis. Thus, we present in the Discussion section of this paper the most accurately measured $s$-electron binding energies, plotted
as a function of the number of $d$ electrons for each of the	hree transition series. These plots exhibit remarkably
smooth trends and strong similarities across the three
transition metal series.

While there have been few accurate measurements of
the electron affinities of transition metals, there have
been even fewer measurements of the spin–orbit splittings
of the negative ions of these elements. Including this
investigation there have been measurements for only
the spin–orbit splittings in Co$^-$, $^{32}$ in Ni$^-$, $^{32}$ in Rh$^-$, and
in Ta$^-$. Using the method of ratio isoelectronic extrapola-
tion, $^{3}$ we have calculated the spin–orbit separations for
most of the transition metal negative ions. By com-
paring the extrapolated values with experimental num-
bers for Co$^-$, Ni$^-$, Rh$^-$, and Ta$^-$, we have arrived at what
we believe to be reliable error bars on the extrapolated
values.

II. EXPERIMENTAL

The apparatus and technique of laser photoelectron
spectrometry have been previously described in de-

tail. $^{31}$ The major difference between the previously re-
ported experiments with this apparatus and the present
ones is the use of a sputter type ion source $^{35,32}$ to pro-
duce the atomic negative ions. This sputter source is
depicted schematically in Fig. 1. Briefly, neutral cesium
is surface ionized on a porous tungsten disk heated to
1200°C. The Cs$^+$ beam (typically 100 $\mu$A) is
accelerated to 4 keV and focused by an einzel lens onto
a target of the metal of interest. The sputtered negative ions
which make it through a 1 mm aperture in the tar-
get are accelerated to 680 eV, focused, and mass se-
lected by a Wien velocity filter. The most intense mass
selected negative ion beam currents (0.5 pA–1 nA de-
pending on the metal target) were obtained using targets
of hollow cone geometry with a 1 mm aperture at the
apex; for some studies a flat disk target was employed.
The limited mass resolution of the Wien filter (one part
in 40) means that in general one cannot distinguish MH$^-$
from M$^-$ ions. The mass selected negative ion beam is
crossed at 90° in a field free interaction region with the
linearly polarized intracavity radiation from a cw argon
ion laser. The typical circulating power is ~100 W at
488 nm (2.540 eV), the wavelength at which data were
usually obtained. Those electrons ejected into a small
solid angle (6.28 $\times$ $10^{-5}$ sr) perpendicular to the plane
of the ion and laser beams are collected and energy ana-
lyzed in a hemispherical electron monochromator.
The resolution of the electron monochromator (55 meV
FWHM) is such that electron energy groups separated by
greater than 100 meV are generally resolvable.

A conversion to absolute, center–of–mass, electron
kinetic energy in the photoelectron spectrum is achieved
by detaching O$^-$ as a calibration and applying the energy
balance expression $^{11}$

$$E_m = h\nu - E.A.(O) - \gamma(\Omega_{O^-} - \Omega_{M^-}) - mW\left(\frac{1}{M_O} - \frac{1}{M_M}\right).$$

(1)

In this equation, $h\nu$ is the photon energy, $E.A.(O)$
$=1.465 \pm 0.003$ eV is the “effective” electron affinity of

the oxygen atom, $^{13,23}$ $\gamma$ is an energy scale compres-
sion factor (typically $\sim 1.02$), $^{31}$ and $(\Omega_{O^-} - \Omega_{M^-})$ is the mea-
sured energy difference between the O$^-$ peak center and
a position in the M$^-$ spectrum. Qualitatively, $\gamma$ is be-
lieved to be a result of aberrations in the electron optics
and empirically is found to be primarily dependent on
the position of the laser focus across the interaction re-
gion. Thus, once alignment of the laser is achieved,
the value of $\gamma$ remains constant throughout subsequent
experiments. In the present set of experiments, $\gamma$ is
determined either independently or self–consistently by

$\gamma$ is determined either independently or self–consistently by

calibrating the observed splittings in the M$^-$ spectrum
against the well–established spectroscopic splittings
of the neutral atom. $^{32}$ In particular, the spectrum of W$^-$
provides an excellent determination of $\gamma$. As will be
seen below, uncertainties in the value of $\gamma$ make only a
minor contribution to errors in E.A.'s. The last term
in Eq. (1) is a small kinematic term resulting from the
fact that the electrons collected perpendicular to the ion
beam must have been backscattered in the center–of–mass
frame. In this kinematic term, $W$ is the ion beam energy,
and $m$, $M_O$, and $M_M$ are the masses of the elec-
tron, oxygen atom, and metal atom M, respectively.
The transition energy $A_M$ associated with any peak in
the photoelectron spectrum can now be obtained by en-
ergy conservation:

$$h\nu = E_m + A_M.$$

(2)

The intensity of the photoelectron spectrum at a par-
ticular electron kinetic energy depends on the angle ($\theta$)
between the polarization vector of the laser light and the
electron collection direction according to

$$I(\theta) = \frac{\sigma_{tot}}{4\pi}[1 + \beta(E)P_2(cos\theta)],$$

(3)

where $\sigma_{tot}$ is the total photodetachment cross section,
$\beta(E)$ is the anisotropy parameter, and $P_2(cos\theta)$ is the
second Legendre polynomial. The spectra presented
here were taken with the laser polarization at the
"magic" angle of 54°44', so that $P_2(cos\theta) = 0$, and the in-
tensity is that of the average photodetachment cross sec-
tion. We can therefore obtain meaningful relative inten-
sities without the necessity for measuring photoelectron
angular distributions.

III. DATA ANALYSIS

In photoelectron spectroscopy of atomic negative ions
there is generally much more known about the structure


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and energy levels of the neutral than is known about the negative ion. For this reason, analysis of the photoelectron spectrum starts with the assignment of the final neutral states associated with the observed photoelectron peaks. The primary basis for the final state assignments is the following: The observed energy differences between any set of peaks thought to arise from transitions from the same initial state of the negative ion, and terminating on different final states, must be consistent (within our error limits) with the spectrscopically determined energy differences of the neutral states. Once the final states in the spectrum are assigned, we then deduce the negative ion states responsible for the spectrum.

For simplicity, let us consider the case where peaks forming only one sequence of final neutral states are observed in the spectrum and hence there is only one detaching negative ion state. In a spectrum where more than one final state neutral sequence is observed, the assignment procedure is repeated for each sequence. The assignment of the initial state follows the hierarchy of atomic structure and starts with the assignment of the electronic configuration of the negative ion. Considering the known near degeneracy of the d and s electrons in the transition metals, three configurations are reasonable for a transition metal negative ion of $k + 2$ valence electrons: $d^{9}s^{2}$, $d^{9}s^{3}$, and $d^{9}s^{2}$. We can determine from the spectrum which one of these possible configurations is correct by recognizing that the major photodetachment features will arise from a single electron process. For example, if the observed neutral sequence contains only $d^{9}s^{2}$ and $d^{9}s^{3}$ configurations, we conclude that the negative ion state responsible for that sequence is a $d^{9}s^{2}$ configuration.

Once the final neutral states and negative ion configuration are assigned, we deduce the angular momenta $L$, $S$, and $J$ of the negative ion state by application of the photodetachment selection rules. These selection rules are $|\Delta L| \leq 1$, $|\Delta S| \leq 1$, and $|\Delta J| \leq 1$, where $L$ is the angular momentum of the orbital shell from which the electron was detached. From the $\Delta L$ selection rule we know that the initial state orbital angular momentum must be the same as that of the final state for an $s$-electron detachment. Thus, once an $s$-electron detachment is assigned, the orbital angular momentum of the negative ion state is known. Similarly, the spin angular momentum of the negative ion state can be readily deduced from the $\Delta S$ selection rule. For example, if the final state neutral sequence contains only singlets and triplets, then the initial state is a doublet.

In principle, the total angular momentum of the negative ion state $J$ can be determined in a similar fashion. To make this determination requires that transitions between fine structure states of the negative ion and the neutral are resolved in the spectrum. However, in many of the spectra presented in this paper, fine structure transitions are not resolved. In these cases we have assumed Hund’s rules apply and that the ordering of the fine structure states of the negative ion term is normal. Thus, we know the configuration, orbital and spin angular momenta, and, if there are no pathologies, the total angular momenta of the negative ion states responsible for the photoelectron spectra. As a final confirmation of the negative ion state assignments, we require that the photoelectron spectrum must contain all those and only those transitions that are allowed by the photoelectron selection rules. As, in principle, a single assigned peak allows the determination of the electron affinity of the species, the requirement of multiple peak confirmation of the negative ion state assignments results in an overdetermined measurement of this quantity.

One problem that has already been alluded to is that we cannot in general separate $MH^{+}$ from $M^{-}$ in the ion beam. We have dealt with this problem in the following fashion: When photodetachment of $MH^{-}$ is suspected to be contaminating the $M^{-}$ spectrum, the $MH^{+}$ concentration in the beam is increased by adding a source of hydrogen ($H_{2}$ or $NH_{3}$) to the ion source and then the spectrum is retaken. This procedure typically enhances the ratio of $MH^{+}/M^{-}$ within the beam by a factor greater than 5. Choosing an $MH^{+}$ peak that is isolated from the $M^{-}$ peaks, we scale the enhanced spectrum such that the intensity of this peak is the same as in the original spectrum. By subtracting this entire spectrum from the originally contaminated one, we obtain a separate photoelectron spectrum of $M^{-}$.

It is useful at this point to elaborate on the basis for the error limits quoted in this paper. Inserting Eq. (1) into the conservation of energy equation $h\nu = E_{M} + A_{M}$ and defining

$$\Delta\Omega = \gamma (\Omega_{O^-} - \Omega_{M^{-}}),$$

we obtain for $A_{M} = E(A,M)$,

$$E(A,M) = E(A,0) + \Delta\Omega + m_{e} \left( \frac{1}{M_{O^{-}}} - \frac{1}{M_{M^{-}}} \right).$$

Applying standard propagation of errors analysis on Eq. (5) yields

$$\epsilon[ E(A,M) ] = \left[ \epsilon[ E(A,0) ]^{2} + \epsilon(\Delta\Omega)^{2} \right]^{1/2},$$

where the (negligible) error associated with the kinematic term has been dropped. The error limits quoted in this paper are predominantly a result of the uncorrelated errors in our measurement of $\gamma$ and the O$^{-}$ and M$^{-}$ peak positions. Concentrating then on $\Delta\Omega$, we see that its error is given by

$$\epsilon(\Delta\Omega) = \Delta\Omega \left[ \left( \frac{\epsilon(\gamma)}{\gamma} \right)^{2} + \left( \frac{\epsilon(\Omega_{O^{-}} - \Omega_{M^{-}})}{\Omega_{O^{-}} - \Omega_{M^{-}}} \right)^{2} \right]^{1/2},$$

where the error in $\gamma$ is typically less than 1%. If the M$^{-}$ peak is not complicated by unresolved multiple transitions, then the least-squares peak fitting procedure conservatively determines $(\Omega_{O^{-}} - \Omega_{M^{-}})$ to $\pm 7$ meV. As the energies of electronic states of the neutral species M are known to much greater accuracy than the measured photoelectron energies, we can choose any identified $M^{-} + e$ transition we wish to determine E(A, M) Normally, it is possible to find an M$^{-} + e$ transition whose photoelectron energy is sufficiently close to the O$^{-} + e$ reference transition that the uncertainty in $\gamma$ (-1%) does not increase the error in $\Delta\Omega$ to greater than 7-10 meV. Coupling this result with the $\pm 3$ meV uncertainty in the "effective" E(A, O), we obtain an
8–10 meV error in E.A.(M). As a test, this procedure was applied to Pt, giving E.A.(Pt) = 2.128 ± 0.010 eV, in agreement with the threshold photodetachment value of 2.128 ± 0.002 eV.31

The electron affinity is defined as the difference in energy between the lowest fine structure level of the negative ion and that of the neutral ground state. However, in many of the transition metal spectra reported here, the spin–orbit splittings of both the neutral and the negative ion are too small for this transition to be resolved from within a multiplet peak. The problem in these cases is how to choose the position of this single multiplet component within the observed peak. In order to accomplish this determination it is necessary to know the (normally unknown) fine structure level splittings in the negative ion, to know the populations of each of those levels in the ion beam, and to be able to calculate relative intensities of transitions between fine structure levels of the negative ion and the neutral. The negative ion fine structure splittings are estimated by a ratio iso-electronic extrapolation.36 The relative intensities of the transitions are calculated within a “golden rule” approximation coupled with angular momentum analysis,21,22,76 and modified to an assumed 1000 K Boltzmann population of negative ion fine structure levels. This type of relative intensity calculation will be referred to in this paper as the fractional parentage method. The sum of these procedures results in a theoretical line shape, which can then be compared with the observed peak.

Qualitatively, the comparisons have been excellent. Quantitatively, estimates of the errors associated with this procedure must be treated on an individual basis. Thus, the reported errors in the electron affinities range from 12–25 meV in cases where this procedure has been used to determine the position of the electron affinity defining transition within the peak. The results of such multiplet line shape profile calculations are shown for Zr and Nb in the next section, along with the experimental results.

IV. EXPERIMENTAL RESULTS

The individual results given here are presented in the following fashion: All spectra have been corrected via Eq. (1) to an absolute center-of-mass electron kinetic energy. The transition energy can be obtained by simply subtracting the observed peak position from the photon energy at which the spectrum was taken. The appropriate energy level diagram is presented to the left of the spectrum. Energetically accessible states of the neutral which would result only from forbidden transitions from the assigned states of the negative ion have been omitted from the diagram. Where the spectrum presented does not cover the full electron energy range, data were actually obtained across the full spectrum and no additional peaks were observed outside that range. We begin with a case study of the photoelectron spectrum of Pt+, treating in detail the procedures that are generally used in analysis of the reported spectra. The remaining experimental results are grouped according to the columns of the periodic table.

A. Pd: A case study

With a Pd target installed in the sputter source, we measured a spectrum from a 15 pA beam, comprised of Pd+ with an unknown amount of Pd++ contaminant. Addition of H2 to 1 × 10–5 Torr in the source yielded an additional spectrum with an increase of greater than a factor of 10 in the Pd++/Pd+ ratio, allowing a clear identification of which peaks in the original spectrum were due to Pd+ and which were due to Pd++. By scaling the spectrum obtained under the enhanced Pd++/Pd+ ratio conditions to the intensity of the clearly identifiable Pd++ contaminant in the original spectrum and then subtracting, we obtain a photoelectron spectrum of Pd++.

The resulting spectrum of Pd++ measured at 2.540 eV photon energy (488 nm) and the corresponding energy level diagram are shown in Fig. 2. In all, eight peaks corresponding to nine transitions from two states of the negative ion are observed.

Analysis of the measured peak separations reveals two final state sequences in the spectrum. This observation alone indicates that there are at least two states of the negative ion with appreciable population in the beam. This is not an unreasonable conclusion, as modeling of previous measurements has indicated a 1000–2000 K electronic temperature for ions from this source.32 Assuming a Boltzmann distribution, we expect to have adequate excited state populations to observe detachment from states lying up to ~0.5 eV above the negative ion ground state. Peaks B, D, E, F, and H form the Pd sequence of (4d0/0)5S1, the three fine structure components of (4d4/2 5S1/2), and (4d4/2 5S1/2). These assignments are in agreement with the known spacings of these states33 to within 3 meV. As this sequence contains only 4d10 and 4d5S configurations, we conclude that the negative ion state responsible for this sequence is (4d6/2 5S1/2). A second Pd sequence of (4d10/0)5S1, (4d4/2 5S1/2), (4d4/2 5S1/2), and (4d4/2 5S1/2) is formed by peaks A, C, D, and G, respectively. The final state assignments for this sequence are in agreement with the known neutral spacings33 to within 7 meV. The presence of both 4d10 and 4d5S configurations in this second Pd sequence argues for a 4d10 5S negative ion configuration. However, this is the same negative ion configuration that was determined from the first sequence, and there can be only one state of this configuration. To assign the two negative ion states in the Pd++ spectrum, we need to look further than just the final state configurations.

There are only three reasonable states for Pd++: (4d6/2 5S1/2), (4d4/2 5S1/2), and (4d4/2 5S1/2). The photoelectron selection rules indicate which transitions are allowed from each of these three states. From a Pd++ state, s-electron detachment to Pd5S and d-electron detachment to Dg, Dg, Dg, and Dg are allowed. This is exactly the set of states that is observed in the Pd sequence formed by peaks B, D, E, F, and H. The second Pd sequence (peaks A, C, D, and G) does not contain the transition to Dg. It is the absence of this transition that forms the strongest evidence that the negative ion state responsible for this sequence is not the (4d6/2 5S1/2). The allowed transitions from a Pd++
2\text{D}_{5/2} state are the s-electron detachments to 2\text{D}_2$, 3\text{D}_2$, and 3\text{D}_1. A \text{Pd}^+ \text{D}_{5/2} \rightarrow \text{Pd}^+ \text{D}_1 transition would be forbidden as an s-electron detachment. With the exception of 1\text{S}_0, the second final state neutral sequence contains exactly those states that are allowed transitions from a \text{Pd}^+ \text{D}_{5/2} state. The assignment of the peaks forming this sequence as being due to detachment from a \text{Pd}^+ \text{D}_{5/2} state then requires that peak A is the result of a two electron process. There is further evidence for this conclusion in the weakness of peak A.

Peak A is the weakest feature in the entire spectrum. Its intensity is completely contrary to what is expected for the s-electron detachment required of a 4d\text{4s}\text{5s} initial state assignment for this peak. Previous observations indicate s-electron detachments to be the most intense peaks in the spectrum, typically 5–20 times as intense as d-electron detachments. The only conclusion that is in accord with these observations is that peak A is not an s-electron detachment, but rather peak A is due to a two electron process.

The assignment of the \text{Pd}^+ photoelectron spectrum is now complete. Peaks B, D, E, F, and H result from photodetachment from the (4d\text{4s}\text{5s})^2\text{S}_{1/2} state of \text{Pd}^+. Peaks A, C, and G result from photodetachment from the (4d\text{4s}\text{5s})^2\text{D}_{3/2} state of \text{Pd}^+. Peak D is a multiple transition peak composed of both the 2\text{D}_{5/2} \rightarrow 3\text{D}_2 and 2\text{S}_{1/2} \rightarrow 3\text{D}_1 transitions. Whenever there is detachment from two states of the negative ion to the same final state of the neutral, the position of the peak associated with detachment from the upper state appears at higher electron kinetic energy relative to detachment from the ground state. As peak A (\text{Pd}^+ \text{D}_{5/2} \rightarrow \text{Pd}^+ \text{S}_0) is at higher electron kinetic energy than peak B (\text{Pd}^+ \text{S}_{1/2} \rightarrow \text{Pd}^+ \text{S}_0), the ground state of \text{Pd}^+ must be (4d\text{4s}\text{5s})^2\text{S}_{1/2} and E.A. (\text{Pd}) = 0.558 \pm 0.008 eV. The first excited state of \text{Pd}^+, i.e., (4d\text{4s}\text{5s})^2\text{D}_{3/2}, lies 0.136 \pm 0.008 eV above the ground state. While there have been no previous measurements of the electron affinity of \text{Pd}, \text{Pd}^+ has been observed in a mass spectrometer by Middleton.

The observation of the 2\text{D}_{5/2} \rightarrow 1\text{S}_0 transition (peak A) is somewhat surprising, as it arises from a two electron process. A reasonable explanation for its presence could be configuration interaction of the (4d\text{4s}\text{5s})^2\text{D} with a (4d\text{4s}\text{5s})^2\text{D} resonance state of \text{Pd}^+. This should be the lowest lying state that could interact with the (4d\text{4s}\text{5s})^2\text{D} state. We mentioned previously that (4d\text{4s}\text{5s})^2\text{D}_{3/2} was a possible state for \text{Pd}^+. Based on the empirical observation that the $\Delta E(4d\text{4s}\text{5s})(\text{Cu}^{2+} \rightarrow \text{Cu}^+)$\text{Pd} ratio varies by less than 2% for In$^{3+}$/In$^{2+}$, Cd$^{2+}$/Cd$^{3+}$, and Ag$^{+}$/Ag$^+$, we have linearly extrapolated as a function of Z to the isoelectronic \text{Pd}^+/\text{Pd} ratio to obtain $\text{Pd}^+ \Delta E(\text{Cu}^{2+} \rightarrow \text{Cu}^+) = 3450 \pm 350$ cm$^{-1}$. The (4d\text{4s}\text{5s})^2\text{D}_{3/2} state of \text{Pd}^+, not observed in our experiment, is thus predicted to lie 0.006 \pm 0.043 eV above the (4d\text{4s}\text{5s})^2\text{S}_0 state of \text{Pd} if this state is not bound, it should be metastable with respect to autodetachment to the 1\text{S}_0. However, the same CI that gave rise to the 2\text{D}_{5/2} \rightarrow 1\text{S}_0 transition might very well make its lifetime too short (7 less than 30 $\mu$s) for us to observe in our experiment. As this state should lie greater than 0.5 eV above the ground state of \text{Pd}^+, it is not clear whether population or lifetime limitations are responsible for its absence.

### B. Group IV-A elements: Ti, Zr, and Hf

**Ti:** The Ti$^+$ photoelectron spectrum measured at 2.540 eV photon energy (488 nm) and the corresponding energy level diagram are presented in Fig. 3. Contamination peaks, due to TiH$^+$ in the beam, have been subtracted away in the reported spectrum. Three peaks corresponding to transitions to three terms of the neutral (3d$^2$4s$^2$)a$^2$F, (3d$^2$4s)a$^2$F, and (3d$^2$4s)b$^2$F are observed. The only possible assignment of the ground state of Ti$^+$ is (3d$^2$4s$^2$)b$^2$F based on the prescription for assignment given in the database analysis section. Owing to
the extremely small beam current (~0.5 pA), the data shown in Fig. 3 were obtained in two separate data runs and peak A is consequently not normalized. Based on other observations of relative intensities of d- and s-electron detachment, the true intensity of peak A is expected to be smaller than that shown in Fig. 3.

Linear isoelectronic extrapolation of the $\Delta E_3(3d^44s^2) \times (4f_{j_p} - 1f_{j_p})/\Delta E(3d^34s)(2F_3 - 2F_1)$ fine structure ratios for Ti+ / Ti from those in V + V' and Cr+/Cr2+ gives the estimated Ti+ spin-orbit splittings $\Delta E(2F_{3/2} - 2F_{1/2}) = 123$ cm$^{-1}$, $\Delta E(2F_{5/2} - 2F_{3/2}) = 99$ cm$^{-1}$, and $\Delta E(2F_{7/2} - 2F_{5/2}) = 124$ cm$^{-1}$.

All Ti+ fine structure levels are expected to be populated statistically in the beam, at the high temperature limit. The three observed transitions are thus recognized to contain unresolved multiplet structure. We have modeled the positions of individual multiplet components by calculating theoretical multiplet line shape profiles and fitting this composite profile to each peak. By choosing those multiplet components that originate from the same fine structure level of Ti+, we can measure the interterm separations between individual fine structure levels $[\Delta E(3d^44s^2 - 3d^44s)]$ of neutral Ti. The neutral state separations thus obtained are consistent with the spectroscopically known splittings$^{33}$ to within 8 meV for all initial states of Ti+. This agreement is typical of the results obtained using this procedure. We have determined the electron affinity of Ti from the positions of the $2F_{3/2} - a^2F_2$, $a^2F_1$, and $b^3F_2$ transitions and the known neutral spacings, obtaining $0.080 \pm 0.014$ eV. As in Pd, there have been no previous measurements of the electron affinity of Ti, although Ti+ has been observed by Middleton.$^{35}$

The transition to $3d^24s^2a^2P$, which involves ejection of a single d electron and should occur at about 1.40 eV electron kinetic energy, is not identifiable in the Ti+ photoelectron spectrum. While this process is expected to be of lower intensity than s-electron detachment, one still expects$^{31,32}$ that it should be visible. One explanation for its absence appears to be given by the Cox theory$^{36}$ of ionization of open shells of d and f electrons. The theory relates the cross sections for transitions to different terms arising from detaching an electron from the same orbital shell I according to the expression

$$X(\alpha S_2 L_2) = Z(\alpha S_2 L_2 | S_1 L_1) \tilde{X}(l),$$

where S and L have their usual meanings and $\alpha$ distinguishes between possible repeated terms. Thus, the theory assumes that the photodetachment cross section $X(\alpha S_2 L_2)$ can be written as an “average” cross section for detachment from orbital shell I, i.e., $\tilde{X}(l)$, times a numerical coefficient. The numerical coefficient for detachment from a single open shell is given by

$$Z(\alpha S_2 L_2 | S_1 L_1) = \eta_\alpha |(\alpha S_2 L_2 | S_1 L_1)|^2,$$

where $\eta_\alpha$ is the number of electrons initially in the orbital shell I, and is multiplied by the square of the coefficient of fractional parentage.$^{35}$ Thus, the intensity ratio of d-electron detachment to $a^2P$ and $a^2F$ in Ti (and in Zr) is given by$^{36}$

$$\frac{X(d a^2P)}{X(d a^2F)} = \frac{|(a^2P \cdot d)|^2}{|(a^2P \cdot d)|^2} \frac{1}{4}.$$

The main limitations in this result are the neglect of configuration interaction of the $(3d^44s^2)a^2F$ term with the $(3d^44s)b^2F$ term in the neutral, and the effect of differing ejected electron energies for the two states. As s-electron detachments are typically more intense than d-electron detachments,$^{31,22}$ such CI will increase the $a^2F$ intensity even further. Based on the observed intensity ratio of detachment to $a^2F$ and the calculated $a^2P/a^2F$ intensity ratio, one would expect the transition to $a^2P$ to be an extremely weak feature in the spectrum. This same absence of the transition to the $a^2P$ is exhibited in the following spectrum of Zr+ where the experimental intensities are more meaningful.

Zr: The photoelectron spectrum of Zr+ measured at 2.540 eV photon energy and the corresponding energy level diagram are presented in Fig. 4. This spectrum

is again a result of subtracting out a ZrH\(^+\) contaminant from a spectrum obtained with a 3 pA beam of mass 91 ions. The ∼35 count scatter about zero is close to the shot noise limit for the subtraction procedure. As in the spectrum of Tl, transitions to three terms of the neutral (4d\(^5\)5s)\(^1\)F, (4d\(^2\)5s)\(^3\)F, and (4d\(^4\)5s)\(^3\)F are observed. The absence of the transition to (4d\(^2\)5s)\(^1\)F is consistent with the prediction given by application of Cox’s theory.\(^{36}\) The ground state of Zr\(^-\) is identified as a (4d\(^2\)5s)\(^3\)F. The multiplet nature of the three observed peaks is evidenced by peak shape (especially peak A) and peak widths of 120, 70, and 80 meV, for peaks A, B, and C, respectively. While the presence of negative ion fine structure is indicated, splittings are nevertheless unresolved.

Ratio isoelectronic estimates of the fine structure splittings of the (4d\(^5\)5s)\(^1\)F in Zr\(^-\) based upon those in Nb gives \(\Delta E(F_{1/2}-F_{3/2})=250\) cm\(^{-1}\), \(\Delta E(F_{1/2}-F_{1/2})=300\) cm\(^{-1}\), and \(\Delta E(F_{3/2}-F_{1/2})=370\) cm\(^{-1}\). Theoretical line shape profiles calculated using these extrapolated splittings are in agreement with the observed peaks as evidenced by the comparison with the \(^1\)F – \(^3\)F peak shown in Fig. 5. Owing to the small number of counts in this peak, this comparison does not provide a stringent test of the theory. However, it is clear that the calculation does account for the general features of the peak, such as width and symmetry. Using the known neutral spacings and the positions of the \(^1\)F\(_{1/2}\) – \(^3\)F\(_{3/2}\), \(^1\)F\(_{3/2}\), and \(^3\)F\(_{3/2}\) transitions, determined from fitting the calculated multiplets to the observed peaks, we have three determinations of the electron affinity of Zr, with a mean value of 0.427 ± 0.006 eV. Allowing for uncertainties in our spin–orbit estimate for Zr\(^-\), the final result is E.A.(Zr) = 0.427 ± 0.014 eV. This is the first experimental measurement of the electron affinity of Zr, although Zr has been previously observed.\(^{35}\)

Hf: When a Hf target was installed in the source, a small (≤ 0.5 pA) beam of mass ∼178 was obtained. While there was structure in the photoelectron spectrum, the signal-to-noise ratio was not sufficient to achieve the overdetermined spectrum required for definite identification of Hf\(^-\). At this point it remains unclear whether Hf\(^-\) is bound.

C. Group V\(_A\) elements: V, Nb, and Ta

V: The 488 nm photoelectron spectrum of V\(^+\) obtained from a 5 pA beam of mass 51 ions is presented in Fig. 6. The appropriate energy level diagram for the V\(^+\) – V system appears to the left of the spectrum. Transitions to four terms of the neutral (3d\(^3\)4s)\(^1\)F, (3d\(^4\)4s)\(^3\)D, (3d\(^4\)4s)\(^3\)D, and (3d\(^4\)4s)\(^3\)P are observed. The only possible ground state of V\(^+\) consistent with the observation of these four transitions is (3d\(^4\)4s)\(^3\)D. Linear isoelectronic extrapolation of the \(\Delta E(3d^44s^3)(D_{1/2}, -D_{3/2})/ \)

FIG. 4. The Zr\(^-\) 488 nm photoelectron spectrum and atomic energy level diagram. The spectrum shown is a result of subtracting out ZrH\(^+\) contaminates from the originally obtained spectrum. The scatter about zero counts is close to the shot noise limit for the subtraction procedure. All three peaks in the spectrum are identified as unresolved multiplet transitions.

FIG. 5. Comparison of experimental and theoretical Zr\(^-\) \(^1\)F – Zr \(^3\)F\(_{3/2}\) transition. The vertical lines are the calculated positions and intensities of individual components of the unresolved multiplet transition. The position of the calculated multiplet has been adjusted to the point of best agreement with experiment and then used to determine the position of the Zr\(^-\) \(^1\)F\(_{3/2}\) electron affinity defining transition within the peak.
\[ \Delta E(3d^4\ 4s)^6D_{3/2} - \Delta E(4d_{5/2}) \] fine structure ratios from Mn\(^{7+}\)/Mn\(^{7+}\) to Cr/Cr\(^{7+}\) to V\(^{5+}\)/V\(^{5+}\) yields the following estimated V\(^{5+}\) spin-orbit splittings: \[ \Delta E(5D_{3/2} - 5D_{3/2}) = 35 \text{ cm}^{-1}, \]
\[ \Delta E(5D_{3/2} - 5D_{3/2}) = 70 \text{ cm}^{-1}, \]
\[ \Delta E(5D_{1/2} - 5D_{3/2}) = 100 \text{ cm}^{-1}, \]
and \[ \Delta E(5D_{1/2} - 5D_{3/2}) = 125 \text{ cm}^{-1}. \] All four peaks in the spectrum are identified as unresolved multiplets. Line shape profile calculations show the 6D\(^{2}D\) and 5D\(^{2}D\) multiplets to be closely packed, with those components that contribute greater than 75% of the total intensity lying within a 5 meV range. This result is consistent with the observed peak widths of 55 meV FWHM, essentially the resolution of the electron monochromator. The positions of the 7D\(^{2}D\) and 6D\(^{2}D\) components as determined from fitting the calculated multiplets to the observed peaks are in agreement with the 6D\(^{2}D\) neutral spacing\(^{33}\) to within 3 meV. This excellent agreement of the line shape calculations with the observed spectrum allows us to determine E.A. (V) = 0.528 ± 0.012 eV. While there have been no previous measurements of the electron affinity of V, V\(^{5+}\) has been observed by Middleton.\(^{23}\)

**FIG. 6.** The 488 nm photoelectron spectrum of V\(^{5+}\) and energy level diagram for the V\(^{5+}\)-V system.

\[ \text{Nb: When a target of Nb metal was installed in the ion source, a 50 mA Nb\(^{+}\) beam was obtained. The resulting 488 nm photoelectron spectrum of Nb\(^{+}\) and the relevant energy level diagram are shown in Fig. 7. As in V\(^{5+}\), transitions to terms of the neutral (4d\(^{6}\) 5s\(^{6}\) 5D, (4d\(^{6}\) 5s\(^{6}\) 5F, (4d\(^{6}\) 5s\(^{6}\) 5P, and (4d\(^{6}\) 5s\(^{6}\) 4D are observed. The peak at ~0.80 eV electron kinetic energy is possibly due to NbH\(^{+}\). The ground state of Nb\(^{+}\) is assigned as (4d\(^{6}\) 5s\(^{5}\) 5D). Ratio isoelectronic estimates of the fine structure splittings in Nb\(^{+}\) from those in Mo gives\(\Delta E(4D_{3/2} - 4D_{3/2}) = 110 \text{ cm}^{-1}, \Delta E(4D_{1/2} - 4D_{1/2}) = 200 \text{ cm}^{-1}, \Delta E(4D_{1/2} - 4D_{1/2}) = 250 \text{ cm}^{-1}, \) and \[ \Delta E(4D_{1/2} - 4D_{3/2}) = 310 \text{ cm}^{-1}. \] While these calculated splittings are considerably larger than those obtained for V\(^{5+}\), individual components of the multplet transitions remain unresolved. Evidence for the multiplet nature of the observed peaks is given by the high resolution data (5 meV per channel) for the s-electron detachments to (4d\(^{6}\) 5s\(^{5}\) 5D and (4d\(^{6}\) 5s\(^{5}\) 4D) shown in Fig. 8. The peaks assigned to these transitions are broader than the electron analyzer resolution and show considerable structure within the peaks. A comparison of the theo-

**FIG. 7.** The 488 nm photoelectron spectrum of Nb\(^{+}\) and energy level diagram for the Nb\(^{+}\)-Nb system. While the spin-orbit splittings in Nb\(^{+}\) and Nb are considerably larger than in V\(^{5+}\) and V, individual multiplet components are still not resolved in the Nb\(^{+}\) spectrum.
retical calculation of the line shape profiles and these data is also presented in Fig. 8. In this comparison the two calculated multiplets have been linked by the known \( ^4D_{13} - ^4D_{12} \) neutral spacing\(^{23} \) and then positioned to the point of best agreement with the observed peaks. As shown in the figure, the calculation accounts for not only the position of the peak maximum but also the direction of peak asymmetry. However, there are some structural details, especially in the \( ^4D - ^4D \) peak, which do not seem to be accounted for by the calculation. As the relative positions of the multiplet components are solely determined by the fine structure splittings, it is possible that errors in the extrapolated fine structure splittings are responsible for these discrepancies. For Ta\(^+\) and Rh\(^+\), where the negative ion fine structure splittings were measured, it will be shown that individual extrapolated splittings (splitting of levels differing in \( J \) by 1)

can be in error by as much as 20\%. We conclude from our comparison of calculated vs observed multiplets that, while there is no doubt as to the accuracy of our assignments, there is some uncertainty in the positions of individual multiplet component positions within a peak in the Nb\(^+\) spectrum. We therefore report the electron affinity of Nb to be 0.894 ± 0.025 eV. This number compares with that of Scheer\(^{21} \) of ~1.0 eV from a self-surface ionization experiment.

**Ta:** The richness of low-lying states of Ta and Ta\(^+\) results in the most complex atomic photoelectron spectrum reported to date. The spectrum obtained from detaching a 2 pA beam of Ta\(^+\) with 2,540 eV (488 nm) photons is presented in Fig. 9. The corresponding energy level diagram for the Ta\(^+\)-Ta system is shown in Fig. 10. In all, 15 peaks comprised of 23 transitions from four states of the negative ion have been assigned! The spectrum shown is a result of subtracting out TaH\(^+\) impurity originally in the spectrum. However, there remain two regions of the spectrum (~0.3–0.8 and 1.2–1.4 eV) originally contaminated with hydride peaks, where even after this procedure we do not feel confident about making additional assignments. Even with this limitation, we can still identify consistently at least four transitions originating from each of the negative ion states. By consistently we mean that in general the agreement with the neutral spacings\(^{23} \) is to within 20 meV for all assignments in the Ta\(^+\) spectrum that do not involve highly convoluted peaks. Such agreement is a reasonable expectation based on the 10 meV spacing between data points, the small number of counts in the spectrum, and the general overlap of peaks due to the complexity of the spectrum. For all the abnormally shaped peaks that have widths greater than our electron analyzer resolution, the assignment predicts that

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**Fig. 8.** Comparison of the calculated Nb\(^+\) \( ^4D \rightarrow ^4D \) and Nb\(^+\) \( ^5D \rightarrow ^5D \) multiplets with high resolution data. The calculation accounts for both the observed peak widths and peak asymmetries. The asterisk denotes the Nb\(^+\) \( ^5D_2 \rightarrow ^5D_{1/2} \) electron affinity defining transition.

**Fig. 9.** The 488 nm photoelectron spectrum of Ta\(^+\). The complexity of the spectrum is due to transitions from four bound negative ion states to a plethora of low lying Ta states (see Fig. 10).

**Fig. 10.** The atomic energy level diagram of the Ta\(^+\)-Ta system. At least four transitions have been assigned from each of the four negative ion states.
FIG. 11. The Cr⁺ 488 nm photoelectron spectrum and energy level diagram. Data were actually obtained over the full electron energy range and no peaks were observed other than those shown in the spectrum.

they are comprised of more than one transition. Equally important confirmation of this assignment is that those transitions that are forbidden are absent from the spectrum. The sum of these observations is unambiguous evidence for the assignments chosen.

As the photoelectron spectrum of Ta⁺ is the most complex atomic spectrum yet obtained, we present the arguments leading to the assignment of four negative ion states. Peaks D, F, K, and M (Fig. 9) fit the neutral spacings between (5d⁶6s⁵)⁴F₇/₂, (5d⁶6s⁴)⁴F₅/₂, (5d⁶6s⁴)⁴F₅/₂, (5d⁶6s⁴)⁴F₇/₂, and (5d⁶6s⁴)⁴F₇/₂. These four peaks, which form the most intense neutral sequence in the spectrum, are attributed to detachment from the (5d⁶6s⁴)⁴D₃ ground state of Ta⁺. The only possible negative ion term consistent with the observation of these four transitions is (5d⁶6s⁵)⁴D. The ⁴D₃ ground state assignment is based on application of Hund’s rules. We have determined the electron affinity from each of these four peaks and obtained a mean value of E.A.(Ta) = 0.323 ± 0.012 eV. The only other measurement of the electron affinity of Ta is 0.8 ± 0.3 eV, obtained in a self-surface ionization study.

The assignment of peak D as the Ta⁺ ⁴D₃–Ta⁺ ⁴F₇/₂ transition implies that peaks A, B, and C are due to transitions from excited states of the negative ion. Additional analysis yields neutral sequences starting from peaks C and A (see Figs. 9 and 10) attributed to detachment from the excited fine structure states ⁴D₁ and ⁴D₂, respectively. Using the known Ta⁺ ⁴F₇/₂ ⁴F₅/₂ splitting, the lowest fine structure splitting in Ta⁺ is found from peaks D and E to be ΔE(⁴D₁–⁴D₂) = 1070 ± 110 cm⁻¹. Similarly, the ⁵D₃ splitting in Ta⁺ is determined from peaks H and K to be ΔE(⁵D₃–⁵D₂) = 2240 ± 120 cm⁻¹. Ratio isoelectronic estimates of the fine structure splittings in Ta⁺ based upon those in W yield ΔE(⁴D₁–⁴D₂) = 980 cm⁻¹ and ΔE(⁴D₃–⁴D₅) = 1960 cm⁻¹. The estimated ⁴D₁–⁴D₂ splitting is within the error limits of the measurement and the calculated ⁵D₃–⁵D₂ separation is in error by 15%, attesting to the accuracy of the ratio isoelectronic method.

The neutral sequence observed starting from peak B is quite different than those previously encountered in the spectrum. The most radical difference is the observation of transitions to (5d⁶6s⁵)⁴D₇/₂ and (5d⁶6s⁵)⁴F₇/₂. These clearly cannot be due to transitions from a member of the ⁴D₃, as that would require a spin forbidden process. That the neutral sequence contains states of only (5d⁶6s⁵) configuration indicates a negative ion state of (5d⁶6s⁵) configuration. As this neutral sequence contains only quartets and doublets, the negative ion state must be a triplet. However, as there are no s-electron detachments in this sequence, we need to invoke the selection rule to complete the negative ion state assignment. As can be seen from Fig. 10, this final state neutral sequence contains only the J levels ½, ½, and ¾. In particular, a transition to ⁴F₇/₂ which would occur between peaks F and G is missing. We therefore infer from the selection rule for d-electron detachment |ΔJ| ≤ ½ that the J value for this negative ion state is zero. There is only one triplet term with a fine structure level of J = 0 that can be formed from the coupling of four d electrons ³P. The ³P term also is the lowest energy excited term of (5d⁶6s⁵) configuration in neutral tungsten, which is isoelectronic with Ta⁺. The assignment of this neutral sequence as arising from transitions from (5d⁶6s⁵)³P₅ now accounts for all of the observed peaks in the sequence. The position of this excited electronic state of Ta⁺ relative to the ⁴D₃ ground state is ΔE(³P₅–⁴D₃) = 1750 ± 110 cm⁻¹.

The atomic structure of Ta⁺ is now clear. There exist four bound states of the negative ion: three fine structure components of (5d⁶6s⁵)⁴D and the excited electronic state (5d⁶6s⁵)³P₅. The spacing between the levels indicates that Ta⁺ is a good example of intermediate coupling, where the electrostatic interaction is comparable to the spin-orbit splitting.

D. Group VIA elements: Cr, Mo, and W

Cr: Figure 11 shows the 488 nm photoelectron spectrum of Cr⁺ obtained with a 5 pA ion beam. The corre-
FIG. 12. The 488 nm photoelectron spectrum of Mo⁺ and atomic energy level diagram for the Mo⁺–Mo system.

Corresponding energy level diagram is shown to the left of the spectrum. Three peaks, associated with transitions to the three lowest terms of neutral Cr, (3d⁴ 4s)⁹S₂, (3d³ 4s)⁷S₅/₂, and (3d⁴ 4s)⁵D are observed in the spectrum.

The only possible ground state of Cr⁺ consistent with the observation of these three transitions is (3d⁴ 4s)⁹S₂. Transitions to all five fine structure levels of (3d⁴ 4s)⁵D are allowed and evidenced by the structure in peak C. In particular, the maximum of this peak and the shoulder to the left of maximum are identified as arising from detachment to the two highest lying fine structure levels of the ⁵D₁, ⁵D₄, and ⁵D₅. Considering the simplicity of the Cr⁺–Cr system, there can be little doubt as to the accuracy of our assignments. The position of the Cr⁺ ⁸S₅/₂ – Cr ⁷S₅/₂ peak in the spectrum yields E.A.(Cr) = 0.867 ± 0.010 eV. This value is in good agreement with the previous measurement of Feldmann et al. of 0.86 ± 0.05 eV.

Mo: With a Mo target in the ion source, a 1 pA beam of mass 96 ions was obtained. The resulting 488 nm photoelectron spectrum of Mo⁺ and the corresponding energy level diagram are shown in Fig. 12. Two main features, assigned to s-electron detachment from Mo⁺ (4d⁴ 5s)⁹S₂ to Mo (4d³ 5s)⁷S₅/₂ (peak A) and Mo (4d³ 5s)⁹S₂ (peak B), are observed in the spectrum with a peak separation in agreement with the known ΔE(⁷S₅/₂–⁹S₂) splitting of to within 6 meV. There is evidence for photodetachment to (4d⁴ 5s)⁵D in region C of the spectrum; however, the signal-to-noise ratio is not sufficient to permit assignment of any peaks as specifically coming from that process. While confirmed assignment of detachment to the ⁵D would have verified the ⁵S ground state assignment, there is other evidence to indicate that this choice is the correct one. The only other reasonable ground state hypothesis (4d³ 5s)⁷D would lead to broadened peaks in the spectrum due to population of excited fine structure states in the beam. The observed peak width of 50 meV FWHM for peak A indicates that this peak is due to a single transition, requiring the (4d³ 5s)⁷S₅/₂ ground state of Mo⁺. We obtain the electron affinity of Mo from the position of the Mo⁺ ⁷S₅/₂ – Mo ⁷S₅/₂ transition as 0.747 ± 0.010 eV. This result compares with the self-surface ionization measurement of Scheer of E.A.(Mo) = 1.0 ± 0.2 eV.

W: The 488 nm photoelectron spectrum of W⁺ obtained from a 5 pA beam of sputtered tungsten negative ions is presented in Fig. 13, along with relevant positions of a W⁺–W energy level diagram. In the spectrum four single transition peaks are assigned to d-electron detachment from W⁺ (5d⁴ 6s)⁹S₂ to four of the five fine structure components of (5d⁴ 6s)⁷D in W. The prominent peak in the center of the spectrum is composed of two overlapping peaks attributed to detachment to the ⁷D₂ state and s-electron detachment to W⁴d 6s)⁹S₂. The fitted peak positions are again consistent with the known neutral spacings of the above final state assignments to within 6 meV. The (5d⁴ 6s)⁹S₂ ground state assignment for W⁺ is the only possible assignment consistent with the observation of detachment to both (5d⁴ 6s)⁷D and (5d⁴ 6s)⁷S₅/₂ in neutral tungsten. The electron affinity of W, obtained from both peaks A and B, is E.A.(W) = 0.816 ± 0.009 eV. The only other measurement of the electron affinity of W is by Scheer and Fine of 0.5 ± 0.3 eV.

One particularly interesting result in the photoelectron spectrum of W⁺ is the relative intensities of d-electron detachment to the five fine structure levels of the ⁷D. A comparison of the observed and calculated intensities is given in Table I. Both the fractional parentage method in pure LS coupling and the statistical method predict the same 2J + 1 relative intensity pattern. Experimentally, however, the maximum intensity peak is detachment to the ⁷D₂, with decreasing intensity to lower and higher J values. One obvious weakness in the fractional parentage calculation is the assumption of the pure LS coupling. A more serious attempt at explaining the observed intensities would have to invoke an intermediate coupling scheme in the calculation. As all other states of (5d⁴ 6s) configuration in neutral tungsten are either ΔS or ΔL forbidden from the ⁷S₅/₂ in W⁺, the observed intensity pattern is probably due to varying degrees of mixing of these states with the fine structure levels of the ⁷D in an intermediate coupling scheme.
E. Group VIII elements: Rh and Ir

Rh: The photoelectron spectrum of Rh\(^+\) obtained from detaching a 30 \(\mu\)A beam of mass 103 ions with 2.540 eV (488 nm) photons is presented in Fig. 14. The corresponding energy level diagram is shown to the left of the spectrum. The photoelectron spectrum of Rh\(^+\) presents a case where there is resolved fine structure in both the neutral and the negative ion. Seven peaks, comprised of 11 transitions from all three fine structure levels of the \((4d^8 5s)^2F\) state in Rh\(^+\) to various fine structure levels of the \((4d^8 5s)^2F\) and \((4d^8 5s)^4F\) state of Rh, are observed in the spectrum. The presence of detachment to only states of \(4d^8 5s\) configuration in the neutral would seemingly allow either a \(4d^8 5s\) or a \(4d^8 5s^2\) configuration for the negative ion. However, each of the Rh sequences observed in the spectrum, with the exception of one transition, contain only those fine structure levels of the \(5^F\) and \(5^P\) which differ in \(J\) by one. This final state \(J\) dependence is precisely what is allowed for by the photoelectron selection rule for \(s\)-electron detachment\(^{16}\) \(|\Delta J| \leq 1\). The selection rules for the \(d\)-electron detachment required of a \(4d^8 5s\) assignment for Rh\(^+\) would allow for many more transitions than are observed. Thus, these selection rules form the basis for the assignment of the three negative ion states observed in the spectrum as the three fine structure levels of \((4d^8 5s)^2F\).

Peaks B, C, D, and G fit the neutral spacings of the \((4d^8 5s)^2F_{7/2}, 4F_{7/2}, 4F_{5/2},\) and \(4F_{7/2}\) states of Rh and are assigned to detachment from the \((4d^8 5s)^2F_{7/2}\) ground state of Rh\(^+\). The Rh\(^+(4d^8 5s)^2F_4\) - Rh\(^+(4d^8 5s)^4F_{7/2}\) transition (peak D) is \(\Delta J\) forbidden as an \(s\)-electron detachment, but is allowed through configuration interaction of the Rh\(^+(4d^8 5s)^2F_4\) with the low lying (~13 000 cm\(^{-1}\)) Rh\(^+(4d^8 5s)^4F_{7/2}\) excitation state. Using the known \((4d^8 5s)^2F_{7/2}-(4d^8 5s)^4F_{7/2}\) splitting in Rh and the position of the Rh\(^+(4d^8 5s)^2F_4\) - Rh\(^+(4d^8 5s)^4F_{7/2}\) transition in the spectrum (peak C), we obtain E. A. (Rh) = 1.138 ± 0.008 eV. While there have been no previous measurements of the electron affinity of Rh, Rh\(^+\) has been observed by Middleton.\(^{23}\)

Peaks A, B, E, and G fit the neutral spacings of the \((4d^8 5s)^4F_{7/2}, 4F_{5/2}, 2F_{7/2},\) and \(2F_{5/2}\) states of Rh, respectively, and are assigned to detachment from the \((4d^8 5s)^2F_4\) fine structure state of Rh\(^+\). Using the known \((4d^8 5s)^2F_{7/2}-(4d^8 5s)^4F_{7/2}\) spacing, we have determined the Rh\(^+(4d^8 5s)^2F_4\) fine structure splitting from peaks C and E to be 2370 ± 65 cm\(^{-1}\) (0.294 ± 0.008 eV). Peaks A, B, F, and G also fit the neutral spacings of the \((4d^8 5s)^4F_{7/2}, 4F_{5/2},\) and \(2F_{7/2}\) states of Rh, respectively, and are assigned to detachment from the \((4d^8 5s)^2F_4\) excited fine structure state of Rh\(^+\). Using the known \((4d^8 5s)^2F_{7/2}-(4d^8 5s)^2F_{7/2}\) splitting, we have measured the Rh\(^+(4d^8 5s)^2F_4\) fine structure splitting from peaks E and F to be 1000 ± 65 cm\(^{-1}\) (0.124 ± 0.008 eV).

Isoelectronic extrapolation of the \(\Delta E(4d^8 5s)^4F_j-(4d^8 5s)^4F_{j'}/\Delta E(4d^8 5s)^4F_4-(4d^8 5s)^4F_{7/2}\) fine structure ratios from Cd\(^+\)/Cd\(^2+\) to Ag\(^+\)/Ag\(^2+\) to Pd\(^+\)/Pd\(^2+\) to Rh\(^+\) gives the estimated Rh\(^+\) \(3P\) spin-orbit splittings of \(\Delta E(F_2-F_4) = 2160\) cm\(^{-1}\) and \(\Delta E(F_2-F_3) = 1200\) cm\(^{-1}\). These extrapolated values disagree with our experimental result by 10% and 20%, respectively. However, the extrapolated full splitting \((E(F_2)-F_3)\) of 3360 cm\(^{-1}\) is in good agreement with our experimental value of 3370 ± 65 cm\(^{-1}\).

The method of ratio isoelectronic extrapolation of the fine structure splittings of transition metal negative ions will be discussed in Sec. V.

We have previously noted that the Rh\(^+(4d^8 5s)^2F_4\) states of Rh\(^+\) are assignments of the three negative ion states observed in the spectrum as the three fine structure levels of \((4d^8 5s)^2F_4\).

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**TABLE I.** \(W(5d^6 6s^1)^8S_{1/2} \rightarrow W(5d^6 6s^1)^8D\) relative intensities.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed intensity</th>
<th>Calculated intensity*</th>
<th>Statistical intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6S_{1/2} \rightarrow D_2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(6S_{1/2} \rightarrow D_3)</td>
<td>1.6 ± 0.1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(6S_{1/2} \rightarrow D_4)</td>
<td>5.0 ± 0.5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>(6S_{1/2} \rightarrow D_3)</td>
<td>3.8 ± 0.2</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>(6S_{1/2} \rightarrow D_4)</td>
<td>2.9 ± 0.2</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>

*Calculated by the fractional parentage method (Refs. 21, 22, and 20).
Rh(4d^5 5s) 1F

"forbidden" transition (peak D) could be explained in terms of configuration interaction of the (4d^5 5s) 1F with the (4d^5 5s) 1F excited state of Rh. The question arises as to why other forbidden transitions, which could be made allowed by the same interaction, are not observed in the spectrum. There are five transitions that are not observed, which could be made allowed by this process. They are 3F_2 1F_3/2, 3F_3 1F_1/2, 3F_4 1F_1/2, 3F_4 1F_3/2, and 3F_4 1F_5/2. Of these, the transitions that originate from both the 3F_2 and 3F_3 states of Rh should be reduced in intensity from peak D by a factor greater than 20, based on Boltzmann population factors. The 3F_4 1F_3/2 transition should also be reduced in intensity from peak D by a factor greater than 20 based on angular momentum considerations. Thus, it is reasonable that the only configuration interaction allowed transition observed in the spectrum is Rh* 3F_4 1F_3/2.

Ir: The 457.9 nm (2.707 eV) photoelectron spectrum of Ir* obtained from a 100 pA beam of sputtered iridium negative ions is presented in Fig. 15. Four peaks, corresponding to transitions to four terms of the neutral (5d^6 6s) a^1F_3/2, a^1F_5/2, a^1F_7/2, and (5d^6 6s) b^4F_3/2, are observed in the spectrum. There is no evidence of a transition to the (5d^6 6s) a^4F_5/2 state of Ir, which would appear at 0.42 eV. An additional peak at 0.25 eV results from detachment to the (5d^6 6s) b^4F_7/2 state, but is badly distorted as a result of being near the low energy transmission cutoff of the electron analyzer.

The assignment of the negative ion state for Ir* presents a somewhat different problem than encountered for the other transition metal ions discussed in this paper. The problem is that the (5d^6 6s) a^1F and the (5d^6 6s) b^4F states of Ir are the only energetically accessible states of the system within the photon energy range, and these two states are strongly interacting. If we ignore this interaction, the presence of transitions to both the (5d^6 6s) a^1F and (5d^6 6s) b^4F neutral terms would argue for a (5d^6 6s) a^1F negative ion state. However, when configuration interaction is considered, a (5d^6 6s) a^1F negative ion state could also give rise to transitions to both the (5d^6 6s) a^1F and (5d^6 6s) b^4F states of Ir.

FIG. 14. The Rh* 488 nm photoelectron spectrum and energy level diagram. Transitions from all three fine structure levels of Rh* 1F are resolved in the spectrum.

FIG. 15. The 457.9 nm photoelectron spectrum of Ir* and atomic energy level diagram. In addition to the four assigned peaks, the peak at 0.25 eV is due to detachment to Ir b^4F_7/2. However, the relative intensity of this peak is inaccurate as it lies close to the low energy cutoff of the electron analyzer.
which is isoelectronic with Ir\(^{\text{III}}\), the ground state is \((5d^66s^1)D_3\) with the \((5d^66s^1)F_3\) state lying 824 cm\(^{-1}\) above this. \(^{33}\) Thus, both the \((5d^66s^1)D\) and the \((5d^66s^1)F\) are reasonable terms for Ir\(^{\text{III}}\) and are feasible consistently with our data. This ambiguity of negative ion state assignment was resolved for the other members of the Ir column (Co\(^{\text{II}}\) and Rh) by the observation that in addition to transitions to the \(F\) states, only those transitions to the \(l\)d\(2\)(n+1)\(\ell\)\(F\) which are allowed by the photoelectron selection rules for \(s\)-electron detachment were observed. This type of evidence does not exist for Ir\(^{\text{III}}\). However, there is indirect evidence that the state responsible for our observed spectrum, the ground state of Ir\(^{\text{III}}\), is \((5d^66s^1)F_4\).

All of the transition metal negative ions studied, with one exception, have had a \(d^5\) ground state configuration. The exception occurred for Pd\(^{\text{II}}\) [\(4\text{d}^6\text{5s}^2\)]\(1\text{S}_{1/2}\) ground state] and yet neighboring Rh\(^{\text{II}}\) had an unambiguous \(4\text{d}^6\text{5s}^2\)\(2\text{F}_4\) ground state. Pt\(^{\text{II}}\) is known from previous threshold measurements to have \(5\text{d}^6\text{6s}^1\)\(2\text{D}_{3/2}\) ground state. \(^{33}\) If Ir\(^{\text{III}}\) had a \(5\text{d}^6\text{6s}^1\)D\(_{3/2}\) ground state term, one would expect a \(5\text{d}^6\text{6s}^1\)\(2\text{S}_{1/2}\) ground state for Pt\(^{\text{II}}\), contrary to what is known. Additional evidence for a \(5\text{d}^6\text{6s}^1\)F over a \(5\text{d}^6\text{6s}^1\)D assignment for Ir\(^{\text{III}}\) lies in the expected fine structure splittings of these states. The \(\Delta\text{E}(D_{3/2} - D_{5/2})\) splitting in isoelectronic Pt is 776 cm\(^{-1}\). \(^{33}\) Thus, one would expect probability of both the \(D_3\) and \(D_{5/2}\) states in the ion beam, if Ir\(^{\text{III}}\) had a \(5\text{d}^6\text{6s}^1\) configuration. While the \(D_{3/2} - D_{5/2}\) fine structure splitting might not be resolvable in the spectrum, some broadening of the peak due to transitions from both of these fine structure components certainly would be expected. The observed peak widths are ~55 meV FWHM, consistent with the interpretation of all the peaks in the spectrum being single transition peaks. A ratio isoelectronic estimate of the \(5\text{d}^6\text{6s}^1\)(\(2\text{F}_3 - \text{F}_2\)) splitting for Ir\(^{\text{III}}\) based on the Pt fine structure splittings gives \(\Delta\text{E}(F_3 - F_2) \approx 7600\) cm\(^{-1}\). Thus, one would expect only single transition peaks from an \(\text{Ir}^{\text{III}}\) \(5\text{d}^6\text{6s}^1\) configuration, consistent with the observed peak widths. Based on this evidence, the ground state of Ir\(^{\text{III}}\) is \((5d^66s^1)F_2\) and the electron affinity of Ir can be obtained directly. Subtracting the measured position of the \(\text{Ir}^{\text{III}}(5d^66s^1)F_4 - \text{Ir}(5d^66s^1)F_2\) transition from the photon energy of 2.707 eV (457.9 nm), we obtain E.A. (Ir) = 1.566 ± 0.006 eV. This ion has apparently not been previously observed.

Photodetachment of Ir\(^{\text{III}}\) provides a case in which the two energetically accessible terms \((5d^66s^1)A^1F\) and \((5d^66s^1)B^2F\) are strongly interacting. In order to investigate the effect of this interaction on the photoelectron intensities we have measured the spectrum of Ir\(^{\text{III}}\) at three wavelengths: 514.5, 488.0, and 457.9 nm. The relative intensities of the various transitions measured at these wavelengths together with the calculated relative intensities for d-electron detachment\(^{31,38}\) to the fine structure components of the \((5d^66s^1)A^2F\) term in Ir are presented in Table II. The calculated intensities for d-electron detachment are not expected to compare favorably with the experimental data, owing to the neglect of configuration interaction. However, the calculated intensities do provide a measure by which one can judge which fine structure components of the \(a^2F\) are most affected by final state coupling.

We expect the following effects of configuration interaction of \((5d^66s^1)A^2F\) with \(\text{Ir}(5d^66s^1)B^2F\) on the \(\text{Ir}^{\text{III}}(5d^66s^1)F_4 - \text{Ir}(5d^66s^1)A^2F\) intensities: Using perturbation theory to determine which states in the neutral can interact, there is configuration interaction only between states of the same \(J\). This is a direct result of the electron–electron repulsion scalar operator commutating with the total angular momentum operator. As both \(\text{Ir}^{\text{III}}F_4 - \text{Ir}b^4F_{3/2}\) and \(\text{Ir}^{\text{III}}F_4 - \text{Ir}b^4F_{5/2}\) are \(\Delta J\) forbidden as \(s\)-electron detachments, the mixing of \(a^2F_{3/2}\) with \(b^4F_{3/2}\) and \(a^2F_{5/2}\) with \(b^4F_{5/2}\) serves to decrease the intensities of detachment to \(a^2F_{3/2}\) and \(a^2F_{5/2}\), relative to those calculated for pure \(d\)-electron detachment. Similarly, as both \(\text{Ir}^{\text{III}}F_4 - \text{Ir}b^4F_{3/2}\) and \(\text{Ir}^{\text{III}}F_4 - \text{Ir}b^4F_{5/2}\) are allowed \(s\)-electron detachments, and as \(s\)-electron detachments are typically more intense than \(d\)-electron detachments, the mixing of \(a^2F_{3/2}\) with \(b^4F_{3/2}\) and \(a^2F_{5/2}\) with \(b^4F_{5/2}\) increases the intensity of transitions to \(a^2F_{3/2}\) and \(a^2F_{5/2}\), relative to those calculated assuming a pure configuration. Qualitatively, the observed intensities are consistent with these expectations with one exception, the \(3^2F_1 - a^2F_{3/2}\) transition. Not only is it mildly surprising that we observe it at all, but this transition also has a curious photon energy dependence. It is probably more than just a coincidence that the observed ~sevenfold decrease in the relative intensity of this transition with change of wavelength occurs after the channel opening of detachment to the \((5d^66s^1)b^4F_{1/2}\). The manner in which this channel opening could affect the intensity of the transition to \(a^2F_{3/2}\) is through interaction of states of the same "total" angular momentum,
where total is the sum of detached electron plus final neutral state in a $j$-$j$ coupled sense. Such an interaction has been previously reported in photodetachment of the alkali negative ions\textsuperscript{23} and theoretically investigated by Lee,\textsuperscript{44} and by Moore and Norcross.\textsuperscript{41} When this type of interaction is allowed, the number of possible mixings that can affect the intensity increases considerably with the interaction of $(a^3F_{y2} + e^-)$ and $(b^3F_{y2} + e^-)$ by being the source of the anomalous $^3F_4 - a^3F_{y2}$ transition intensity.

This first investigation of the photoelectron spectroscopy of Ir\textsuperscript{-} does not answer all the questions of the nature and extent of final state couplings in photodetachment of Ir\textsuperscript{-}. Rather, it suggests that Ir\textsuperscript{-} could be an interesting negative ion to study in order to investigate final state coupling in a complex system.

\section*{V. DISCUSSION}

The ground state configurations of all the transition metal negative ions studied in this paper, with the exception of Pd\textsuperscript{-}, have been $d^3s^2$. This finding is in contrast to the transition metal neutrals which have ground state configurations of $d^2s^2$, $d^{11}s$, and $d^{10}$. Clearly, there is an increased stability of the $s$ orbital relative to the $d$ orbital in going from the neutrals to the negative ions. This increased stability can be predicted by a simple model. The $d$- and $s$-electron orbital energies for one electron interacting with an effective nuclear charge are given by

$$E_{nd}(Z) = -\frac{R(Z - S_{nd})^2}{n^2}$$  \hspace{1cm} (11)

and

$$E_{ns+(1)}(Z) = -\frac{R(Z - S_{ns+(1)})^2}{(n + 1)^2},$$  \hspace{1cm} (12)

where $R = +13.6$ eV, and $S_{nd}$ and $S_{ns+(1)}$ are the $d$- and $s$-electron screening constants, respectively.

Assuming that for some neutral transition metal these orbital energies are degenerate, we solve for the $s$-electron screening constant in terms of the $d$-electron screening constant, and obtain

$$S_{ns+(1)} = [(n + 1)S_{nd} - Z]/n.$$  \hspace{1cm} (13)

As the screening constant is a slowly varying function of $Z$ in an isoelectronic sequence,\textsuperscript{42} substitution of this value for an isoelectronic negative ion [the $(Z - 1)$ case] and simplification yields

$$E_{ns+(1)}(Z - 1) = -\frac{R(Z - 1 - S_{nd} + \frac{1}{n + 1})^2}{n^2}$$  \hspace{1cm} (14)

and

$$E_{sd}(Z - 1) = -\frac{R(Z - 1 - S_{sd})^2}{n^2}.$$  \hspace{1cm} (15)

Since $Z - S_{nd}$ is the effective nuclear charge felt by one $d$ electron in the neutral, it can be screened by at most $Z - 1$ electrons, implying $Z - S_{sd} > 1$. Both the Slater rules\textsuperscript{45} for screening and the Clementi and Raimondi extensions\textsuperscript{46} to these rules give a value greater than 1 for this quantity. Therefore,

$$\left(Z - 1 - S_{nd} + \frac{1}{n + 1}\right)^2 > (Z - 1 - S_{sd})^2,$$  \hspace{1cm} (16)

implying that the $(n + 1)s$ orbital has increased stability relative to the $nd$ orbital in going from the neutral to the isoelectronic negative ion. It is interesting to note that, based on the relative positions of the $(4d^3s^2)^2D_{y2}$ and $(4d^3s^2)^2S_{1/2}$ states in Pd\textsuperscript{2+} (this work) and in isoelectronic Ag,\textsuperscript{43} this added stability amounts to 30 000 cm\textsuperscript{-1} for Pd\textsuperscript{2+}. While clearly a simplistic model, it does predict the preponderance of $d^3s^2$ configurations observed in transition metal negative ions. In addition, this same model can be extended to predict increased stability of the $nd$ orbital over the $(n + 1)s$ orbital in going from the neutral to the isoelectronic positive ion.

The added stability of the $s$ orbital in the transition metal negative ions is chemically relevant to the electronic structure of transition metal complexes with formal negative oxidation states, such as Fe(CO)\textsubscript{5}. The metal-ligand bond in these complexes is viewed as a cooperative effect of a dative (electron donating) sigma bond and dative back bonding of the metal dx (i.e., dp\textsubscript{x}) orbital and the $\pi^*$ orbital of the ligand.\textsuperscript{44} The net effect of this binding on the electron distribution in the metal is a decrease of electron density in the dx orbital and an increase of electron density in the $\sigma$ orbitals (primarily of s and p origin). The stability of these complexes has been largely attributed to the electron withdrawing capability of the $\sigma$-acceptor ligands.\textsuperscript{45} However, it should also be recognized that the additional effect of the transfer of electron density from the $dx$ to the $\sigma$ orbitals on the metal contributes to the stability of these compounds by analogy to the increased stability of the $s$ orbital in the transition metal negative ions.

Prior to this investigation there have been few accurate experimental measurements of the electron affinities of the transition metal elements. Due to this lack of accurate experimental values, the best estimates of the electron affinities of these elements have come from extrapolation techniques, such as the horizontal analysis employed by Zollweg\textsuperscript{28} and by Hotop and Lineberger.\textsuperscript{13} As applied to the transition metal negative ions, horizontal analysis assumes that the "$s$-electron binding energies" of elements of the same series are approximately related by

$$\Delta(d^3s(0) - d^3s^2(-)) = ab + k, \quad b = 0, 1, \ldots, 10.$$  \hspace{1cm} (17)

The quantities $a$ and $b$ are constants for any given row of the transition metals. Note that this $s$-electron binding energy is not equal to the electron affinity in all cases, as the $d^3$ configuration is not always the ground state configuration of the neutral.\textsuperscript{33} In addition, for the extrapolation to provide information on the electron affinity requires that the ground state of the negative ion be a $d^3$ configuration, which we have seen to be true for all elements studied with the exception of Pd (even here, Pd$^{4d^3s^2}2D_{y2}$ exists as a bound excited state).

Figures 16–18, show experimental s-electron binding energies for each of the three transition metal series, as a function of $k$. The $s$-electron binding energy $\Delta(d^3s(0) - d^3s^2(-))$ is defined as the difference between the lowest fine structure level of the lowest energy term of the appropriate configuration in the neutral and the negative ion. The data used in these plots come from
FIG. 16. Plot of the experimental $s$-electron binding energies of the negative ions of the first transition series as a function of the number of $d$ electrons. The $s$-electron binding energy is defined as the difference between the lowest energy states of the neutral $d^8s$ configuration in the neutral and the $d^2s^2$ configuration in the negative ion. Where these states are also the ground states of the neutral and ion, the $s$-electron binding energy is also the electron affinity. The data used in this plot for Ca' come from an electron scattering resonance and the rest come from photodetachment experiments.

FIG. 17. Experimental $s$-electron binding energies of the second transition series negative ions plotted as a function of the number of $d$ electrons. The energy scale of this plot is identical to that of the first transition series, showing the striking similarity between the plots for the two series.

FIG. 18. Plot of the experimental $s$-electron binding energies of the third transition series negative ions vs the number of $d$ electrons. The large difference in the slope of this plot as compared to those of the first and second series plots is presumed to be a result of the filled $f$ shell of the lanthanides.

several sources. The $d^2s^2$ negative ion energy levels for K', Rb', Cs', and Pt' are from threshold photodetachment measurements, and Ca' is from an observed $d$-wave resonance in the electron scattering data of Johnston and Burrow, and the rest are from photodetachment measurements. The necessary neutral energy levels were taken from "Atomic Energy Levels."

Focusing first on behavior common to all three transition series, we can see two striking features in these plots. The first is the remarkably good fit of the available data for $k > 6$ to the line connecting the alkalis and the noble metals. Since the error bars on these measured $s$-electron binding energies are typically 10 meV, it is amazing how accurately this simple relationship holds. Equally interesting is the dispersion-like behavior for $1 < k < 5$ for all three plots. If we focus on the plot of the first transition series, the inclusion of Ca gives us what appears to be a skewed dispersion curve. At this point we know of no simple model that would account for this trend.

Another rather curious point is the relationship between the slopes for the different transition series. The slopes for the first and second transition series of 0.073 eV/($d$ electron) and 0.082 eV/($d$ electron), respectively, are quite similar. In fact, the plots of the first and second transition series are so similar as to indicate that the physics behind the observed trends is independent of principal quantum number. However, the slope for the third transition series is 0.184 eV/($d$ electron), more than twice that of the first two series. This difference presumably arises from the effect of the filled $f$ shell in
the third transition series. However, as the f-shell filling occurs between La and Hf, it is not obvious that Cs is a suitable end point in the graph. When more data become available, we hope to be able to make a quantitative statement about the effect of a filled f shell on the s-electron binding energy.

The observed trends in the s-electron binding energies for the three transition series pose some interesting questions. The foremost of these concerns the mechanism responsible for the linear behavior and the dispersion type deviation from linearity in the plots. In order to further substantiate these trends it would be of interest to have data on Sc\textsuperscript{+} and Mn\textsuperscript{+}, completing the plot for the first transition series. If the trends observed so far continue for these ions, the d\textsuperscript{5}s\textsuperscript{2} configuration for both of these should not be bound and the positions of states of this configuration need to come from electron scattering experiments. We hope this work will encourage more measurements on temporary negative ion resonances\textsuperscript{15,46} such as the measurement on Ca\textsuperscript{-}. Also of interest will be whether the large deviation for Ca is repeated for Sr and Ba in the second and third transition series. Depending on how strongly this deviation is repeated, the 5d6s\textsuperscript{2} configuration might be bound for Ba\textsuperscript{-}, contrary to earlier estimates\textsuperscript{15,48}.

Of the 11 transition metal negative ions studied, eight have had bound terms with fine structure. In only two of these were the fine structure splittings sufficiently large to afford a direct measurement. Furthermore, of all of the transition metal negative ions, there have been measurements of the spin–orbit splittings only for Co\textsuperscript{-},\textsuperscript{22} Ni\textsuperscript{-}, Rh\textsuperscript{-}, and Ta\textsuperscript{-}. Just as was the case for the electron affinities of the transition metals, where the extrapolation techniques gave the best estimates of those numbers until accurate measurements could be made, extrapolation methods such as ratio isoelectronic extrapolation\textsuperscript{19} must provide estimates of the fine structure splittings of these elements until higher-resolution experiments are possible. Thus, it is important to know how accurate these extrapolated values are expected to be.

The experimentally measured and extrapolated values presented in this paper on the fine structure splittings of transition metal negative ions, together with some previous extrapolations\textsuperscript{13} and measurements,\textsuperscript{22} are summarized in Table III. The error bars assigned to the extrapolated values are based on comparisons between extrapolations and the Co\textsuperscript{-}, Ni\textsuperscript{-}, Rh\textsuperscript{-}, and Ta\textsuperscript{-} measurements. We believe that the individual extrapolated splittings (splittings between adjacent levels) are accurate to better than ±10\% for the first transition series negative ions and to better than ±20\% for the second and third transition series ions. Considering the complexity of the transition metals, this remarkable accuracy for a simple method. Furthermore, the extrapolated full term splitting (largest energy separation of any two fine structure levels) appears to have half the uncertainty of any individual separation.

### Table III. Fine structure splittings of transition metal negative ions.

<table>
<thead>
<tr>
<th>Negative ion</th>
<th>Fine structure interval</th>
<th>Extrap. separation ( \Delta E_{\text{cm}^{-1}} )</th>
<th>Measured separation ( \Delta E_{\text{cm}^{-1}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti\textsuperscript{-}\textsuperscript{4}(F)</td>
<td>3/2 – 5/2</td>
<td>72 ± 7</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>5/2 – 7/2</td>
<td>96 ± 10</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>7/2 – 9/2</td>
<td>124 ± 12</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>3/2 – 9/2</td>
<td>295 ± 15</td>
<td>...</td>
</tr>
<tr>
<td>V\textsuperscript{-}\textsuperscript{2}(D)</td>
<td>0 – 1</td>
<td>35 ± 4</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>1 – 2</td>
<td>70 ± 7</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>2 – 3</td>
<td>106 ± 10</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>3 – 4</td>
<td>125 ± 13</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>4 – 0</td>
<td>330 ± 17</td>
<td>...</td>
</tr>
<tr>
<td>Fe\textsuperscript{-}\textsuperscript{2}(F)</td>
<td>9/2 – 7/2</td>
<td>540 ± 50</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>7/2 – 5/2</td>
<td>390 ± 40</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>5/2 – 3/2</td>
<td>270 ± 30</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>3/2 – 1/2</td>
<td>1200 ± 60</td>
<td>...</td>
</tr>
<tr>
<td>Co\textsuperscript{-}\textsuperscript{2}(F)\textsuperscript{b}</td>
<td>4 – 3</td>
<td>925 ± 90</td>
<td>910 ± 50</td>
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<td></td>
<td>3 – 2</td>
<td>625 ± 60</td>
<td>650 ± 50</td>
</tr>
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<td></td>
<td>4 – 2</td>
<td>1550 ± 80</td>
<td>1560 ± 50</td>
</tr>
<tr>
<td>Ni\textsuperscript{-}\textsuperscript{2}(D)\textsuperscript{b}</td>
<td>5/2 – 3/2</td>
<td>1450 ± 70</td>
<td>1470 ± 100</td>
</tr>
<tr>
<td>Zn\textsuperscript{-}\textsuperscript{2}(F)</td>
<td>3/2 – 5/2</td>
<td>250 ± 50</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>5/2 – 7/2</td>
<td>330 ± 70</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>7/2 – 9/2</td>
<td>370 ± 70</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>3/2 – 1/2</td>
<td>950 ± 100</td>
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<tr>
<td>Nb\textsuperscript{-}\textsuperscript{2}(D)</td>
<td>0 – 1</td>
<td>110 ± 20</td>
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<tr>
<td></td>
<td>1 – 2</td>
<td>200 ± 40</td>
<td>...</td>
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<tr>
<td></td>
<td>2 – 3</td>
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<td>3 – 4</td>
<td>310 ± 60</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>4 – 0</td>
<td>860 ± 90</td>
<td>...</td>
</tr>
<tr>
<td>Rh\textsuperscript{-}\textsuperscript{2}(F)</td>
<td>4 – 3</td>
<td>2160 ± 430</td>
<td>2370 ± 65</td>
</tr>
<tr>
<td></td>
<td>3 – 2</td>
<td>1200 ± 240</td>
<td>1000 ± 65</td>
</tr>
<tr>
<td></td>
<td>4 – 2</td>
<td>3360 ± 340</td>
<td>3370 ± 65</td>
</tr>
<tr>
<td>Pd\textsuperscript{-}\textsuperscript{2}(D)</td>
<td>5/2 – 3/2</td>
<td>3450 ± 350</td>
<td>...</td>
</tr>
<tr>
<td>Ta\textsuperscript{-}\textsuperscript{2}(D)</td>
<td>0 – 1</td>
<td>980 ± 200</td>
<td>1070 ± 110</td>
</tr>
<tr>
<td></td>
<td>1 – 2</td>
<td>980 ± 200</td>
<td>1170 ± 120</td>
</tr>
<tr>
<td></td>
<td>2 – 3</td>
<td>980 ± 200</td>
<td>Not bound</td>
</tr>
<tr>
<td>Ir\textsuperscript{-}\textsuperscript{2}(F)</td>
<td>4 – 3</td>
<td>7600 ± 1500</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>3 – 2</td>
<td>4400 ± 900</td>
<td>...</td>
</tr>
<tr>
<td></td>
<td>4 – 2</td>
<td>12000 ± 1200</td>
<td>...</td>
</tr>
<tr>
<td>Pt\textsuperscript{-}\textsuperscript{2}(D)\textsuperscript{c}</td>
<td>5/2 – 3/2</td>
<td>10000 ± 1000</td>
<td>...</td>
</tr>
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</table>

\*This work except where noted.
\#Measured separations, Ref. 22.
\$Reference 13.

VI. SUMMARY AND CONCLUSIONS

A summary of all of the experimental negative ion energy levels and states presented in this paper is given in Table IV. In all, the electron affinities of 11 transition metals and energy levels of six excited states of negative ions of these elements have been measured. With the measurement of the fine structure splittings of Rh\textsuperscript{-} and Ta\textsuperscript{-} presented, the experimental spin–orbit separations of four transition metal negative ions have been reported to date. As the majority of the transition metal negative ions have bound excited fine structure states, we have presented extrapolated spin–orbit splittings for most of the transition metal negative ions, with appropriate limits on the accuracy of these calculations.

With the measurements reported in this paper, there
TABLE IV. Summary of experimental results.

<table>
<thead>
<tr>
<th>Element</th>
<th>Negative ion state</th>
<th>E. A. (eV)</th>
<th>Level (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>$(3d^{10}4s^{1})F_{3/2}$</td>
<td>0.080 ± 0.014</td>
<td>0.0</td>
</tr>
<tr>
<td>V</td>
<td>$(3d^{10}4s^{2})P_{3/2}$</td>
<td>0.526 ± 0.012</td>
<td>0.0</td>
</tr>
<tr>
<td>Cr</td>
<td>$(3d^{9}4s^{2})S_{3/2}$</td>
<td>0.667 ± 0.010</td>
<td>0.0</td>
</tr>
<tr>
<td>Zr</td>
<td>$(4d^{2}5s^{2})F_{3/2}$</td>
<td>0.427 ± 0.014</td>
<td>0.0</td>
</tr>
<tr>
<td>Nb</td>
<td>$(4d^{4}5s^{2})F_{3/2}$</td>
<td>0.894 ± 0.025</td>
<td>0.0</td>
</tr>
<tr>
<td>Mo</td>
<td>$(4d^{6}5s^{2})F_{3/2}$</td>
<td>0.747 ± 0.010</td>
<td>0.0</td>
</tr>
<tr>
<td>Rh</td>
<td>$(4d^{6}5s^{2})F_{3/2}$</td>
<td>1.138 ± 0.008</td>
<td>0.0</td>
</tr>
<tr>
<td>Pd</td>
<td>$(4d^{8}5s^{2})P_{3/2}$</td>
<td>0.558 ± 0.008</td>
<td>0.0</td>
</tr>
<tr>
<td>Ta</td>
<td>$(5d^{6}6s^{2})P_{3/2}$</td>
<td>0.323 ± 0.012</td>
<td>0.0</td>
</tr>
<tr>
<td>W</td>
<td>$(5d^{6}6s^{2})D_{5/2}$</td>
<td>0.133 ± 0.014</td>
<td>0.0</td>
</tr>
<tr>
<td>Ir</td>
<td>$(5d^{7}6s^{2})F_{3/2}$</td>
<td>0.816 ± 0.008</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Now exist accurate experimental values for the electron affinities of 18 of the transition metals. While this is by no means a complete set, one can begin to consider the relationships in the binding of transition metal negative ions. Thus, we have investigated the series trends in the s-electron binding energies of the transition metal negative ions. It has been found that there are marked similarities in the series trends of the s-electron binding energies of the three long periods. In the data for the first transition series, which is the most complete, a dispersion-like deviation from an overall linear behavior has been observed. Further experiments are necessary before one can conclude whether this behavior is repeated in the second and third transition series. As detailed understanding of the observed series trends in the s-electron binding energy of these negative ions is not yet available, it would appear to merit some theoretical interest.

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J. C. Slater, Phys. Rev. 36, 57 (1930).


