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RELATIVISTIC AND CANCELLATION EFFECTS IN THE LINE STRENGTH RATIOS OF THE ALUMINIUM GROUP ELEMENTS SPECTRA*

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Results of calculations for relativistic line strength ratios in the spectra of aluminium group elements are given and compared with the available experimental and other theoretical data. The radial integrals were computed by employing the wave functions obtained from a semiempirical approach that included exchange effects. The influence of the spin-orbit interaction as well as of the cancellation of the positive and negative contribution in the radial transition integral on the line strengths is presented and discussed.

1. Introduction

The rapid development of "beam-foil" technique and its application to the measurements of lifetimes of atoms or ions in excited states increased considerably the amount of available experimental lifetime data. These data permit the extraction of experimental absolute oscillator strengths provided the experimental or theoretical branching ratios are known. Thus a strong need exists for accurate knowledge of theoretical branching ratios or more precisely speeking: for the line strength ratios. The aim of this study is to demonstrate, using the group spectra of aluminium as an example, those effects that are of great importance for precise line strength ratio calculations. The simplest way to evaluate the line strength ratios is to include only the Coulomb and exchange interaction in the Schrödinger equation and to assume that the radial integral remains constant within the multiplet. Under this assumption the line strength ratios can be evaluated from the angular parts of transition integrals only. Values obtained in this way are frequently called statistical ratios. However, experimental numeral investigations [6, 13–14, 16–18], exhibited that the values of line strength ratios in the sharp and principle series of the aluminium group spectra differ from the statistical ratio's value of 2. Analogous deviations observed

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in the alkali metal spectra were ascribed by Fermi [2] to the spin-orbit interaction for the optical electron. Nevertheless, a simple extension of the Fermi method to the case of the spectral series of aluminium group elements by Hanus [4] and Lubowiecka [7] led to results incompatible with the experimental data, particularly for the sharp series. Nowadays it is possible to perform computations of line strength ratios that much more precisely account for the spin-orbit interaction.

2. Calculations

The relativistic line strength ratios were computed by employing the following formula [15]:

$$S(nlj-n'l'j') = (2j+1)(2j'+1)W^2(ljl'j';\tfrac{1}{2}1)l_{\max}|R^{n'l'j'}_{nlj}|^2,$$

where

$$R^{n'l'j'}_{nlj} = \int_0^\infty [P_{nlj}(r)P_{n'l'j'}(r)+Q_{nlj}(r)Q_{n'l'j'}(r)]rdr.$$

$P(r)$, $Q(r)$ are large and small components of the relativistic wave function,

$$l_{\max} = \max(l, l'),$$

and W is the Racah coefficient.

To evaluate the magnitude of cancellation in the transition integral the coefficient φ was computed for each transition.

$$\varphi = \begin{cases} x & \text{if } x \leqslant 1 \\ x^{-1} & \text{if } x > 1, \end{cases}$$

where x is the ratio of positive to negative contributions in the radial integral.

To determine the relativistic wave functions, the Dirac homogeneous equations were numerically solved with the effective potential as follows:

$$V(r) = -\frac{Z}{r} + \frac{1}{r}\int_0^r \varrho^c(r_1)dr_1 + \int_r^\infty \frac{\varrho^c(r_1)}{r_1}dr_1 + V_{\text{exch}}(r)$$

$$V_{\text{exch}}(r) = -\frac{\lambda}{r}\left[\frac{81r\varrho^c(r)}{32\pi^2}\right]^{1/3}, \qquad \varrho^c(r) = \sum_\gamma N_\gamma[P^2_\gamma(r)+Q^2_\gamma(r)], \qquad \gamma = (nlj).$$

N is a number of electrons in the γ shell of the core. The exchange potential used was similar to that of Slater but the electron radial density of the core $\varrho^c(r)$ was employed in the electrostatic and exchange part of the potential. So there is no need for Latter's correction. The λ parameter in the exchange part of the potential was adjusted to fit the eigenvalues of Dirac equations to the experimental values of ionization energy of an atom. Experimental ionization energies were taken from Erikson and Isberg [1] for Al I, from Johansson and Litzen [5] for Ga I and In I and from Moore's tables [12] for Tl I. This

adjustment was performed for each (nlj) state. The data required to construct the electron radial density $\varrho^c(r)$ were taken from the simplified SCF calculations of Gombas and Szondy [3]. These computations are essentially the same as described in [10]. However, there are non important differences in the resulting line strengths ratios due to the fact that the Rydberg constant for the motionless nucleus was used in the present study ($R_\infty = 109737.6\ \mathrm{cm}^{-1}$) instead of the measured value ($R_M = 109677.8\ \mathrm{cm}^{-1}$) employed by the author in [10].

3. *Results and conclusions*

The relativistic line strength ratios computed in the present study are shown in Tables I–IV together with results obtained by Hanus [4] and Lubowiecka [7]. The values of φ and ζ_{nl} coefficients are also included. This last coefficient represents the magnitude of the spin-orbit interaction.

$$\zeta_{nl} = \frac{2\Delta E_{nlj}}{2l+1},$$

where ΔE_{nlj} is a fine structure splitting.

In Figs 1 and 2 the behaviour of theoretical line strengths ratios along the sharp and principal series are presented (n^* is the effective main quantum number of the upper

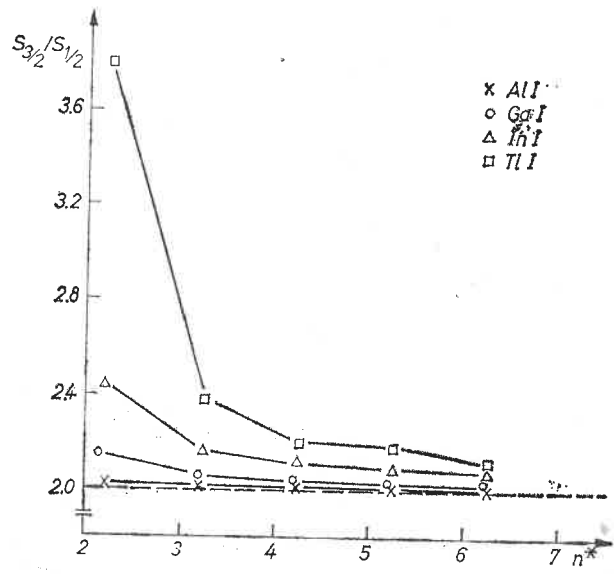

Fig. 1. The behaviour of relativistic line strengths ratios along the sharp series in Al I, Ga I, In I and Tl I spectra

state). The results obtained for the sharp and principal series of Al, I, Ga I, In I and Tl I spectra confirm fairly the experimentally observed deviations in the line strength ratios. The largest deviations exist in the spectra of the heavy atoms, In I and Tl I, particularly

for the first doublet of the sharp series and for the higher doublets of the principal series. For light atoms, like Al I, the deviations are negligibly small for all the transitions in both series.

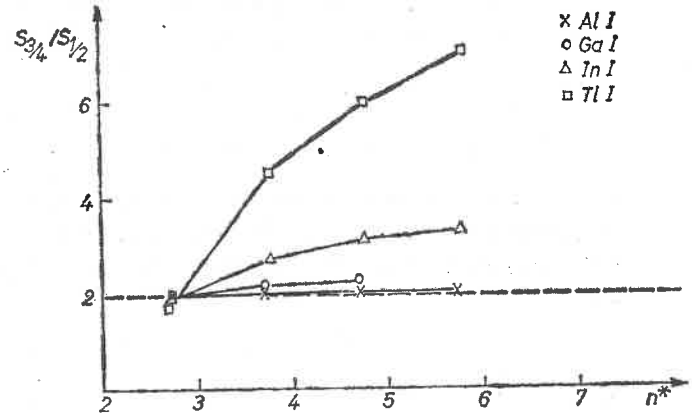

Fig. 2. The behaviour of relativistic line strengths ratios along the principal series in Al I, Ga I, In I and Tl I spectra

TABLE I

Al I

Transition	Line strengths ratios			φ_j [%]	ζ_{nl} [cm^{-1}]
	Q-rel. [a]	Rel. [b]	Experiment		
Sharp series					
$3p\,^2P^0_{1/2,\,3/2}$ — $4s\,^2S_{1/2}$	1.97	2.021	2.01[c], 2.0±0.3[d]	12.0, 11.9	
— $5s\,^2S_{1/2}$	1.82	2.023	0.10[c], 2.0±0.3[d], 2.03±0.03[c]	34.4, 34.1	
— $6s\,^2S_{1/2}$	1.64	2.017		40.3, 40.3	74.6
— $7s\,^2S_{1/2}$	1.45	2.013		42.9, 42.9	
— $8s\,^2S_{1/2}$	1.51	2.011		44.2, 44.2	
— $9s\,^2S_{1/2}$		2.010		44.8, 44.8	
— $10s\,^2S_{1/2}$		2.010		44.8, 44.8	
Principal series					
$4s\,^2S_{1/2}$ — $4p\,^2P^0_{1/2,\,3/2}$	2.00	1.998		0.3, 0.3	10.5
— $5p\,^2P^0_{1/2,\,3/2}$	2.04	2.039		65.6, 65.3	4.0
— $6p\,^2P^0_{1/2,\,3/2}$	2.07	2.056		77.3, 77.0	1.9
— $7p\,^2P^0_{1/2,\,3/2}$	2.12	2.064		81.6, 81.3	1.0

[a] Hanus [4]; [b] present study; [c] Kunisz [6]; [d] Voorhoeve [17].

TABLE II

Ga I

Transition	Line strengths ratios			φ_j [%]	ζ_{nl} [cm^{-1}]
	Q-rel. [a]	Rel. [b]	Experiment [c]		
Sharp series					
$4p\,^2P^0_{1/2,\,3/2}$ — $5s\,^2S_{1/2}$		2.150	2.15	10.6, 10.0	
— $6s\,^2S_{1/2}$	1.06	2.046	2.04	34.5, 35.2	
— $7s\,^2S_{1/2}$	0.57	2.031	1.89	40.8, 41.5	
— $8s\,^2S_{1/2}$	0.62	2.027	1.88	43.5, 44.0	550.6
— $9s\,^2S_{1/2}$		2.025		44.8, 45.5	
— $10s\,^2S_{1/2}$		2.024		45.5, 46.3	
— $11s\,^2S_{1/2}$		2.024		45.9, 46.7	
Principal series					
$5s\,^2S_{1/2}$ — $5p\,^2P^0_{1/2,\,3/2}$		1.980		0.4, 0.5	74.0
— $6p\,^2P^0_{1/2,\,3/2}$		2.217		59.9, 58.1	27.4
— $7p\,^2P^0_{1/2,\,3/2}$		2.305		71.3, 69.5	13.2

[a] Lubowiecka [7]; [b] present study; [c] Penkin and Shabanova [14].

TABLE III

In I

Transition	Line strengths ratios			φ_j [%]	ζ_{nl} [cm^{-1}]
	Q-rel. [a]	Rel. [b]	Experiment		
Sharp series					
$5p\,^2P^0_{1/2,\,3/2}$ — $6s\,^2S_{1/2}$	1.52	2.453	2.40[d], 2.44 ± 0.04[c], 2.35 ± 0.09[e]	12.2, 10.5	
$7s\,^2S_{2/i}$	0.33	2.156	2.13[d]	34.8, 36.1	
$8s\,^2S_{1/2}$	0.04	2.103	2.12[d]	41.0, 42.7	
$9s\,^2S_{1/2}$	0.001	2.084	2.00[d]	43.7, 45.5	1475.1
$10s\,^2S_{1/2}$		2.075		45.0, 46.7	
$11s\,^2S_{1/2}$		2.069		45.9, 47.6	
— $12s\,^2S_{1/2}$		2.066		46.3, 48.1	
Principal series					
$6s\,^2S_{1/2}$ — $6p\,^2P^0_{1/2,\,3/2}$	2.00	1.945		0.4, 0.5	198.8
— $7p\,^2P^0_{9/2,\,3/2}$	2.95	2.763	2.52 ± 0.3 [c]	64.4, 58.9	74.4
— $8p\,^2P^0_{1/2,\,3/2}$	3.57	3.130	3.3 ± 0.1 [c]	75.6, 70.1	36.2
— $9p\,^2P^0_{1/2,\,3/2}$	3.61	3.337	4.0 ± 0.5 [c]	79.9, 74.6	20.4

[a] Hanus [4]; [b] present study; [c] Kunisz [6]; [d] Penkin and Shabanova [14]; [e] Payne-Scott [13].

TABLE IV

Tl I

Transition	Line strengths ratios			φ_j [%]	ζ_{nl} [cm^{-1}]
	Q-rel. [a]	Rel. [b]	Experiment		
Sharp series					
$6p\,^2P^0_{1/2,\,3/2}$ — $7s\,^2S_{1/2}$	0.91	3.809	3.20 [d], 2.57 ± 0.03 [e]	11.6, 7.1	
— $8s\,^2S_{1/2}$	0.02	2.339	1.94 [d]	31.3, 38.2	
— $9s\,^2S_{1/2}$	0.10	2.165	1.90 [d]	37.3, 45.0	
— $10s\,^2S_{1/2}$	0.20	2.165		39.2, 46.5	5195.2
— $11s\,^2S_{1/2}$		2.093		41.2, 49.0	
— $12s\,^2S_{1/2}$		2.094		41.8, 49.5	
— $13s\,^2S_{1/2}$		2.094		42.2, 50.0	
Principal series					
$7s\,^2S_{1/2}$ — $7p\,^2P^0_{1/2,\,3/2}$	2.01	1.790		0,3. 1.0	667.4
— $8p\,^2P^0_{1/2,\,3/2}$	6.45	4.516	4.5 ± 0.44 [e], 4.4 [f]	62.9, 47.1	248.5
— $9p\,^2P^0_{1/2,\,3/2}$	11.7	5.993	5.8 ± 2 [c], 5.7 ± 0.92 [e], 6.6 ± 0.25 [f]	74.1, 57.9	121.2
— $10p\,^2P^0_{1/2,\,3/2}$	17.5	7.067	6.4 [e], 6.0 ± 0.2 [f]	78.5, 62.3	69.6

[a] Hanus [4]; [b] present study; [c] Kunisz [6]; [d] Penkin and Shabanova [14]; [e] Voonwiller [16]; [f] Williams and Herlihy [18].

It may be deduced from the analysis of calculated line strength ratios, fine structure splittings of the upper or lower state and ratios of the positive to negative contributions in the radial integral that the observed deviations are due to the superposition of the spin-orbit interaction for the optical electron and mutual cancellation of the contributions with opposite signs in the radial integral. The superposition of these two effects permits the explanation of the characteristic behaviour of the line strength ratios along the spectral series and the strong increase in deviations for corresponding transitions in the various atoms with increasing atomic Z value. The last variation is almost entirely due to the influence of spin-orbit interaction as the cancellation effects barely change with Z for the homologous atoms. The same effect is mostly responsible also for the values of line strength ratios and their behaviour in the sharp series where cancellation is rather moderate (30—40%). For the first doublet it is about 10%. For the principal series, however, the cancellation is very strong (except for the first doublet of the series) and reaches 70—80% for higher transitions. This strong cancellation reflects the rapid decrease in the probabilities of electron transitions from higher p-states. Because of almost complete cancellation, the line strengths ratio is extremely sensitive, even to the weak influence of the spin-orbit interaction, what results in large deviations in this case. The growth of cancellation along the principal series results in an increase in line strength ratio deviations despite the decreasing influence of relativistic effects. Thus the existence of strong cancellation amplifies the influence of the spin-orbit interaction on the line strength ratios.

A question now arises why did the Hanus [4] and Lubowiecka [7] calculations fail to yield results in good agreement with experiment. The first two reasons are obvious. The zero-order wave functions obtained in the Coulomb approximation as well as the estimation of the matrix element of the perturbing spin-orbit hamiltonian originally introduced by Fermi [2] are only very rough approximations. However, the reasons mentioned above do not explain the complete failure of this approach for the sharp series of spectra. Moreover, the author had performed earlier the perturbational calculations [8] where more reliable zero-order wave functions, obtained by the linear core deformation method, were used and the matrix element of the spin-orbit hamiltonian was directly evaluated. These computations, though significantly improved agreement with experiment over those of Hanus [4] and Lubowiecka [7], still overestimated the influence of the spin-orbit interaction particularly for the sharp series. A similar effect was observed in the theoretical line strength ratios for the spectra of singly ionized silicon group elements [9, 11]. The overestimation of the spin-orbit influence for higher transitions of the sharp series as well as other perturbations in calculated line strength ratios are due to the poor convergence of the series expansion of the quasi-relativistic radial integral $\tilde{R}^{n'l'j'}_{nlj}$ in terms of non-relativistic radial integrals $R^{n'l'}_{nl}$. The quasi-relativistic radial integral for the transition between $(\bar{n}s\bar{j})$ and (npj) states may be represented as

$$\tilde{R}^{npj}_{ns\bar{j}} = R^{np}_{ns} + \sum_{n' \neq n} c^{j}_{n'p} R^{n'p}_{ns},$$

where

$$\tilde{R}^{n'l'j'}_{nlj} = \int_0^\infty P_{nlj} P_{n'l'j'} r dr,$$

$$R^{n'l'}_{nl} = \int_0^\infty P_{nl} P_{n'l'} r dr.$$

In the case of the sharp series ($\bar{n} > n$) the zero-order radial integrals $R^{np}_{n\bar{s}}$ are for the higher transitions of the series, much lower than the radial integrals $R^{n'p}_{n\bar{s}}$ with $n' \geqslant \bar{n}$ (corresponding to the principal series transition), which can occur in the higher terms of the expansion. Therefore, the convergence of the $\tilde{R}^{n'l'j'}_{nlj}$ expansion for higher transitions of the sharp series is usually very poor. Thus, the superiority of the approach, in which the wave functions for the (nlj) states and consequently the line strength ratios are determined directly from the Dirac equation, is clearly apparent.

Finally it may be concluded that though the influence of the spin-orbit interaction for the optical electron is the direct reason for the existence of deviations in the line strength ratios, the resulting deviation depends not only on the magnitude of this interaction but also on the degree of cancellation in the radial integral.

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