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LETTER TO THE EDITOR

Intermediate coupling branching fractions for UV transitions in ions of the Si and Ge sequences

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Abstract. The use of lifetime measurements for the specification of transition probabilities along isoelectronic sequences is hindered by the fact that virtually no branching fraction measurements exist for multiply charged ions. Part of the reason for this lies in the lack of calibration standards for intensity as a function of wavelength in the ultraviolet region. It has been shown that transitions of the form ns^2np^2–ns^2npn's in Si I and Ge I are virtually free of configuration interaction, hence their branching fractions can be accurately predicted from intermediate coupling amplitudes deduced from measured spectroscopic energy level data. Reported here is the extension of these semiempirical methods to the ions P II, S III, Cl IV and Ar V in the Si sequence and As II, Se III and Br IV in the Ge sequence. This provides a set of branching fractions that can both specify transition probability rates from lifetime measurements for these ions, and serve as a set of lines of known relative intensities for use in the calibration of detection apparatus in the UV region.

Atomic transition probability rates can be reliably determined without the need for absolute calibration through the combined measurement of relative branching fractions and level lifetimes [1]. These quantities are, in turn, required to deduce elemental abundances from astrophysical spectra, to determine impurity concentrations from fusion plasma spectra, and to make transition by transition comparisons between experiment and theory. When studied along an isoelectronic sequence, transition probability rates can be freed of wavelength dependences by conversion to line strengths. Scaled line strengths have been found to provide predictive interpolative and extrapolative parametrizations through their regular and slowly varying behaviour [2]. This is in contrast to lifetime data, which contain a reciprocal sum of transition probability rates with many different wavelength and nuclear charge dependences producing strong variations that are not isoelectronically regular.

While lifetime measurements now exist which extend along many isoelectronic sequences, the corresponding line strength studies are effectively limited to low-lying unbranched $\Delta n = 0$ transitions, since virtually no branching fraction data exist for multiply charged ions [1]. While there are many difficulties which contribute to the dearth of ionic branching fraction data, one strong limitation lies in the lack of accepted standard lines in the ultraviolet (UV) region for use in the intensity calibration of detection systems as a function of wavelength.

It has been shown earlier [3] that transitions of the form ns^2np^2–$ns^2np(n+1)s$ in neutral Si I, Ge I, Sn I and Pb I are virtually free of configuration interaction (CI), and can thus be semiempirically specified using intermediate coupling (IC) amplitudes obtained from measured spectroscopic energy level data alone. It was also shown [3] that these semiempirical values agree to within narrow tolerances with precision branching fraction measurements that are available for these neutral atoms.

We have therefore extended these semiempirical methods to the ions P II, S III, Cl IV and Ar V in the Si sequence ($n = 3$) and As II, Se III and Br IV in the Ge sequence ($n = 4$).

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This has been done both to test the applicability of the single configuration picture to these ions, and to specify their corresponding branching fractions. The values obtained for these branching fractions provide both a means for deducing transition probability rates from lifetime measurements for these ions, and a set of UV lines of known relative intensities for possible use as calibration standards.

In nominal LS coupling notation, configurations of the form p^2 and sp consist of singlets and triplets which mix due to the effects of IC. However, these particular configurations are particularly simple since neither has more than two levels with the same total angular momentum J, so the normalized mixing amplitudes for each pair can be characterized by a single mixing angle. Thus for the ns^2np^2 ground configuration the $^3P'_0$, $^3P_1$, $^3P'_2$, $^1D'_2$, $^1S'_0$ levels can be characterized by two mixing angles: θ_0, coupling $^3P'_0$ and $^1S'_0$, and θ_2, coupling $^3P'_2$ and $^1D'_2$. Similarly, for the $ns^2npn's$ excited configuration the $^3P_0$, $^3P^{o\prime}_1$, $^3P_2$, $^1P^{o\prime}_1$ levels can be characterized by a single mixing angle, θ_1, coupling $^3P^{o\prime}_1$ and $^1P^{o\prime}_1$. (Primes are attached to the nominal LS spectroscopic symbols for levels in which CI mixing occurs.)

For both of these configurations the IC equations are overdetermined, providing a test of the presence or lack of CI and thus of the corresponding validity of the single configuration model. For both cases the splittings of the levels are determined by just two Slater parameters (F_2 and ζ_{pp} for ns^2np^2, G_1 and ζ_p for $ns^2npn's$), and there are four independent splittings for ns^2np^2 and three independent splittings for $ns^2npn's$. Since both configurations contain three values of J, the number of independent splittings for each is reduced to two if one considers the J-centroid energies. Thus, one effective way to utilize this overdetermination as a test of CI is to (a) reduce the number of independent splittings to two by averaging the singlet and triplet energies of the mixed levels for each J, in terms of which the mixing angles are uniquely specified, then (b) compute the singlet–triplet splittings for each J from these mixing angles to determine the degree to which they reproduce the corresponding measured values. A set of formulae for deducing θ_0, θ_2, θ_1 from the measured J-centroid energies is given in equations (26)–(29) of [3].

In the nonrelativistic 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 wavefunctions alone, which can easily be constructed from the LS wavefunctions and the singlet–triplet mixing angles. For the p^2–sp system this results in the set of trigonometric expressions that are given as equations (10)–(25) of [3]. A relativistic extension of this treatment has also been developed in [5], but it was shown there that these corrections are small except in regions where there are substantial cancellation effects in the radial transition matrix.

The results obtained by this method in [3] are reproduced for Si I and Ge I in table 1, together with two independent sets of high precision measurements. This comparison clearly demonstrates that these branching fractions are very accurately specified from spectroscopic energy level measurements alone. If higher members of these sequences have a similar single configuration nature, then they should be predicted to similar accuracy.

The database of measured energy levels used as inputs to this calculation is given in table 2, together with the bibliographic sources. In cases where a critical compilation from multiple sources is available on the NIST online database [11], those values were used. In the Ge sequence the data were incomplete: values for the $4s^24p5s$ levels are not available above Br IV, and the $4s^24p^2\ ^1S_0$ levels are not connected to the triplet system for Se III and Br IV. However, an accurate measurement for the $^1S_0$ excitation energy in Kr V is available [15], which permitted interpolated values to be obtained for Se III and Br VI. The database was reduced using equations (26)–(29) of [3] to obtain the empirical values for the mixing angles, given in table 3.

Table 1. Comparison of semiempirical and measured branching fractions (in %) for Si I and Ge I. SE denotes the semiempirical estimates of [3]. Expt denotes experimental measurements as cited, with parentheses indicating quoted uncertainties in the last figure.

	Si I			Ge I		
Transition	SE	Expt [6]	Expt [7]	SE	Expt [8]	Expt [9]
$^3P'_0 \leftarrow {}^3P^{o\prime}_1$	33.3	33.3(17)	33.3(3)	31.2	32.5(16)	32.9
$^3P_1 \leftarrow$	24.7	24.7(13)	24.7(4)	21.2	22.1(11)	20.3
$^3P'_2 \leftarrow$	41.1	40.6(21)	40.7(4)	38.3	37.1(19)	36.1
$^1D'_2 \leftarrow$	0.88	1.20(11)	1.2(1)	8.8	8.1(8)	10.3
$^1S'_0 \leftarrow$	0.06	<0.20(6)	<0.20(6)	0.52	0.23(2)	0.38
$^3P_1 \leftarrow {}^3P^o_2$	25.2	24.6(13)	24.6(3)	26.4	27.2(14)	31.0
$^3P'_2 \leftarrow$	74.8	75.4(36)	75.4(3)	73.1	72.1(14)	67.8
$^1D'_2 \leftarrow$	0.020	0.027(4)	0.027(4)	0.53	0.72(7)	1.3
$^3P'_0 \leftarrow {}^1P^{o\prime}_1$	0.24	0.34(3)	0.30(2)	2.9	4.6(5)	4.5
$^3P_1 \leftarrow$	0.25	0.27(3)	0.20(2)	3.3	3.6(4)	3.6
$^3P'_2 \leftarrow$	0.15	0.25(3)	0.20(2)	1.0	1.68(17)	1.7
$^1D'_2 \leftarrow$	92.0	93.4(47)	93.4(2)	86.2	86.1(14)	83.2
$^1S'_0 \leftarrow$	7.4	5.7(3)	5.70(12)	6.6	4.0(4)	7.0

Table 2. Energy level database. Sources of spectroscopic data: P II, [10]; S III, Cl IV, Ar V, [11]; As II, [12]; Se III, [13]; Br IV, [14]. Parentheses denote interpolated values.

Level	P II	S III	Cl IV	Ar V	As II	Se III	Br IV
$^3P'_0$	0	0	0	0	0	0	0
$^3P_1$	164.90	298.69	492.0	765.23	1 063.49	1 741	2 622
$^3P'_2$	469.12	833.08	1 341.9	2 028.80	2 541.35	3 937	5 611
$^1D'_2$	8 882.31	11 322.7	13 767.6	16 298.9	10 095.82	13 032	18 115
$^1S'_0$	21 575.63	27 161.0	32 547.8	37 912.0	22 598.6	(28 482)	(34 017)
$^3P^{o\prime}_0$	86 597.55	146 697.37	215 026.0	295 731	78 730.893	126 276.9	179 993.6
$^3P^{o\prime}_1$	86 743.96	146 737.55	215 389.3	296 227	79 128.33	126 781.4	181 840.0
$^3P^{o\prime}_2$	87 124.60	147 147.11	216 468.1	297 878	81 508.925	130 391.0	185 960.7
$^1P^{o\prime}_1$	88 893.22	148 398.97	219 454	301 291	82 819.214	131 655.9	187 101.6

Table 3. Empirical singlet–triplet mixing angles (in degrees) and percentage errors introduced into the J splittings by the mixing angle formulation.

				% Differences		
Ion	θ_0	θ_2	θ_1	$^1S'_0$–$^3P'_0$	$^1D'_2$–$^3P'_2$	$^1P^{o\prime}_1$–$^3P^{o\prime}_1$
Si I	−0.951	1.221	6.007	+0.12	−1.07	−0.004
P II	−1.259	1.630	6.685	+0.06	−1.06	−0.014
S III	−1.851	2.437	8.193	+0.15	−1.31	−9.54
Cl IV	−2.482	3.236	9.773	+0.21	−1.75	−0.02
Ar V	−3.188	4.358	11.820	+0.27	−2.13	−0.31
Ge I	−4.385	6.198	21.297	−0.27	+1.42	+0.12
As II	−5.622	8.223	22.421	−0.66	+2.34	+0.64
Se III	−6.765	10.203	25.501	−1.32	+3.68	+2.39
Br IV	−8.251	12.924	24.253	−1.46	+3.21	+42.75

To test the validity of the single configuration model, these mixing angles were used to compute the splitting of the mixed-J levels, which can be shown from equations in [3,4] to be (denoting the energy levels by their spectroscopic symbols)

$$^1S'_0 - ^3P'_0 = \sqrt{1 + \cot^2(2\theta_0)}\; 2\sqrt{2}\zeta_{pp} \tag{1}$$

$$^1D'_2 - ^3P'_2 = \sqrt{1 + \cot^2(2\theta_2)}\; \sqrt{2}\zeta_{pp} \tag{2}$$

$$^1P'_1 - ^3P'_1 = \sqrt{1 + \cot^2(2\theta_1)}\; \sqrt{2}\zeta_{p} \tag{3}$$

where ζ_{pp} and ζ_p are obtained from the J centroid energies using equations (16) and (8) of [4]. Values for these splittings were computed from the values of θ_0, θ_2, θ_1 given in table 3 using equations (1)–(3) above, and were then compared with the measured energy levels. The percentage differences between the calculated and measured values are also given in table 3. With the exception of the $^1P_1$–$^3P_1$ interval in Br IV, all splittings are very well described by the single configuration model. (It should be noted that the early analysis of Br IV [16] was completely revised by Joshi and Bhadiraja in 1971 [14], and the isoelectronic inconsistency noted here suggests the need for further study of the $4s^24p5s$ levels.)

With this confirmation of the validity of the single configuration model to characterize these transitions, the empirical mixing angle values in table 3 were combined with the transition rate formulae in equations (10)–(25) of [3] to compute the desired branching fractions. Table 4 presents the branching fractions for P II, S III, Cl IV and Ar V in the Si sequence. Table 5 presents the corresponding quantities for As II, Se III and Br IV in the Ge sequence. Since these results involve an extrapolation to systems for which no experimental data currently exist, they should be used with some degree of caution. However, this very lack of measured data, coupled with the success of the method in describing the neutral counterparts and the challenges to *ab initio* theory presented by these complex systems, certainly justifies the use of these results in current physical applications.

These results could be of use in obtaining branching fractions from fast ion beam excitation methods. An intensity calibration of the detection apparatus as a function of wavelength presents special problems for in-beam studies, since there are Doppler broadenings and

Table 4. Transition wavelengths and semiempirical branching fractions (BF, in %) for ions in the Si sequence.

	P II		S III		Cl IV		Ar V	
Transition	λ (Å)	BF	λ (Å)	BF	λ (Å)	BF	λ (Å)	BF
$^3P'_0 \leftarrow ^3P^{o\prime}_1$	1115.82	33.1	681.49	32.8	464.28	32.4	337.58	31.9
$^3P_1 \leftarrow$	1155.01	24.5	682.88	24.2	465.34	23.8	338.45	23.2
$^3P'_2 \leftarrow$	1158.82	41.0	685.38	40.8	467.19	40.7	339.91	40.5
$^1D'_2 \leftarrow$	1284.33	1.3	784.47	1.9	495.98	2.7	357.24	3.8
$^1S'_0 \leftarrow$	1534.49	0.12	836.28	0.22	546.92	0.32	387.12	0.49
$^3P_1 \leftarrow ^3P^o_2$	1149.96	25.2	680.97	25.2	463.01	25.2	336.57	25.3
$^3P'_2 \leftarrow$	1153.73	74.8	683.46	74.7	464.84	74.6	338.01	74.4
$^1D'_2 \leftarrow$	1278.08	$<10^{-3}$	736.25	0.11	493.34	0.21	355.14	0.37
$^3P'_0 \leftarrow ^1P^{o\prime}_1$	1124.95	0.22	673.86	0.27	455.68	0.34	331.91	0.47
$^3P_1 \leftarrow$	1127.04	0.25	675.22	0.34	456.70	0.46	332.75	0.65
$^3P'_2 \leftarrow$	1130.66	0.11	677.66	$<10^{-3}$	458.48	$<10^{-3}$	334.16	$<10^{-3}$
$^1D'_2 \leftarrow$	1249.83	88.8	729.52	87.2	486.18	86.1	350.89	85.2
$^1S'_0 \leftarrow$	1485.50	10.6	824.82	12.1	535.03	13.0	379.68	13.6

Table 5. Transition wavelengths and semiempirical branching fractions (in %) for ions in the Ge sequence.

	As II		Se III		Br IV	
Transition	λ (Å)	BF	λ (Å)	BF	λ (Å)	BF
$^3P'_0 \leftarrow {}^3P^{o\prime}_1$	1263.77	29.8	788.76	28.1	549.93	28.8
$^3P_1 \leftarrow$	1280.99	20.0	799.74	18.4	557.98	18.6
$^3P'_2 \leftarrow$	1305.70	38.7	814.04	38.6	567.45	40.8
$^1D'_2 \leftarrow$	1448.59	10.5	879.13	13.4	603.68	10.5
$^1S'_0 \leftarrow$	1768.98	0.99	1017.30	1.5	676.48	1.3
$^3P_1 \leftarrow {}^3P^o_2$	1243.08	26.2	777.30	26.1	545.44	26.1
$^3P'_2 \leftarrow$	1266.34	72.7	790.80	72.0	554.48	70.8
$^1D'_2 \leftarrow$	1400.30	1.1	852.09	1.87	589.03	3.1
$^3P'_0 \leftarrow {}^1P^{o\prime}_1$	1207.45	2.34	759.56	2.70	534.47	1.9
$^3P_1 \leftarrow$	1223.16	2.95	769.74	3.50	542.07	3.0
$^3P'_2 \leftarrow$	1245.67	0.41	782.97	0.32	551.00	$<10^{-5}$
$^1D'_2 \leftarrow$	1375.07	84.4	843.00	82.2	585.08	82.6
$^1S'_0 \leftarrow$	1660.56	9.90	968.24	11.3	663.23	12.6

shifts, polarizations due to anisotropic excitation, wavelengths not amenable to reflective and transmissive optical elements, differential downstream decays and repopulations of the levels, etc. Thus the use of a lab-fixed standard lamp is not particularly suitable for an intensity versus wavelength calibration of a detection system that views a moving beam. However, the use of an in-beam ionic standard such as the systems reported here could eliminate some of these problems. The ionic beam used for calibration could be tuned to the same velocity as that of the ion beam to be studied, thus providing a standard with the same Doppler shifts and the same range of intensities as the ion beam to be studied.

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