PHYSICAL REVIEW A VOLUME 19, NUMBER 1 JANUARY 1979

Laser photoelectron spectrometry of Fe$^-$: The electron affinity of iron and the "nonstatistical" fine-structure detachment intensities at 488 nm

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(Received 6 September 1978)

With a fixed-frequency Ar II laser (488 nm), the photoelectron spectrum of Fe$^-$ has been obtained. The electron affinity of iron is 0.164 ± 0.035 eV. It has been found that the cross section for detachment of *s* electrons is much larger than that for detachment of *d* electrons at this wavelength. Also, the various fine-structure transitions do not occur in the $(2J''+1)(2J'+1)$ statistical weighting of the neutral (J') and ion (J'') spin-orbit states. An explanation for this result extends previous calculations, deriving explicit, usable expressions for fine-structure transition intensities, which are then found to agree with those observed experimentally.

I. INTRODUCTION

Iron, one of the most abundant terrestrial elements, occupies a central position in the Periodic Table and in technology, but until recently[1] there has been no direct experimental determination of the electron affinity (EA) of atomic iron. Although calculable[2] in principle, the electron affinity of iron is a particular challenge to theory, for its small value makes even a small absolute error in any calculation into a large relative error. Furthermore, most theoretical estimates of the EA (Refs. 3–5) depend on extrapolations from either end of a transition-metal series, but in the center of a series these methods often disagree. We have made an attempt to reduce the uncertainty of this number, and in this paper present the direct determination of the iron electron affinity by fixed-frequency laser photoelectron spectrometry.

Basically, in the experiment a beam of Fe$^-$ ions crossed a single-wavelength (488 nm) laser beam, and the resulting photoelectrons emitted in a direction perpendicular to both beams were energy analyzed to produce a photoelectron spectrum. The apparatus has been described elsewhere in detail.[6]

Figure 1 shows the energy levels of atomic iron[7] with those of the negative ion sketched in. Photodetachment with 488-nm radiation will raise the energy of the negative ion by 2.54 eV to a "virtual" level from which it will be able to eject an electron, leaving an atom in either the ^5D ground state or the ^5F or ^3F excited states. Actually a fourth, ^5P state, is energetically accessible, but the electrons are left with too little energy to pass the low-energy cutoff (0.25 eV) of the electron optics. Thus three "peaks" should occur in the photoelectron spectra associated with electrons leaving the atom in these three accessible states. Furthermore, the j-level fine structure resulting from the spin-orbit splitting of these levels should produce structure in each of the three photoelectron peaks. The true electron affinity is the difference between the neutral $^5D_4$ level and the ionic $^4F_{4\,1/2}$ level.

II. EXPERIMENTAL

The apparatus and techniques have been previously[6] described in detail. Iron pentacarbonyl (Apache Chemicals) is dissociated in a low-pres-

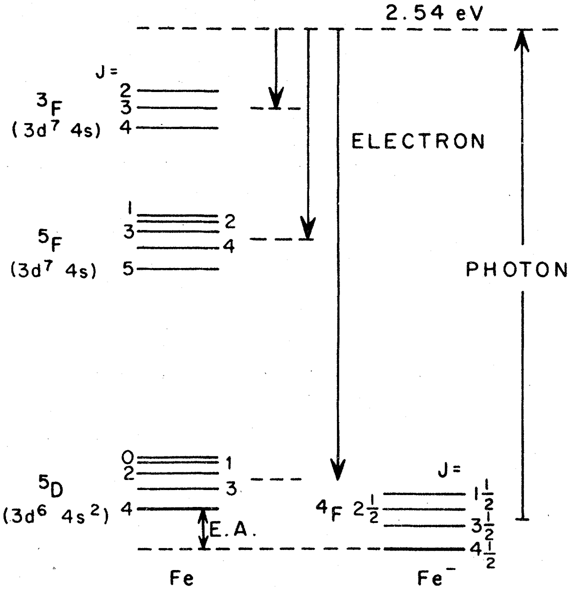

FIG. 1. Schematic of atomic energy levels in iron observed in this experiment. Absorption of a 2.54-eV photon (488 nm) can detach an electron from Fe$^-$ and leave the resulting neutral atom in either a ^3F, ^5F, or ^5D state. Although the fine-structure splitting is large, there is little evidence of it in the photoelectron spectrum.

sure electrical discharge ion source to produce beams of Fe^- ions. The ions are extracted from the source, accelerated to 680 eV, and mass analyzed by a Wien filter. The 0.5-nA mass selected ion beam is crossed in a field-free interaction region by the intracavity beam of a 4880-Å (2.540 eV) cw Ar II laser, and electrons ejected into the acceptance angle of a hemispherical electrostatic monochromator are energy analyzed [resolution of 55-meV full width at half-maximum (FWHM)].

The absolute, center-of-mass, electron kinetic energies of peaks in the detachment spectra are determined using simultaneously produced O^- as a calibration ion and the expression[6]

$$E_x = 2.540\ \text{eV} - \text{EA(O)} - 1.0215(\Omega_{O^-} - \Omega_{X^-}) - mW(1/M_O - 1/M_X); \qquad (1)$$

$\text{EA(O)} = 1.465$ eV is the "effective"[5,8] electron affinity of the oxygen atom, determined from the center of the O^- photodetachment peak; $(\Omega_{O^-} - \Omega_{X^-})$ is the laboratory energy difference between the O^- peak center and a particular X^- peak center. The factor 1.0215 is an energy scale compression factor described previously, determined by calibrating an NH^- photodetachment spectrum against the known values for the NH $a^1\Delta - X^3\Sigma$ splitting.[9] The final term in Eq. (1) accounts for the fact that the electrons we detect must be backscattered (in the c.m. frame) into the energy analyzer and thus have a c.m. component of energy perpendicular to the analyzer axis; W is the kinetic energy of the ion beam (680 eV), and m, M_O, and M_X are the masses of electron, oxygen atom, and molecule X, respectively.

The intensity of the photoelectrons at a given electron energy E depends upon the angle θ between the electric vector of the linearly polarized laser light and the electron collection direction according to[10]

$$I(\theta) = (\sigma/4\pi)[1 + \beta(E)P_2(\cos\theta)], \qquad (2)$$

where σ is the average photodetachment cross section, β is the anisotropy parameter, and P_2 is the second Legendre polynomial. A half-wave plate could be inserted to rotate the laser polarization, allowing measurement of the anisotropy of the detached electrons. The spectra shown in this paper were obtained with θ such that $P_2(\cos\theta)$ was zero, and thus reflect an average photodetachment cross section.

III. RESULTS AND DISCUSSION

The Fe^- photodetachment spectrum taken with 488-nm radiation is shown in Fig. 2. Comparison of the observed energy spacings between peaks with known Fe term energies allows immediate identification of the various processes, as shown in Fig. 2. Note the ratio of intensities: the $^5D \leftarrow {}^4F$ peak (which results from detachment of a d electron) is reduced an order of magnitude from the other $^5F \leftarrow {}^4F$ and $^3F \leftarrow {}^4F$ peaks (which result from detachment of an s electron). Again, at higher resolution (Figs. 3 and 4) the $^5D \leftarrow {}^4F$ shows itself to be qualitatively different from the others: it is twice as broad and has considerable structure that is not quite resolvable with the 60-mV resolution of our spectrometer. The ^5F and ^3F peaks each have a shoulder that is barely noticeable; the shapes of the peaks do not change with a change from 488- to 514.5-nm radiation. Apparently, a selection rule is narrowing these transitions.

The most surprising result of the Fe^- data is the small relative intensity of the $^5D \leftarrow {}^4F$ line. If the proposed $3d^7 4s^2$ electron configuration is taken for the ^4F negative-ion ground state, a one-electron transition to the $3d^6 4s^2$ configuration of the ^5D by ejection of a d electron might appear just as likely (if not more likely) as a transition to the $3d^7 4s$ configuration of both the ^5F and ^3F states by ejection of an s electron.

One possible explanation for the anomalous intensity ratios would abandon the assignment of a $3d^7 4s^2$ configuration to the negative ion in favor of a $^4F(3d^8 4s)$ configuration, making detachment to the $3d^7 4s$ configuration of the F states one-electron allowed, while making detachment to the $^5D(3d^6 4s^2)$ a two-electron process, with less intensity.

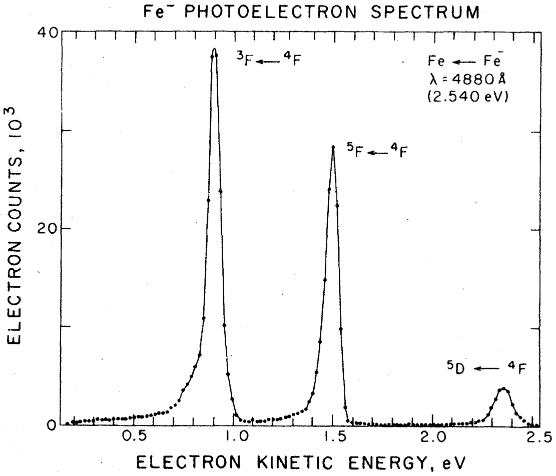

FIG. 2. Iron photodetachment spectrum taken at 488 nm.

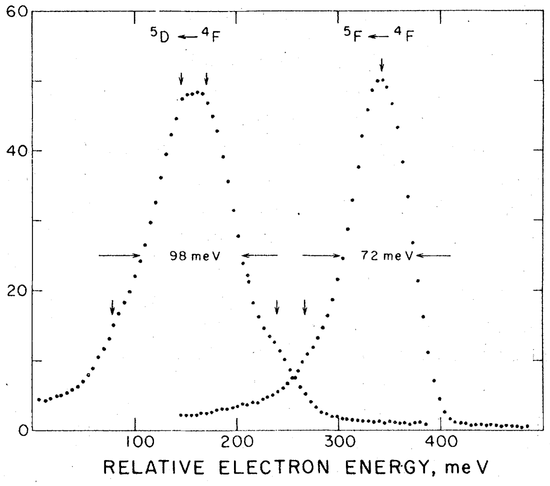

FIG. 3. ${}^5D \leftarrow {}^4F$ and ${}^5F \leftarrow {}^4F$ detachment peak shapes plotted against a relative energy scale. Some tailing to low energies is characteristic of the electron analyzer. Arrows point to incipient structure in these peaks.

However, the polarization measurements do not support this. Detachment to both F states occurs with a $\beta \geq 1.9 \pm 0.1$; that is, the electrons detach preferentially in the polarization direction of the radiation electric field. This is only consistent with either (i) detachment of an s electron giving a pure p wave or (ii) detachment of a d electron with fortuitously equal p- and f-wave contributions of the right phase.[10] The second explanation is unlikely, especially in two cases (both F lines) which compels the first of these two explanations: the detachment is of an s electron. These polarization data support the expected $3d^7 4s^2$ configuration for the stable negative ion, and all peaks in the spectrum result from single-electron promotions out of this configuration.

A rationale can be given for the reduced intensity of the ${}^5D(3d^6 4s^2) \leftarrow {}^4F(3d^7 4s^2)$ transition, the d-electron detachment. In both of these states, five of the d electrons are high-spin coupled in a half-filled shell; in fact this is true of all the low-lying states of iron observed in this experiment. These five electrons remain coupled together, permitting only either of two d electrons to detach from the ion. Thus while the d electrons out number the valence s electrons, those d electrons capable of leaving the ion in a one-electron process are equal in number to the s electrons and enjoy no statistical advantage.

This can be made more quantitative in the analysis developed by Cox based upon the fractional parentage coefficients for these states.[11,12] In this theory the electrons are assumed to be Russell-Saunders coupled. The relative intensity for detachment from an ion state consisting of a single open shell ${}^{2S+1}L_J$ to neutral state ${}^{2S'+1}L'_{J'}$ is proportional to

$$n_l \, |\langle (S'L'), l\} SL \rangle|^2 \sum_{l'} |\langle l' \| V^1 \| l \rangle|^2 ,$$

the number of electrons in the ion's l shell, times the square of the fractional parentage coefficient of the ion made from the neutral, times the sum of the reduced matrix elements for the promotion of a bound electron of type l into the continuum l'.

Of the three peaks observed in the spectrum the

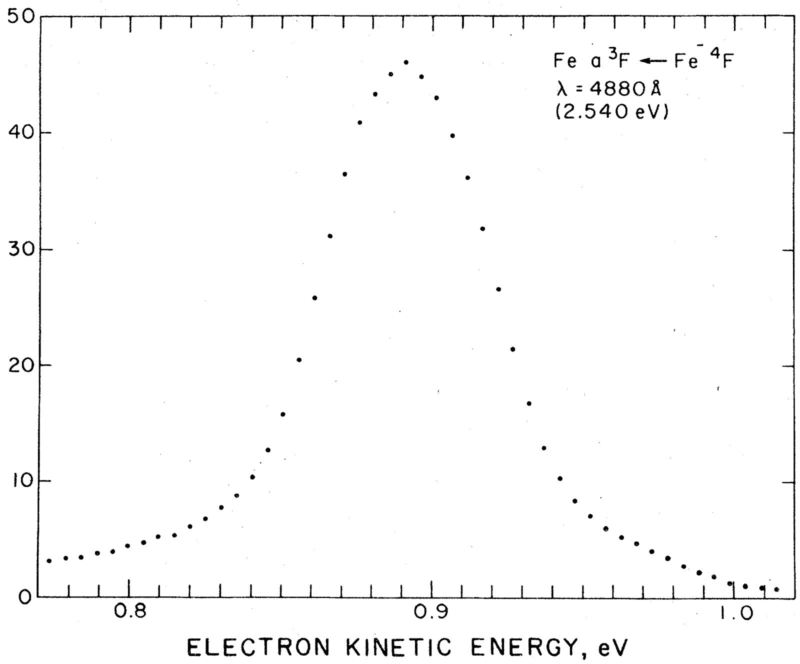

FIG. 4. ${}^3F \leftarrow {}^4F$ detachment peak. The peak width is comparable to the electron analyzer's resolution, while the tailing to low energies is characteristic of the analyzer.

two resulting from the s-electron detachment (^3F and ^5F) should have a total intensity of

$$2|\langle p\| V^1 \| s\rangle|^2 ,$$

while the sole peak representing a d-electron ejection (to give ^5D) should have an intensity of

$$7(\tfrac{5}{14})[\,|\langle p\| V^1\| d\rangle|^2 + |\langle f\| V^1\| d\rangle\,|^2].$$

Thus the only way to explain the intensity ratios observed is to invoke a difference in the reduced matrix elements for s- versus d-electron detachment.

Calculations should be helpful on this point, since evaluating the reduced matrix elements involves the radial dependence of the orbitals. A similar disparity in band intensities has been noted before in the photoionization of metallic compounds[13] and also appears in the photodetachment of FeO anions.[14] In the photoelectron spectra of these metal-ligand systems the peaks resulting from detachment of the metal pure d electrons are noticeably weak, while the ligand and ligand-metal bonding electrons dominate the spectrum.

The widths of the three (J unresolved) photodetachment peaks pose the second issue. All of the states involved have fine-structure[7] levels spanning the order of 150 meV, yet exhibit linewidths narrower than this. This is especially striking in the narrow ^3F and ^5F peaks. A feasible explanation for this, recognized in other systems,[15-17] is that the transitions from different J levels occur with "nonstatistical" weights. Thus, although photodetachment of a d electron occurs with $|\Delta L| \leq 2$, and $|\Delta S| \leq \frac{1}{2}$, resulting in a $|\Delta J| \leq \frac{5}{2}$ selection rule, the line intensities need not occur with $(2J+1)$ weights; Rau[18] points out that the fine-structure intensities are determined by purely "geometrical" factors determined by angular momentum coupling in the problem. This appears to be sufficient to explain the narrow peaks observed in the photoelectron spectrum.

We will examine the process for one peak

$$\mathrm{Fe}^{-}\,{}^4F_{J''}\,(3d^7\,4s^2) + h\nu \rightarrow \mathrm{Fe}\,{}^3F_{J'}\,(3d^7 4s) + e^-(kp)\,.$$

We will assume a one-electron process of photodetachment is occurring.

The Appendix presents the derivation of the intensity expression for a one-electron detachment from an L-S coupled ion. In this particular case, we find an expression for the individual fine-structure components of the photodetachment:

$$I_{J'J''} \sim (2J'+1)(2J''+1) \begin{Bmatrix} J'' & \frac{3}{2} & 3 \\ 1 & J' & \frac{1}{2} \end{Bmatrix}^2 \,.$$

A comparison of this expression with a simple product of the statistical degeneracy factors of the initial and final states $(2J'+1)$ $(2J''+1)$ indicates a substantial effect on the photodetachment fine structure. A mock line shape is shown in Fig. 5 (cf. Fig. 4) using intensities derived from the angular momentum recoupling coefficients and the statistical weights of the upper and lower states. These intensities have been convolved with a 55-meV width Gaussian instrumental function. Also shown for contrast is the relatively broad photodetachment structure calculated with just the statistical weights of the initial and final states. Since the negative-ion fine-structure intervals have not been measured, we have estimated the fine-structure splitting in the negative-ion $^4F_J(3d^7\,4s^2)$ state to be 0.6 of that found in the same state of cobalt, based on an extrapolation procedure[19] applied to the isoelectronic series Fe^-, Co, Ni^+, ... The optimum fit to the data was with a spin-orbit splitting between 0.5 and 0.6 of the splitting in the cobalt ground state, but even 20% variations in this estimate produce little change in the calculated line shape.

Changes in the line shape produced by population changes in the fine-structure levels of the negative ion are also small. The above calculations were made with a $(2J+1)$ statistical weighting of the initial-state levels; that is, an infinite effective temperature was assumed. When a Boltzmann factor was used corresponding to 1000 K (more representative of the relative populations of the fine-structure levels in the experiment), the linewidth narrowed by only 5 meV. This small change resulted from shifting more intensity into the al-

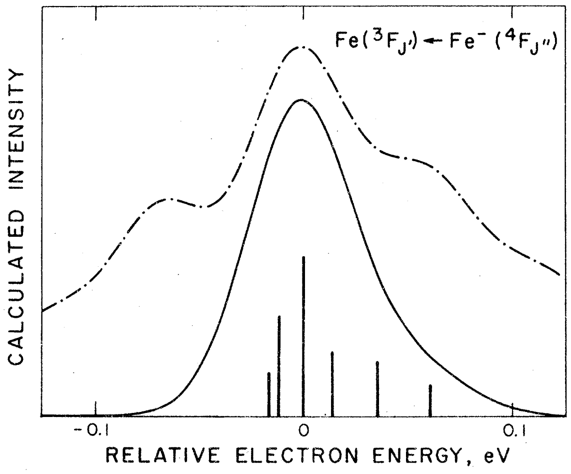

FIG. 5. Theoretical $^3F \leftarrow {}^4F$ line shapes. The solid line is the fine-structure calculation of this paper (stick spectrum) convoluted with a 55-meV wide Gaussian. The dot-dash line would be expected from a statistical $(2J'+1)(2J''+1)$ weighting of the fine-structure components of this transition. Zero relative energy here corresponds to the $J'=4 \leftarrow J''=4\frac{1}{2}$.

ready dominant $J=4\frac{1}{2}\rightarrow J'=4$ transition, increasing its contribution from 35% to almost 60% of the total intensity, and comparably reducing the contributions from all five other allowed $J\rightarrow J'$ transitions.

This analysis now permits the determination of the electron affinity of iron with confidence. Regardless of the error in estimating the value of the unknown fine-structure constant of the ion, the $\mathrm{Fe}^-\,{}^4F_{4\,1/2}\rightarrow \mathrm{Fe}\,{}^3F_4$ photodetachment, giving the ${}^4F_4$ electron affinity, is very close to the maximum of the actually observed peak. We can be certain within very generous limits if we assign this process to the experimentally observed peak, plus or minus the peak halfwidth. Then, by subtracting the difference between ${}^3F_4$ and the ${}^5D_5$ ground state of iron (known by optical spectroscopy[7]) we obtain the ground-state electron affinity of iron (0.164 ±0.035 eV).

Estimates of the Fe electron affinity include the 0.58-eV value from the calculation of Clementi,[2] and the 0.11- and 0.09-eV values from improvements to the respective methods of Charkin and Dyatkina,[3] and Zollweg.[4] (The original authors estimated the EA at $\frac{1}{2}$ eV higher.) On a weighted average of the above values, Hotop and Lineberger[5] based a recommended 0.25 ±0.20 eV electron affinity, and in agreement with this average, one experimental number exists in the work of Compton and Stockdale.[1] They combine the appearance potential of Fe^- from electron bombardment on $\mathrm{Fe(CO)_5}$ with the dissociation energy of the Fe-C bonds in that compound to find again EA(Fe) = 0.25 ± 0.2 eV. Thus an EA of 0.164 ±0.035 eV is consistent with this earlier work, and is more accurate.

Further experiments on transition metals should prove to be stringent tests of the assumptions underlying these methods of predicting detachment intensities. The data concerning[19] Pt^- and recently Cr^- and Ni^- (Ref. 20) have come from threshold experiments which do not have adequate resolution to check the consistency of the theory. Nor is this study of iron a stringent test of these methods, since the fine structure was not resolved. More delicate tests are needed, and these could be supplied by the photoelectron spectra of the ions of the elements just to the right of iron in the Periodic Table, cobalt and nickel. These have larger spin-orbit splittings than iron,[7] so the spectra of Co^- and Ni^- should be resolvable into individual fine-structure components. Also, because of the increase in spin-orbit effects, these measurements should provide information on the sensitivity of this theoretical framework to breakdown of L-S coupling. This breakdown of Russell-Saunders coupling in the rare gases has been investigated by photoionization,[15,21] where it was noticed that strong departures from LS predictions were observed for the heavy elements. The same techniques are applicable here to the photodetachment of the transition metals, and it can be hoped that an interplay of theory and experiment could refine our understanding of photodetachment (and photoionization) of the transition metals.

IV. CONCLUSIONS

The electron affinity of atomic iron has been directly measured to be 0.164 ±0.035 eV; the ground state of the ion is $3d^7 4s^2({}^4F_J)$. Two unusual features are present in the data. The first is the large s-electron detachment cross section in preference to d-electron detachment. The second is the "nonstatistical" weighting of the J component lines, giving rise to quite narrow photo lines nearly devoid of spin-orbit structure. The narrowing of the fine structure in the photodetachment of iron negative ions is explained for the simple case of electrons ejected out of a closed s shell. In addition to finding a selection rule for detachment of an s electron, $\Delta J=\pm\frac{1}{2}$, we are able to calculate intensities of individual fine-structure components, in agreement with experiment. Finally, we can now conclude that the electron affinity of iron is 0.164 ±0.035 eV.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation through Grants Nos. AER74-20552 and PHY76-04761 to the University of Colorado. One of us (W.C.L.) acknowledges support from a Camille and Henry Dreyfus Teacher-Scholarship, and appreciation for the stimulating atmosphere of the Aspen Center for Physics during the preparation of the manuscript.

APPENDIX: FINE STRUCTURE IN PHOTODETACHMENT OF AN *L-S* COUPLED NEGATIVE ION

We begin with the matrix element expressed as a reduced matrix element and a Clebsch-Gordon factor,[22]

$$\langle J'M'\,|\,T^j_m|\,J''M''\rangle=(2J'+1)^{-1/2}\langle J'\|\,T^j\,\|J''\rangle \times\langle J''jM''m|J'M'\rangle\ .$$

Thus the intensity of a transition to a final J' from an initial J'' gives, after summing over M', M'', m, and j,

$$I(J',J'')=\sum_j|\langle J'\|\,T^j\|\,J''\rangle|^2\ .$$

Now we concentrate on the structure of the reduced matrix element itself. The ion state $^{2S'+1}L'_{J'}$ is assumed to be well described by L-S coupling. Detachment is assumed to be a direct, one-electron process, and the action of the photon "annihilates" an electron of spin $\frac{1}{2}$ and angular momentum l by promoting it into the continuum. Then the reduced matrix element factors:

$$\begin{aligned}\langle J' \| T^j \| J'' \rangle &= \langle S'L'J' \| T^j \| S''L''J'' \rangle \\ &= \langle S' \| t^-_{1/2} \| S'' \rangle \langle L' \| t^- \| L'' \rangle \\ &\quad \times [(2J'+1)(2j+1)(2J''+1)]^{1/2} \\ &\quad \times \begin{Bmatrix} S'' & L'' & J'' \\ \frac{1}{2} & l & j \\ S' & L' & J' \end{Bmatrix} \langle (S',L')l\} S'',L'' \rangle .\end{aligned}$$

Proportional to annihilation operators, $t^-_{1/2}$ and t^- act on the spin and space wave function of an electron, respectively. The last factor is a parentage coefficient for forming the ion term by adding an electron to the neutral term, its "parent." When the ion or neutral is not well described by a single-electron configuration, a sum over configurations is required, and the matrix element on the left is a sum over expressions on the right. However, this does not affect the results to be obtained here concerning the relative intensities of the fine-structure components. As long as spin-orbit effects are small and L-S coupling holds, configurations of different L and S will not mix, and we can factor the configuration independent 9-j symbol and the J factors out of the sum.

Now, the relative intensity for a fine-structure component of a specific transition between L-S states becomes

$$I(J',J'') \sim \sum_{j=l-1/2}^{l+1/2} (2J'+1)(2J''+1)(2j+1) \times \begin{Bmatrix} S'' & L'' & J'' \\ \frac{1}{2} & l & j \\ S' & L' & J' \end{Bmatrix}^2 .$$

We have suppressed the common factors independent of J (the reduced matrix elements and parentage coefficients). This final formula for relative intensities of the fine-structure components assumes all J'' levels of the initial negative ion have been populated by their degeneracy, and as such this result applies when kT is much greater than the fine-structure splitting. Otherwise, a weighting function peculiar to the particular experiment, such as a Boltzmann factor $\exp[-E(J'')/dT]$, must be applied to these relative intensities.

One important selection rule is immediately found from the triangle relationship which the components of the 9-j matrix must satisfy: $|\Delta J| \leq l+\frac{1}{2}$.

A special case occurs when $l=0$, the photodetachment of an s electron. The intensity expression contains but one term, and the 9-j symbol simplifies to

$$\begin{Bmatrix} S'' & L'' & J'' \\ \frac{1}{2} & 0 & \frac{1}{2} \\ S' & L' & J' \end{Bmatrix}^2 = \delta_{L'L''} [2(2L'+1)]^{-1} \begin{Bmatrix} S'' & J'' & L'' \\ J' & S' & \frac{1}{2} \end{Bmatrix}^2 .$$

Thus when $l=0$,

$$I(J',J'') \sim (2J'+1)(2J''+1) \begin{Bmatrix} S'' & J'' & L'' \\ J' & S' & \frac{1}{2} \end{Bmatrix}^2 .$$

From this selection rule $|\Delta J| \leq \frac{1}{2}$ immediately follows.

We have derived explicitly the relative intensity expression for fine-structure transitions because of a discrepancy between methods already in the literature.[12,18] The cause of this discrepancy is now understood. One derivation,[18] along different lines from those presented here, neglected fractional parentage coefficients which should have appeared in the final expression for the relative fine-structure intensities. Neglecting these coefficients gives incorrect expressions.[23] On the other hand, the expressions we derive are almost identical to those of Cox,[12] differing only in the addition of a factor of $(2J''+1)$ to account for the statistical degeneracy of the initial fine-structure levels. We hope a stringent test of these various expressions will be the photodetachment of Ni^- and Co^-.

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