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LETTER TO THE EDITOR

Use of intermediate coupling relationships to test measured branching fraction data

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Abstract. The extensive arc emission measurements of transition probabilities by Corliss and Bozman are known to contain errors due to flaws in the determination of level populations in the source. However, if no similar errors were present in the photometric calibration, then branching fractions from the same upper level deduced from these measurements should be valid. It is shown that the branching fractions for the ns^2np^2–$ns^2np(n+1)s$ transitions in Si I, Ge I, Sn I and Pb I can be accurately estimated using intermediate coupling amplitudes obtained from spectroscopic data, and thus provide a test of the validity of these measurements. The results of Corliss and Bozman are examined in the context of comparisons with these estimated values and with other measurements, and it is demonstrated that branching fractions from the same upper level obtained from these data can be quite reliable.

Atomic oscillator strengths can be determined experimentally either by absolute emission, absorption or dispersion measurements, or through the combined measurement of relative branching fractions and level lifetimes. The absolute measurements require sample equilibrium, a knowledge of the absolute number density and an absolute photometric calibration, and the lifetime measurements yield oscillator strengths only in cases where a single decay channel exists. Thus high-precision measurements have often involved the combined measurement of lifetimes and branching fractions [1].

While many methods have been brought to bear on the precision measurement of lifetimes [2] and much progress has been made in the measurement of branching ratios [3], branching fraction data remain sparse and urgently needed. A very extensive tabulation of transition probability data derived from arc spectra line intensities exists in the monograph of Corliss and Bozman [4]. However, it is well known [5] that these transition probabilities provide neither an absolute nor a self-consistent set of values, so care must be exercised in their use. In general, the normalization must be corrected for two types of errors. The first is in the determination of the concentration of radiating atoms in the arc source (which can be corrected by summing transition probabilities over final states and renormalizing to match measured lifetime data). The second is in the determination of the level populations in the arc source due to either a lack of thermodynamic equilibrium or an inaccurate temperature determination, which causes the renormalization factor to depend on the excitation energy of the upper level. Since branching ratios involve the comparison of relative transition probabilities from the same upper level, neither the overall normalization nor the arc temperature should affect their validity. However, it does require an accurate photometric calibration of the detection equipment over the very wide range of wavelengths spanning the decay channels.

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In general, the comparison of experimental branching fractions with theoretical calculations requires the specification of radial transition moments, which are sensitive to the details of the potential. However, in the non-relativistic approximation, the relative intensities of the lines within a supermultiplet all involve the same radial transition moment, which cancels when branching ratios are formed. If there is no significant branching to other configurations the branching fractions can be specified from angular factors and the intermediate coupling (IC) mixing amplitudes, which can be determined from spectroscopic energy level data. The ns^2np^2–$ns^2np(n+1)s$ manifold of transitions in Si I, Ge I, Sn I and Pb I provide such a case, and comprehensive measurements for this supermultiplet are contained both in the tabulation of Corliss and Bozman [4], and in more recent studies [6–9]. While the lack of configuration interaction (CI) in these systems simplifies the calculational specification of the branching fractions, the transitions cover a wide range of both wavelength regions and intensity ratios, and are no less challenging to experimental measurement than any other system studied in [4]. We have therefore made data-based empirical IC calculations of these branching fractions and compared them with the measurements of [4] and others, in order to evaluate the reliability of the tabulation of Corliss and Bozman as a source of branching fraction data.

For a pure configuration, the intermediate coupling amplitudes are manifested both by the energy levels and by the transition probabilities of the levels. Thus, if the single-configuration picture is valid, the measured energy level splittings within the upper and the lower configuration can be used to determine the mixing amplitudes, and these can then be used to specify (to within factors of the radial transition matrix) the relative transition probabilities. In the case of the sp and p^2 configurations, there are at most two normalized mixing amplitudes for a given value of J, which can be characterized by a singlet–triplet mixing angle θ_J. For sp the mixing between $^3P_1$ and $^1P_1$ can be characterized by θ_1 (primes denote that the LS notation is only nominal for the physical states)

$$|^3P_0^{o\prime}\rangle = |^3P_0^o\rangle \tag{1}$$

$$|^3P_1^{o\prime}\rangle = \cos\theta_1|^3P_1^o\rangle - \sin\theta_1|^1P_1^o\rangle \tag{2}$$

$$|^3P_2^{o\prime}\rangle = |^3P_2^o\rangle \tag{3}$$

$$|^1P_1^{o\prime}\rangle = \sin\theta_1|^3P_1^o\rangle + \cos\theta_1|^1P_1^o\rangle \tag{4}$$

whereas for p^2 the mixing can be characterized between $^3P_0$ and $^1S_0$ by θ_0 and between $^3P_2$ and $^1D_2$ by θ_2:

$$|^3P_0'\rangle = \cos\theta_0|^3P_0\rangle - \sin\theta_0|^1S_0\rangle \tag{5}$$

$$|^3P_1'\rangle = |^3P_1\rangle \tag{6}$$

$$|^3P_2'\rangle = \cos\theta_2|^3P_2^o\rangle - \sin\theta_2|^1D_2\rangle \tag{7}$$

$$|^1D_2'\rangle = \sin\theta_2|^3P_2^o\rangle + \cos\theta_2|^1D_2\rangle \tag{8}$$

$$|^1S_0'\rangle = \sin\theta_0|^3P_0\rangle + \cos\theta_0|^1S_0\rangle. \tag{9}$$

A formalism has been developed previously [10, 11] by which these mixing angles are first extracted from measured energy level data and then used to predict transition probabilities. For a p^2–sp manifold, the transitions from the upper level sp to the levels of the ground configuration p^2 can be deduced from this formalism using the LS-coupling angular transition matrices [12, 13]. The nonvanishing values are

$$\langle^3P_0^o|r|^3P_1\rangle = -\langle^1P_1^o|r|^1S_0\rangle = \langle^3P_1^o|r|^3P_0\rangle = -\sqrt{20} \tag{10}$$

$$-2\langle^3P_2^o|r|^3P_1\rangle = 2\langle^3P_1^o|r|^3P_2\rangle = \langle^1P_1^o|r|^1D_2\rangle = 10 \tag{11}$$

$$\sqrt{5}\langle^3P_1^o|r|^3P_1\rangle = \langle^3P_2^o|r|^3P_2\rangle = \sqrt{75}. \tag{12}$$

These equations yield, for the upper level $^3P_1^{o\prime}$

$$\langle {}^3P_0'|\boldsymbol{r}|{}^3P_1^{o\prime}\rangle = -\sqrt{20}\cos(\theta_1+\theta_0)\ \langle p^2|r|sp\rangle \tag{13}$$

$$\langle {}^3P_1'|\boldsymbol{r}|{}^3P_1^{o\prime}\rangle = \sqrt{15}\cos\theta_1\ \langle p^2|r|sp\rangle \tag{14}$$

$$\langle {}^3P_2'|\boldsymbol{r}|{}^3P_1^{o\prime}\rangle = 5(2\sin\theta_1\sin\theta_2+\cos\theta_1\cos\theta_2)\ \langle p^2|r|sp\rangle \tag{15}$$

$$\langle {}^1D_2'|\boldsymbol{r}|{}^3P_1^{o\prime}\rangle = -5(2\sin\theta_1\cos\theta_2-\cos\theta_1\sin\theta_2)\ \langle p^2|r|sp\rangle \tag{16}$$

$$\langle {}^1S_0'|\boldsymbol{r}|{}^3P_1^{o\prime}\rangle = -\sqrt{20}\sin(\theta_1+\theta_0)\ \langle p^2|r|sp\rangle \tag{17}$$

for the upper level $^3P_2^{o\prime}$

$$\langle {}^3P_1'|\boldsymbol{r}|{}^3P_2^{o\prime}\rangle = -5\ \langle p^2|r|sp\rangle \tag{18}$$

$$\langle {}^3P_2'|\boldsymbol{r}|{}^3P_2^{o\prime}\rangle = 5\sqrt{3}\cos\theta_2\ \langle p^2|r|sp\rangle \tag{19}$$

$$\langle {}^1D_2'|\boldsymbol{r}|{}^3P_2^{o\prime}\rangle = 5\sqrt{3}\sin\theta_2\ \langle p^2|r|sp\rangle \tag{20}$$

and for the upper level $^1P_1^{o\prime}$

$$\langle {}^3P_0'|\boldsymbol{r}|{}^1P_1^{o\prime}\rangle = -\sqrt{20}\sin(\theta_1+\theta_0)\ \langle p^2|r|sp\rangle \tag{21}$$

$$\langle {}^3P_1'|\boldsymbol{r}|{}^1P_1^{o\prime}\rangle = \sqrt{15}\sin\theta_1\ \langle p^2|r|sp\rangle \tag{22}$$

$$\langle {}^3P_2'|\boldsymbol{r}|{}^1P_1^{o\prime}\rangle = -5(2\cos\theta_1\sin\theta_2-\sin\theta_1\cos\theta_2)\ \langle p^2|r|sp\rangle \tag{23}$$

$$\langle {}^1D_2'|\boldsymbol{r}|{}^1P_1^{o\prime}\rangle = 5(2\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2)\ \langle p^2|r|sp\rangle \tag{24}$$

$$\langle {}^1S_0'|\boldsymbol{r}|{}^1P_1^{o\prime}\rangle = \sqrt{20}\cos(\theta_1+\theta_0)\ \langle p^2|r|sp\rangle. \tag{25}$$

It should be noted that in a fully relativistic Dirac treatment the corresponding expressions will involve two separate jj-coupled radial transition matrices, and reduce to equations (13)–(25) only if these two radial matrices are equal. Theoretical studies of these relativistic corrections have been presented elsewhere [14].

For pure sp and p^2 configurations the energy levels (and thereby the mixing angles) are specified [10] by three parameters (F_0, G_1, ζ_p for sp and F_0, F_2, ζ_{pp} for p^2, in the notation of [13]). Since the sp and p^2 configurations contain four and five levels, respectively, the specification of these three parameters is overdetermined. Here this was treated by using the average energies ε_J of the $J = 0, 1, 2$ levels to make an exactly determined parametrization, computing the singlet–triplet splittings from this parametrization, and then using the deviations as a measure of the validity of the single-configuration picture. Within this framework, the mixing angles θ_J can be determined from the relationships [10]

$$\cot(2\theta_J) = W_J \tag{26}$$

where the sp mixing $J = 1$ level is given by

$$W_1 = [\varepsilon_2 - 3\varepsilon_1 + 2\varepsilon_0]/[\sqrt{2}(\varepsilon_2 - \varepsilon_0)] \tag{27}$$

and the p^2 mixing of the $J = 0$ and $J = 2$ levels is given by

$$W_0 = -[10\varepsilon_2 - 21\varepsilon_1 + 11\varepsilon_0]/[4\sqrt{2}(5\varepsilon_2 - 3\varepsilon_1 - 2\varepsilon_0)] \tag{28}$$

$$W_2 = -[5\varepsilon_2 + 3\varepsilon_1 - 8\varepsilon_0]/[2\sqrt{2}(5\varepsilon_2 - 3\varepsilon_1 - 2\varepsilon_0)]. \tag{29}$$

In terms of the transition elements $\langle k|\boldsymbol{r}|i\rangle$ given by equations (13)–(25), the transition probabilities are obtained from

$$A_{ik}(ns^{-1}) = \tfrac{1}{3}[1265.38/\lambda(\text{Å})]^3\ |\langle k|\boldsymbol{r}|i\rangle|^2 \tag{30}$$

Table 1. Spectroscopic database and intermediate coupling parametrization of energy levels (in cm^{-1}). Sources of spectroscopic data: Si I [15]; Ge I [16]; Sn I [17, 18]; Pb I [19].

Level	E_{obs}	E_{IC}	ΔE	E_{obs}	E_{IC}	ΔE
	Si I			Ge I		
$6p^2\ ^3P'_0$	0	0	0	0	21.8	+21.8
$6p^2\ ^3P_1$	77.115	77.12	0	557.1341	557.1	0
$6p^2\ ^3P'_2$	223.157	255.5	+32.4	1 407.9609	1 369.4	−40.5
$6p^2\ ^1D'_2$	6 298.850	6 266.5	−32.4	7125.2989	7165.8	+40.5
$6p^2\ ^1S'_0$	15 394.370	15 412.1	17.7	16 367.3332	16 345.5	−21.8
$6p7s\ ^3P^o_0$	39 683.163	39 683.2	0	37 451.6893	37 451.7	0
$6p7s\ ^3P^{o\prime}_1$	39 760.285	39 760.3	0	37 702.3054	37 700.9	−1.4
$6p7s\ ^3P^o_2$	39 955.053	39 955.1	0	39 117.9021	39 117.9	0
$6p7s\ ^1P^{o\prime}_1$	40 991.884	40 991.9	0	40 020.5604	40 022.0	+1.4
	Sn I			Pb I		
$6p^2\ ^3P'_0$	0	107.5	+107.5	0	0	0
$6p^2\ ^3P_1$	1 691.806	1 691.8	0	7 819.2626	7 819.3	0
$6p^2\ ^3P'_2$	3 427.673	3 341.0	−86.6	10 650.3217	10 812.3	+161.9
$6p^2\ ^1D'_2$	8 612.955	8 699.6	+86.6	21 457.7982	21 295.9	−161.9
$6p^2\ ^1S'_0$	17 162.6	17 055.1	−107.5	29 466.8303	29 493.9	27.0
$6p7s\ ^3P^o_0$	34 640.76	34 640.8	0	34 959.9084	34 959.9	0
$6p7s\ ^3P^{o\prime}_1$	34 914.28	34 899.6	−14.7	35 287.2244	35 445.9	+158.7
$6p7s\ ^3P^o_2$	38 628.88	38 628.9	0	48 188.6296	48 188.6	0
$6p7s\ ^1P^{o\prime}_1$	39 257.05	39 271.7	+14.7	49 439.6165	49 281.0	−158.7

Table 2. Empirical singlet–triplet mixing angles (in degrees) and empirically deduced Slater parameters (in cm^{-1}).

Ion	θ_1	θ_2	θ_0	$F_0(p^2)$	$F_2(p^2)$	ζ_{pp}	$F_0(sp)$	$G_1(sp)$	ζ_p
Si I	−0.951	1.22	6.01	5 247.7	1016.0	181.1	40 421.4	557.0	181.3
Ge I	−4.38	6.20	21.3	6 081.4	1016.9	879.8	39 139.1	576.6	1110.8
Sn I	−10.2	16.8	29.7	7 333.3	918.6	2096.9	37 750.4	450.8	2658.7
Pb I	−22.2	39.8	32.2	16 074.8	921.9	7292.2	44 568.2	789.2	8819.1

and the branching fractions are defined as

$$BF_{ik} = A_{ik} / \sum_{k'} A_{ik'}. \tag{31}$$

The measured energy level data (obtained from [15–19]) are given in table 1, together with values obtained from the J-averaged IC parametrization and the subtracted differences. The agreement between the observations and the values obtained from the parametrization indicates that the single-configuration approximation is valid. The extracted mixing angles and Slater parameters are given in table 2.

Table 3 presents the branching fractions, computed from equations (13)–(25), by the reduction of the measured transition probabilities of Corliss and Bozman [4], and from other published experimental studies [6–9]. In Si I the agreement between the IC semiempirical values and the high-precision measurements of Smith *et al* [6] is quite striking, and gives additional credence to the single-configuration model for this system. Larger deviations exist

Table 3. Comparison of semiempirical and measured branching fractions (in per cent). SE denotes semiempirical estimates from this work, and CB denotes the measurements of [4]. Other measurements are from [3] for Si I, [7] for Ge I, [8] for Sn I and [9] for Pb I.

	Si I			Ge I			Sn I			Pb I		
Transition	SE	CB	Other	SE	CB	Other	SE	CB	Other	SE	CB	Other
$^3P'_0 \leftarrow {}^3P^{o\prime}_1$	33.3	32	33.3	31.2	29	32.9	31.8	37	55	48.9	15	32
$^3P_1 \leftarrow$	24.7	24	24.7	21.2	27	20.3	17.4	27	13	12.8	11	18
$^3P'_2 \leftarrow$	41.1	40	40.7	38.3	36	36.1	41.0	22	19	38.1	74	49
$^1D'_2 \leftarrow$	0.88	0.4	1.2	8.8	7	10.3	9.3	14	13	0.29	0.5	0.5
$^1S'_0 \leftarrow$	0.06	—	$\leqslant$0.2	0.52	0.6	0.38	0.52	0.3	—	0.01	—	—
$^3P_1 \leftarrow {}^3P^o_2$	25.2	33	24.6	26.4	29	20.3	28.5	30	30	36.0	15	16
$^3P'_2 \leftarrow$	74.8	67	75.4	73.1	69	67.8	67.7	64	62	51.2	37	41
$^1D'_2 \leftarrow$	0.020	—	0.027	0.53	1.4	1.3	3.8	6	9	12.8	48	43
$^3P'_0 \leftarrow {}^1P^{o\prime}_1$	0.24	—	0.3	2.9	7	4.5	4.7	21	10	2.7	1	3
$^3P_1 \leftarrow$	0.25	—	0.2	3.3	6	3.6	6.8	13	4	11.5	11	10
$^3P'_2 \leftarrow$	0.15	—	0.2	1.0	2	1.7	0.03	—	—	24.9	35	25
$^1D'_2 \leftarrow$	92.0	95	93.4	86.2	75	83.2	81.8	60	76	55.2	48	50
$^1S'_0 \leftarrow$	7.4	5	5.7	6.6	10	7.0	6.7	6	—	5.8	6	13

between the semiempirical and measured values for Pb I, but it has been shown [14] that this occurs because of unusually large differences between the two relativistic radial transition integrals caused by fortuitous cancellation effects, and not because of any breakdown in the single-configuration approximation.

The results of [4] generally agree quite well with both the semiempirical estimates and with subsequent experimental measurements. These transitions involve branches with wavelengths from 2000 Å to over 7000 Å so, irrespective of any problems with either the relative or absolute normalization of the transition probabilities in the measurements of Corliss and Bozman [4], the results presented here demonstrate that the photometric intensity calibration was accurate. It is therefore concluded that branching fractions from a common upper level that are deduced from the measurements of [4] can be expected to be reliable to the accuracies indicated in table 3.

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References

[1] Curtis L J 1996 Precision oscillator strength and lifetime measurements *Atomic, Molecular, & Optical Physics Handbook* ed G W F Drake (New York: AIP) pp 206–12
[2] Wiese W L 1987 *Phys. Scr.* **35** 846
[3] Lawler J E, Bergeson S D and Wamsley R C 1993 *Phys. Scr.* T **47** 29
[4] Corliss C H and Bozman W R 1962 *Experimental Transition Probabilities for Spectral Lines of Seventy Elements (NBS Monograph 53)* (Washington, DC: US Govt Printing Office)
[5] Whaling W, Martinez-Garcia M and Mickey D L 1970 *Nucl. Instrum. Methods* **90** 363
[6] Smith P L, Huber M C E, Tozzi G P, Griesinger H E, Cardon B L and Lombardi G G 1987 *Astrophys. J.* **322** 573
[7] Lotrian J, Cariou J, Guern Y and Johannin-Gilles A 1978 *J. Phys. B: At. Mol. Phys.* **11** 2273
[8] Lotrian J, Cariou J and Johannin-Gilles A 1976 *J. Quant. Spectrosc. Radiat Transfer* **16** 315
[9] Lotrian J, Guern Y, Cariou J and Johannin-Gilles A 1979 *J. Quant. Spectrosc. Radiat Transfer* **21** 143

[10] Curtis L J 1989 *Phys. Rev.* A **40** 6958
[11] Henderson M, Curtis L J, Ellis D G, Irving R E and Wahlgren G M 1996 *Astrophys. J.* **473** 565
[12] Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley, CA: University of California Press)
[13] Condon E U and Shortley G H 1935 *The Theory of Atomic Spectra* (Cambridge: Cambridge University Press)
[14] Curtis L J, Ellis D G, Matulioniene R and Brage T 1997 *Phys. Scr.* **56** 240
[15] Martin W C and Zalubas R 1983 *J. Phys. Chem. Data* **12** 323
[16] Sugar J and Musgrove A 1993 *J. Phys. Chem. Data* **22** 1213
[17] Brown C M, Tilford S G and Ginter M L 1977 *J. Opt. Soc. Am.* **67** 607
[18] Moore C E 1957 (Reissued 1971) *Atomic Energy Levels* vol III (NSRDS-NBS 35) (Washington, DC: US Govt Printing Office)
[19] Wood D R and Andrew K L 1968 *J. Opt. Soc. Am.* **58** 818