

**Electron Affinities, Magnetic Dipole Decay Rates,
and Hyperfine Structure
for the Excited States of $5p^3 \text{ Sn}^-$**

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Theoretical results have been computed to complement recent measurements by Scheer *et al* [Bull. Am. Phys. Soc. **42**, 1026 (1997)] which yielded electron affinities of excited states of the ground configuration of Sn^- . Our relativistic configuration interaction (RCI) values for the position of the excited Sn^- with respect to the negative ion ground state are $\text{EA}(^2D_{3/2}) = 5903 \text{ cm}^{-1}$ (0.732 eV), $\text{EA}(^2D_{5/2}) = 6493 \text{ cm}^{-1}$ (0.805 eV). Triple excitations make a significant contribution. Magnetic dipole hyperfine structure (hfs) constants (A) and M1 transition probabilities are also reported.

I. METHODOLOGY: ELECTRON AFFINITIES AND HYPERFINE STRUCTURE

Very recently, Scheer *et al* [?] have been able to measure the electron affinities (EA) of excited states of the ground configuration of Sn^- . There are no available theoretical results for these levels. Our approach is to calculate the EA of the two excited states with respect to the negative ion ground state ($^4\text{S}_{3/2}$). This reduces the necessity for a more complete correlation treatment which would be needed to properly position the negative ion levels with respect to the atomic ground state.

Our results in this work are produced by relativistic configuration interaction (RCI) calculations, whose methodology has been more fully detailed elsewhere [?,?]. Briefly, our calculations begin by obtaining Dirac-Fock (DF) results for the $5p^3$ levels, using the program of Desclaux [?]. After the DF (zeroth order) solution is obtained, correlation is introduced with our RCI code [?] by making single and double excitations from the occupied subshells. To keep the calculations simple, all energy differences are obtained relative to the negative ion ground state. Except for the symmetry changing single excitations from the shallow core, this should considerably reduce the role of core-valence correlation effects. Subshells which are unoccupied in the DF function, are designated with a “v” (for “virtual”). These subshells are represented in the RCI calculation as relativistic screened hydrogenic functions ($n = \ell + 1$), whose effective charge (Z^*) is determined as a part of the RCI variational process [?,?].

We make separate runs for each level with Z^* 's determined to minimize the energy of the specified level. Initially, we include all single and double excitations from the $5p$ subshells. A second and third set of virtuals are added in subsequent layers, adding single excitations from $5s$, doubles from $5s\ 5p$ and $5s^2$, and, finally, singles from the $4d$ subshell.

As we add correlation to the $5p^3$ levels, we monitor energy contributions to the various levels from individual correlation configurations. Since the $^2\text{D}_{3/2} - ^2\text{D}_{5/2}$ gap remains quite stable ($\sim 75\text{--}85$ meV) beyond the addition of the second set of virtuals, we pay particular attention to the $^4\text{S}_{3/2} - ^2\text{D}_{3/2}$ energy difference. Though a certain amount of fluctuation

is expected, with most configurations having slightly higher energy contributions as more correlation is added to $5p^3$, a few configurations exhibit dramatic losses to their energy contributions. We attribute this to a “pulling away” of the energetically close excitations as the $5p^3$ levels are more completely and preferentially correlated. The most prominent losses come from $5s^2 5p^2 vf$ and $5s vd 5p^3$, which exhibit relative losses in contribution to the lessening of the ${}^4S_{3/2} - {}^2D_{3/2}$ gap of 23 meV and 56 meV respectively. To lessen the effect of this preferential correlation we remove all configurations which have nearly equal (within 3 meV) contributions to all three levels of interest. This results in removal of 10 configurations (see footnote a of Table I) and ~ 210 meV (net differences are within 1 meV for the three levels) of correlation contribution to the energies of these levels. Since we remove nearly equal amounts from each level, any changes in their relative positions must then come from second order effects through the lessening of the preferential “pulling away” from the $5p^3$ manifold. In fact, we do see a decrease in the ${}^4S_{3/2} - {}^2D_{3/2}$ gap of 8.4 meV, with 8.0 meV coming from $5s^2 5p^2 vf$ and $5s vd 5p^3$.

At this point we have $\sim 3200-3500$ parents, or basis functions, in each of the runs. For each run, we remove $\sim 1200-1500$ of the smallest parents. Calculations using these smaller sets shows changes in the EAs of less than 1 meV. This reduction combined with the configuration removal discussed above, provides us with enough room within the 7000 parental limit of our code for the inclusion of a large number of second order effects (see below).

The two configurations $5s^2 5p^2 vf$ and $5s vd 5p^3$ still show a reduced contribution from earlier runs. In addition, we notice that the energy contribution of $5s^2 5p^2 vp$ to the ${}^2D_{3/2}$ level in the run optimized to ${}^2D_{3/2}$ is half that of the same contribution in the run optimized to ${}^4S_{3/2}$. We attribute this to the differences in the virtual sets present from a differing set of Z^* 's. From consideration of correlation tables from intermediate calculations, it appears that our variational procedure has produced Z^* 's for vp , vp' , and vp'' which maximize the $5s^2 5p^2 vp^2$ contribution at the expense of the much smaller $5s^2 5p^2 vp$ contribution (see Table I). Since the energy contributions of these three configurations ($5s^2 5p^2 vf$, $5s vd 5p^3$, and $5s^2$

$5p^2$ vp) are the most affected by their positioning with respect to the $5s^2$ $5p^3$ manifolds, we more fully correlate these configurations by including configurations corresponding to the same types of excitations present in the $5s^2$ $5p^3$ levels.

We choose certain double excitations which are large or differentially large in the $5p^3$ levels to add to the above configurations (see footnote b of Table I), which are then triple excitations with respect to the $5p^3$ manifolds and thus have zero contribution in first order. In addition, we include two double excitations from $5p^3$ which are also second order effects, $5s^2 \rightarrow vp$ vf and $5s$ $5p \rightarrow vs$ vf . The net effect of these second order additions is to lower ${}^2D_{3/2} \sim 12.5$ meV with respect to ${}^4S_{3/2}$.

The above discussion involves triple excitations involving only the first (dominant) set of virtuals. We add further correlation to these excited states by considering triples involving one or two virtuals from the second set. Our criterion for inclusion involves a more detailed correlation table which separates excitations according to virtual sets. If an excitation involving a virtual from the second set contributes 20% or more of the energy from the corresponding excitation involving only the first set, it is included in our triple excitations. For example, we find that for ${}^2D_{3/2}$ $5s^2 \rightarrow vp$ vp' contributes about 30% the amount of energy as $5s^2 \rightarrow vp^2$, so we include it in our correlation for the excited states.

Note that many of the triples we are adding may look like doubles or singles with respect to other configurations as well. In particular, $5s^2$ $5p$ vp^2 and $5s$ $5p^2$ vp vd , which are themselves single excitations from some of the configurations we are trying to correlate, are greatly affected by these second order additions to the calculation. The final result of all the second order effects is a net reduction of the ${}^4S_{3/2} - {}^2D_{3/2}$ gap by 19.4 meV, with the majority (18.6 meV) coming from $5s^2$ $5p^2$ vp , $5s^2$ $5p^2$ vf , $5s$ vd $5p^3$, $5s^2$ $5p$ vp^2 , and $5s$ $5p^2$ vp vd as expected.

Our final step is the addition of the exclusion effects $4d^2 \rightarrow 5p^2$ and $4d$ $5s \rightarrow 5p^2$, which have a net effect of lowering ${}^2D_{3/2}$ 11.1 meV with respect to ${}^4S_{3/2}$. Based on earlier work [?], these and the single excitations from $4d$ should provide the largest differential effects involving the $4d$ subshell.

II. METHODOLOGY: MAGNETIC DIPOLE TRANSITION RATES

Decay rates of excited states of negative ions have been used [?,?] to help characterize such states. For ground configurations, decays occur by magnetic dipole (M1) and electric quadrupole (E2) processes. Since rates available [?] for the isoelectronic neutral atomic state usually favor the M1 rate over the E2 rate, we concentrate on the former in this work.

Our previous work [?] on transition probabilities has been for the electric dipole (E1) operator. The basic theory was drawn from the work of Grant [?], which was both corrected and extended where necessary. Calculation of M1 rates is both simpler and more complicated than E1 rates. On the “simpler” side, only one gauge is involved [?], for all magnetic poles, and correlation effects are often suppressed [11; also see below], because the two states involved in the transition are similar (i.e. have the same DF configuration, $5p^3$ in this case). The increased “complication” comes in the treatment of non-orthonormality. For us, the two transition states are generated independently, and thus do not have orthonormal one electron basis sets. As is usual, we treat these using the results of King *et al* [?], which creates a set of “corresponding” spinors by diagonalization of 1 or 2 overlap matrices, for each pair of determinantal matrix elements. For E1 transitions, a symmetry (parity) change is guaranteed, and the diagonalizations may be avoided entirely [?] leading to efficiency gains of ~ 1000 . On the other hand, for M1, there is no such guarantee [?], and we have programmed the “full” formulae of King *et al* [?]. Nonetheless, due to a combination of wavefunction size (~ 6900 parents), and computational resources (Alpha 250 4/266), computational times were moderate (25 minutes). Below, we present the essential formulae needed to obtain any magnetic transition probability.

The transition probability for spontaneous emission (in sec^{-1}) is given [?] by:

$$A_{ki} = \frac{6.670 \times 10^{15}}{\lambda^2} \frac{g_i}{g_k} f_{ik} \quad (1)$$

where λ , the wavelength, is given in Angstroms, the g 's are the statistical weights ($2J + 1$) for the upper (k) and lower (i) levels, and f_{ik} is the absorption oscillator strength (dimensionless). Following refs [?,?], f is given by:

$$f_L (J \rightarrow J') = \frac{c^2 |\langle JJ | T_{J-J'}^{(L)} | J'J' \rangle|^2}{\Delta E (2J + 1) \begin{pmatrix} J & L & J' \\ -J & J - J' & J' \end{pmatrix}^2 (2L + 1)} \quad (2)$$

with

$$T_Q^{(L)} = \sum_{k=1}^N t_Q^{(L)}(k) \quad (3)$$

Here, ΔE is the excitation energy (in a.u.), which we extract from experiment (if available; otherwise from the best available theoretical value). The bracket in the denominator is a 3j symbol, and the initial (final) state has $M = +J$ ($M' = +J'$). In the present instance (M1), the rank (L) of the tensor “causing” the transition is 1.

One electron matrix elements of $t_Q^{(L)}$ evaluated over spinors $| n\kappa m \rangle$ for magnetic poles are given by

$$\begin{aligned} \langle n\kappa m | t_Q^{(L)} | n'\kappa' m' \rangle &= (-1)^{L+j-m+j'-\frac{1}{2}} (2L + 1) \sqrt{\frac{(2j + 1)(2j' + 1)}{2L(L + 1)}} \times \\ &\times i^{L+1} (\kappa + \kappa') \begin{pmatrix} j & L & j' \\ -m & Q & m' \end{pmatrix} \begin{pmatrix} j & L & j' \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} I_L^+ \left(\frac{\Delta E r}{c} \right) \end{aligned} \quad (4)$$

For magnetic multipoles [?], $j + j' + L$ is odd (even) if $\kappa\kappa' < 0$ ($\kappa\kappa' > 0$). The radial integral is given by [?]:

$$I_L^+ \left(\frac{\Delta E r}{c} \right) = \int_0^\infty (PQ' + QP') j_L \left(\frac{\Delta E r}{c} \right) dr \quad (5)$$

where P, Q (P', Q') are the major, minor radial functions of the bra (ket) and j_L is a spherical Bessel function. Evaluation of the formula is done using using the newly developed M1 option of our relativistic oscillator strength program [?].

III. RESULTS

In Table I we report energy contributions from correlation configurations. In addition to those configurations discussed in Section I, we note the importance of excitations of the form $5p^2 \rightarrow v\ell v(\ell + 2)$. These excitations, as well as $5p \rightarrow v\ell$, vanish for a pure 4S state, and are thus large contributors to the lowering of the 2D levels (Dirac-Fock LS purities for $^4S_{3/2}$, $^2D_{3/2}$, and $^2D_{5/2}$ are 98.2%, 91.7%, and 100%, respectively). Of particular interest is the use of $v\ell$ in $5p^2 \rightarrow v\ell v\ell$. The importance of extending our virtual sets beyond $\ell = 4$ was known from previous work in Cs II [?], and here affects the EAs of the $^2D_{3/2}$ and $^2D_{5/2}$ levels by over 7.5 meV. We also included the excitation $5p^2 \rightarrow v\ell v\ell$, but this was removed as part of the effort to reduce the non-differential correlation discussed in Section I.

In Table II we report our results for the electron affinities (EA) for the $5p^3$ excited bound states of Sn^- . It can be seen that there are only two main contributors to the EAs, the Dirac-Coulomb contribution, obtained using Desclaux's program [?], and correlation, obtained using our RCI program [?]. As the results of Scheer *et al* [?] are unpublished to date, we have compared to older experimental values where available. These are drawn from the work of Feldman *et al* [?,?] and Hotop and Lineberger [?]. There does exist a more accurate measurement of the EA of $\text{Sn}^- ^4S_{3/2}$ by Miller *et al* [?], but we need the $^2D_{3/2} - ^4S_{3/2}$ energy difference, and for the sake of consistency have used the two Feldman *et al* values [?]. The more recent review of Hotop and Lineberger [?] was useful in assembling these results.

Though the error in the $^2D_{3/2}$ EA is ~ 75 meV, we don't see this as unreasonable considering the Feldman value of 0.8 eV is given to one digit, and we are within 0.1 eV. More accurate experiments should clear up this discrepancy. Likewise, though the $^2D_{5/2}$ EA is off with respect to $^4S_{3/2}$, the $^2D_{3/2} - ^2D_{5/2}$ energy difference is within ~ 25 meV of the experimental difference. Partially correlated results for $5p^3 ^2P_{1/2}$ and $5p^3 ^2P_{3/2}$ place them at $\sim 11,200 \text{ cm}^{-1}$ (1.39 eV) and $13,200 \text{ cm}^{-1}$ (1.64 eV) above the $^4S_{3/2}$ level (EA = 1.112 eV [?]), leaving them quite unbound. Properly speaking, the 2P levels should be treated with shape resonance theory to establish the positions and widths of these states.

In Table III, we report magnetic dipole hfs constants, A , for the three $5p^3$ bound states of Sn^- . The magnetic dipole moment for the hfs is taken from ^{117}Sn [?] (see footnote a of Table III). These hfs constants can be useful in characterizing negative ion states [?]. Though we have no experimental measurements to compare with our hfs A 's, we expect the error in our calculations may be as high as 20% due to lack of excitation from the core, particularly single excitations from the 4s and 4p subshells. We expect the largest error to be in the $^4\text{S}_{3/2}$ A due to its small value.

Finally, in Table IV we report calculations for M1 transition probabilities (see Section II for theoretical background) for the transitions $^4\text{S}_{3/2} \rightarrow ^2\text{D}_{3/2}$, $^4\text{S}_{3/2} \rightarrow ^2\text{D}_{5/2}$, and $^2\text{D}_{3/2} \rightarrow ^2\text{D}_{5/2}$.

TABLE I. Contributions to $\text{Sn}^- 5p^3$ energies (-meV).

Excitation ^a	$^4S_{3/2}$	$^2D_{3/2}$	$^2D_{5/2}$
$5p \rightarrow vp$	3.8	27.4	11.6
$5p \rightarrow vf$	1.1	137.3	150.9
$5p^2 \rightarrow vp^2$ ^b	97.6	174.6	168.4
$5p^2 \rightarrow vd^2$ ^b	273.3	294.9	276.0
$5p^2 \rightarrow vs vd$ ^b	0.4	58.6	58.4
$5p^2 \rightarrow vd vg$ ^b	0.4	26.8	28.2
$5p^2 \rightarrow vp vf$ ^b	0.3	20.4	21.5
$5p^2 \rightarrow vf vh$	0.1	7.8	8.2
$5s \rightarrow vs$	19.0	3.2	4.7
$5s \rightarrow vd$	645.7	613.8	654.1
$5s^2 \rightarrow 5p^2$ ^b	3.5	16.2	N/A
$5s^2 \rightarrow 5p vp$ ^b	105.5	124.6	122.9
$5s^2 \rightarrow vp^2$ ^b	65.6	86.7	85.8
$5s^2 \rightarrow vd^2$ ^b	95.7	91.6	95.8
$5s 5p \rightarrow vs vp$ ^b	153.8	160.7	160.3
$5s 5p \rightarrow vp vd$ ^b	226.1	257.4	250.4
$5s 5p \rightarrow vd vf$ ^b	185.8	172.6	169.9
$4d \rightarrow vs$	0.9	5.4	5.4
$4d \rightarrow vd$	59.7	31.2	31.4
$4d \rightarrow vg$	4.1	19.0	19.3
$4d^2 \rightarrow 5p^2$	1.0	1.1	1.1
$4d 5s \rightarrow 5p^2$	0.1	11.1	12.9
Total	1943.2	2344.2	2334.7

^aContributions represent combinations of configurations with same type of virtuals from all three sets. The following configurations were removed due to lack of differential energy

contributions (see Section I): $5p^2 \rightarrow vs^2 + vf^2 + vg^2 + vg\ vi$, $5s^2 \rightarrow vs^2 + vf^2 + vg^2$, and $5s\ 5p \rightarrow vf\ vg + vg\ vh + vh\ vi$.

^bIndicates excitations used for second order effects (triples). These doubles are applied to $5s^2\ 5p^2\ vp$, $5s^2\ 5p^2\ vf$, and $5s\ vd\ 5p^3$ where applicable (see Section I).

TABLE II. EA ^a (cm⁻¹) for 5p³ Sn⁻ excited bound states.

Contribution	² D _{3/2}	² D _{5/2}
Dirac Coulomb	9131	9656
Magnetic	2	-10
Retardation	-2	-2
Radiative	6	7
Correlation	-3234	-3158
Total Theory	5903 (0.732 eV)	6493 (0.805 eV)
Experiment	6500 ^b	7300 ^c

^aRelative to Sn⁻ 5p³ ⁴S_{3/2}.

^bConverting the Sn⁻ ²D_{3/2} - ⁴S_{3/2} energy difference of 0.8 eV reported by Feldman *et al* [?] to cm⁻¹.

^cAdding to ^c a measured 800 cm⁻¹ as reported by Hotop and Lineberger [?].

TABLE III. Hyperfine structure constants A (MHz)^a and largest contributions^b to A .

A (Dirac-Fock)	93.5	-488	-1156
A (RCI)	198	-311	-1016
1st order (core-polarization) effects			
5p \rightarrow vp	24.7	67.7	15.9
5s \rightarrow vs	413.6	-17.7	102.6
4d \rightarrow vd	-1.1	21.3	28.4
2nd order (configurationally diagonal) effects			
5s \rightarrow vd	-262.3	39.7	-66.0
5s 5p \rightarrow vp vd	-36.7	6.4	-15.9
5s 5p \rightarrow vd vf	-28.0	2.9	-6.1

^a $I=1/2$, $\mu_I = -1.000$ [?]. Results for other isotopes may be obtained by scaling A with the ratio of μ_I/I .

^bTerms shown are those that contribute at least 10 MHz for one or more of the $5p^3$ states.

TABLE IV. M1 transition probabilities (s^{-1}) for $5p^3 \text{Sn}^-$.

Transition	Dirac-Fock	RCI
$^4S_{3/2} \rightarrow ^2D_{3/2}$	0.760	0.744
$^4S_{3/2} \rightarrow ^2D_{5/2}$	0.00294	0.00420
$^2D_{3/2} \rightarrow ^2D_{5/2}$	0.00214	0.00211

IV. ACKNOWLEDGEMENT

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