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PROPERTIES OF THE OSCILLATOR STRENGTHS OF Cu I AND Ag I SPECTRAL LINES*

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Abstract: Using the Coulomb approximation, transition probabilities were calculated for twenty lines of the sharp and diffuse series of neutral copper and silver atoms. The logarithm of the line strength is found to be proportional to the inverse of the principal quantum number of the upper level. The oscillator strengths of the higher members in the series are proportional to the inverse cube of the effective quantum number of the upper levels of the relevant transitions. Available experimental data were used for comparison.

1. Introduction

Transition probabilities of the spectral lines of metal atoms are not sufficiently known[1] because of experimental difficulties. This is the case, in particular, for copper and silver atoms. However, in recent years, more information on the transition probabilities of spectral lines of copper has become available[2,3] while, for silver, the transition probabilities are still largely unknown[4].

In calculating the transition probabilities, one may choose among several approximate methods. The quickest and simplest seems to be the Coulomb approximation of Bates and Damgaard[5], which can be successfully applied to moderately or highly excited lines[6] and, especially, to spectral lines originating in what is called the alkali part of the term diagram of copper and silver atoms. As will be shown bellow, theoretical oscillator strengths, calculated using the Coulomb approximation, exhibit some interesting properties which are generally in accordance with both experimental and detailed theoretical results.

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Table 1

Transition probabilities of Cu I spectral lines calculated in the LS-Coupling-Coulomb approximation.

λ (Å)	Transition	gA (10^8 s^{-1})			
		This work C. A.	K. R.[5]	C. B.[7]	A. A.[3]
8092	$4p\,^2P^o_{3/2} - 5s\,^2S_{1/2}$	0.51	—	2.6	—
7933	$4p\,^2P^o_{1/2} - 5s\,^2S_{1/2}$	0.27	—	1.3	—
5220	$4p\,^2P^o_{3/2} - 4d\,^2D_{3/2}$	0.54	0.6	0.95	—
5218	$4p\,^2P^o_{3/2} - 4d\,^2D_{5/2}$	4.83	4.5	5.8	—
5153	$4p\,^2P^o_{1/2} - 4d\,^2D_{3/2}$	2.69	2.4	4.7	—
4530	$4p\ P - 6s\ S$	0.14	0.17	0.65	—
4480	$4p\ P - 6s\ S$	0.07	0.06	—	0.098
4063	$4p\ P - 5d\ D$	0.2	—	—	—
4062	$4p\ P - 5d\ D$	1.77	1.26	—	—
4022	$4p\ P - 5d\ D$	1.0	0.76	0.77	—
3861	$4p\ P - 7s\ S$	0.062	—	—	—
3825	$4p\ P - 7s\ S$	0.032	—	—	0.064
3687	$4p\ P - 6d\ D$	0.095	—	—	—
3687	$4p\ P - 6d\ D$	0.86	—	—	0.74
3654	$4p\ P - 6d\ D$	0.48	—	—	—
3598	$4p\ P - 8s\ S$	0.031	—	—	—
3566	$4p\ P - 8s\ S$	0.016	—	—	0.026
3512	$4p\ P - 7d\ D$	0.05	—	—	—
3512	$4p\ P - 7d\ D$	0.49	—	—	—
3481	$4p\ P - 7d\ D$	0.28	—	—	0.38

2. Transition probabilities

Transition probabilities are closely connected with the knowledge of the matrix elements of the dipole moment of the radiating electron. Supposing that this (outer) electron is under the influence of a potential which has central symmetry, then the angular part of the relevant matrix element is

Table 2

Transition probabilities of Ag I spectral lines calculated in the LS-Coupling-Coulomb approximation.

λ (Å)	Transition	gA (10^8 s^{-1})		
		This work C. A.	T. S.[9]	C. B.[9]
8273	$5p\ ^2P^o_{3/2} - 6s\ ^2S_{1/2}$	0.5	0.27	2.3
7687	$5p\ ^2P^o_{1/2} - 6s\ ^2S_{1/2}$	0.27	0.17	1.4
5471	$5p\ ^2P^o_{3/2} - 5d\ ^2D_{3/2}$	0.52	0.46	1.6
5465	$5p\ ^2P^o_{3/2} - 5d\ ^2D_{5/2}$	4.66	4.1	16
5209	$5p\ ^2P^o_{1/2} - 5d\ ^2D_{3/2}$	2.68	2.48	15
4668	$5p\ P - 7s\ S$	0.14	0.22	1.4
4476	$5p\ P - 7s\ S$	0.07	0.11	1.1
4212	$5p\ P - 6d\ D$	0.18	—	—
4210	$5p\ P - 6d\ D$	1.65	1.1	2.6
4055	$5p\ P - 6d\ D$	0.97	0.6	—
3981*	$5p\ P - 8s\ S$	0.062*	0.062*	—
3841	$5p\ P - 8s\ S$	0.034	0.034	—
3811	$5p\ P - 7d\ D$	0.09		—
3810	$5p\ P - 7d\ D$	0.8	0.52	—
3682	$5p\ P - 7d\ D$	0.48	0.3	—
3709	$5p\ P - 9s\ S$	0.032	0.03	—
3586	$5p\ P - 9s\ S$	0.018	0.015	—
3624	$5p\ P - 8d\ D$	0.05	—	—
3624	$5p\ P - 8d\ D$	0.45	0.25	—
3508	$5p\ P - 8d\ D$	0.27	0.13	—

easily calculated in an LS-coupling scheme, while the radial part has to be numerically computed with approximate radial wave functions. The transition probability is usually expressed in terms of the absorption oscillator strength, a dimensionless quantity, by the following relation

$$g_n' A_{nn'} = \frac{2 e^2 \omega^2}{m c^3} g_n f_{n'n}, \qquad (1)$$

where $A_{nn'}$ is the transition probability from the level n' to n, ω the angular frequency of the transition, g_n and $g_{n'}$ are the statistical weights of the lower and upper levels, and $f_{n'n}$ is the absorption oscillator strength. When there is only one electron above closed shell, oscillator strength is explicitly given in the LS-coupling scheme by the relation[7]

$$f_{n'n} = \frac{4\pi a_0}{3\alpha\lambda}(2J'+1)\,W^2(LJL'J';\ \tfrac{1}{2}1)\,l_>\,(4l_>+1)\,\sigma^2. \tag{2}$$

Here a_0 is the Bohr radius, α the fine structure constant, and λ the wavelength of the spectral line; $2J'+1$ is the statistical weight of the upper level. $W(LJL'J';\ \frac{1}{2}1)$ denotes the Racah coeficient, J is the total angular momentum, L the total orbital momentum (letters with indices correspond to the upper level), $l_>$ is the larger of the two orbital angular momenta of the jumping electron, and σ^2 is the square of the radial part of the matrix element (in atomic units)

$$\sigma^2 = \frac{1}{4l_>^2 - 1}\left[\int R_{n^*l}\, r\, R_{n^{*\prime}l'}\, r^2\, \mathrm{d}\, r\right]^2. \tag{3}$$

This relation can be obtained by means of linear interpolation from the tables of Bates and Damgaard[5]. R_{n^*l} is the radial wave function in the Coulomb approximation. In order to obtain σ^2, one has to know l, l' the orbital quantum numbers of the jumping electron, and the effective principal quantum numbers of the levels involved in the transition, which are defined by

$$n_l^* = \frac{1}{\sqrt{-2E_{nl}}}. \tag{4}$$

Here E_{nl} is the binding energy of the jumping electron (in atomic units).

In general, it may be stated that if two different atoms from the same column in the periodic system have almost identical term structures, then their transition probabilities of analogous transitions will be almost identical, provided the calculations are made by use of the Coulomb approximation. This condition practically holds for copper and silver atoms if we restrict our calculations to the alkali part of their energy diagrams, where a single electron is jumping above the closed d-shell.

Inspection of the observed Lande factors[8] indicates that the LS-coupling scheme is a good approximation for the alkali part of copper and silver atoms. Therefore, a comparison of the calculated transition probabilities with experimental values can serve as a direct check of the Coulomb approximation.

The transition probabilities of the sharp and diffuse series for twenty lines of copper and silver are given in Tables 1 and 2. For the comparison of copper transition probabilities, three sets of experimental values were chosen[2, 3, 9]. The transition probabilities measured by Kock and Richter[2]

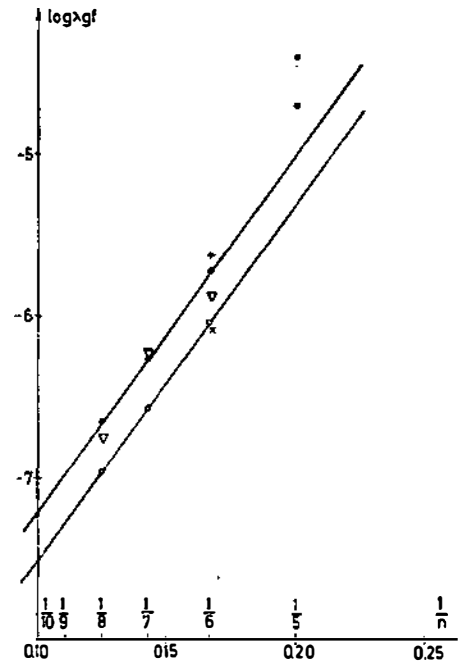

Fig. 1. Logarithm of $\lambda g f$ for the sharp series of Cu I as a function of the inverse principal quantum number.
Coulomb approximation: ● $4p\,^2P^\circ_{3/2} - n s\,^2S_{1/2}$,
○ $4p\,^2P^\circ_{1/2} - n s\,^2S_{1/2}$. Experimental points:
+ $4p\,^2P^\circ_{3/2} - 6s\,^2S_{1/2}$ and × $4p\,^2P^\circ_{1/2} - 6s\,^2S_{1/2}$ from Kock and Richter[2],
▽ $4p\,^2P^\circ_{1/2} - n s\,^2S_{1/2}$ from Allen and Asaad[3].

seem preferable because they used a well-defined plasma source in which thermal equilibrium for copper atoms was established. Although there are only a few lines that can be compared with theoretical values, the comparison is more than satisfactory, which proves the validity of the Coulomb approximation for copper spectral lines. The experimental values of Corliss and Bozman[9] are less accurate. At best, they differ from the calculated values by a factor two or a little less. Recently, Corliss[3] has published a review of Cu I oscillator strengths which corrects previously published data[9] according to the temperature obtained with the help of the transition probabilities measured by Kock and Richter[2]. For the comparison of transitions from

higher levels, we take from this review[3] only the corrected values of the transition probabilities of five appropriate lines measured by Allen and Asaad[10].

For infrared lines of both copper and silver atoms, the Coulomb approximation ceases to be fully valid because both the upper and lower levels are rather low in the energy diagram. For all lines of the sharp series, small extrapolations of the tables[5] were made.

In the case of silver, a comparison with the relative transition probabilities measured by Terpstra and Smit[4] can be made along the whole series of the given spectral lines. Their values were put on the absolute scale with the calulated value of the 3981 Å line (marked by an asterisk in Table 2). Agreement is better than within a factor of two; in several cases, the comparison is quite satisfactory. The absolute experimental values of Corliss and Bozman[9] for silver sometimes differ by an order of magnitude. This disagreement may be attributed to the unknown inhomogeneous structure of their plasma source and to the lack of thermal equilibrium among the atoms of the added elements[11].

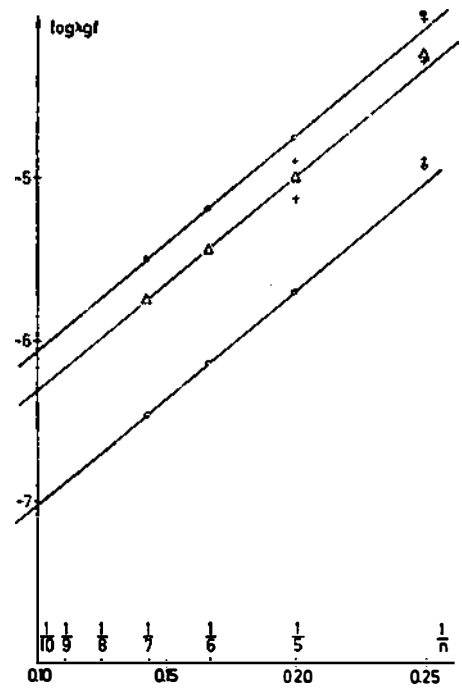

Fig. 2. Logarithm of $\lambda g f$ for the diffuse series of Cu I as a function of the inverse principal quantum number.
Coulomb approximation: ● $4p\,^2P^\circ_{3/2} - n\,d\,^2D_{5/2}$,
△ $4p\,^2P^\circ_{1/2} - n\,d\,^2D_{3/2}$, ○ $4p\,^2P^\circ_{3/2} - n\,d\,^2D_{3/2}$. Experimental points:
+ from Kock and Richter[5].

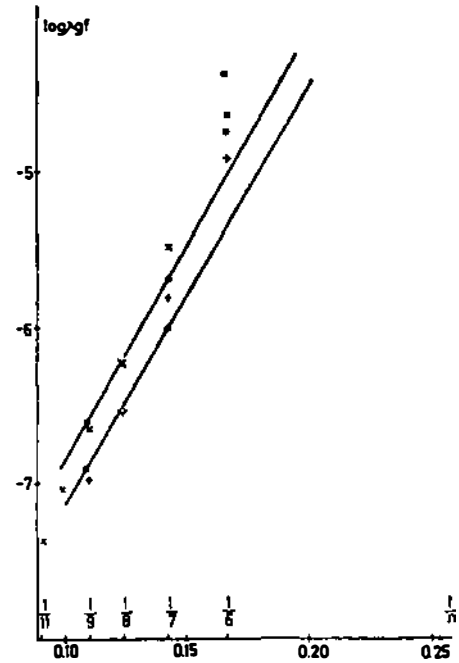

Fig. 3. Logarithm of $\lambda g f$ for the sharp series of Ag I as a function of the inverse principal quantum number. Coulomb approximation: ● $5p\,^2P_{3/2} - n\,s\,^2S_{1/2}$, ○ $5p\,^2P^\circ_{1/2} - n\,s\,^2S_{1/2}$. Experimental points: × $5p\,^2P^\circ_{3/2} - n\,s\,^2S_{1/2}$ and + $5p\,^2P^\circ_{1/2} - n\,s\,^2S_{1/2}$ from Terpstra and Smit[4].

3. *Properties of the line strengths*

The paper of Terpstra and Smit[4] includes two interesting diagrams which show that $\log \lambda^3 g A$ for both the sharp and diffuse series of silver lines is proportional to the inverse of the principal quantum number of the upper level. The quantity $\lambda^3 g A$ is proportional to $\lambda g f$ or to the line strength[7]. Figures 1, 2, 3 and 4 show that, with f-values calculated by the Coulomb approximation, we again obtain straight lines in the diagrams with $\log \lambda g f$ on the ordinate and $(1/n)$ on the abscissa. Thus the empirical relations of Terpstra and Smit appear to be confirmed by semiempirical calculations, now extended to copper lines. The points in Figs. 1 and 3, which belong to infrared spectral lines, deviate from straight lines. The reason of this may lie in the breakdown of the Coulomb approximation. Terpstra and Smit have also stated that the same empirical relation holds for the sharp series of the alkaline elements and that the slopes of straight graphs have the same proportion as the numbers of the rows of the periodic system, i. e. 2 : 3 : 4 : 6 : 8 for Li, Na, K, Rb and Cs, respectively. For the first three elements, this relation can be checked directly with the help of the critical compilation of

transition probabilities published by Wiese et al.[6, 12]. In the case of copper and silver, the ratio of the slopes for the sharp series is 0.78 and for the diffuse series 0.725. The latter value is close to $5/7 = 0.714$.

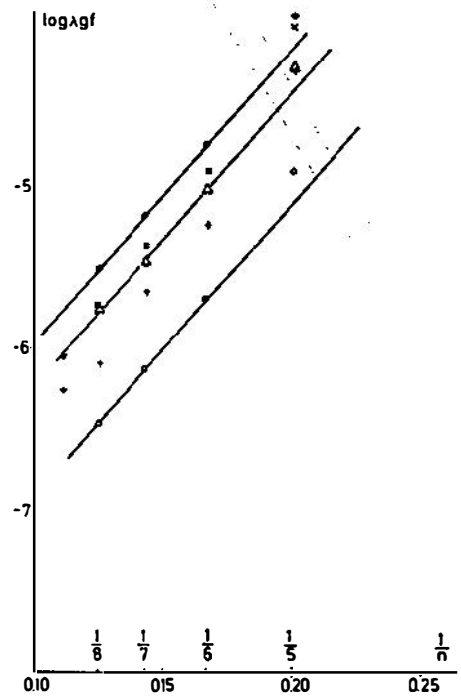

Fig. 4. Logarithm of $\lambda g f$ for the diffuse series of Ag I, as a function of the inverse principal quantum number. Coulomb approximation: ● $5p\,^2P^o_{3/2} - n\,d\,^2D_{5/2}$, △ $5p\,^2P^o_{1/2} - n\,d\,^2D_{3/2}$, ○ $5p\,^2P^o_{3/2} - n\,d\,^2D_{3/2}$. Experimental points: × $5p\,^2P^o_{3/2} - n\,d\,^2D_{5/2}$ and + $5p\,^2P^o_{1/2} - n\,d\,^2D_{5/2}$ from Terpstra and Smit[4].

4. Properties of the oscillator strengths

It is a well-known fact that oscillator strengths for any series of hydrogen lines are proportional to the inverse of the cube of the main quantum number of the upper level. For heavier atoms, one would expect[13] a similar dependance, except that n should be replaced by n^*, i. e. by the effective main quantum number. In order to find whether the same applies to copper and silver oscillator strengths, the product of calculated gf values with n^{*3} was plotted against n^* (Figs. 5 and 6). Because of the limited use of the Bates and Damgaard tables for transitions from very high levels, additional points were taken from the extrapolation of the straight lines from Figs. 1, 2, 3 and 4. The straight-line extrapolation is justified in the case of silver, as is shown

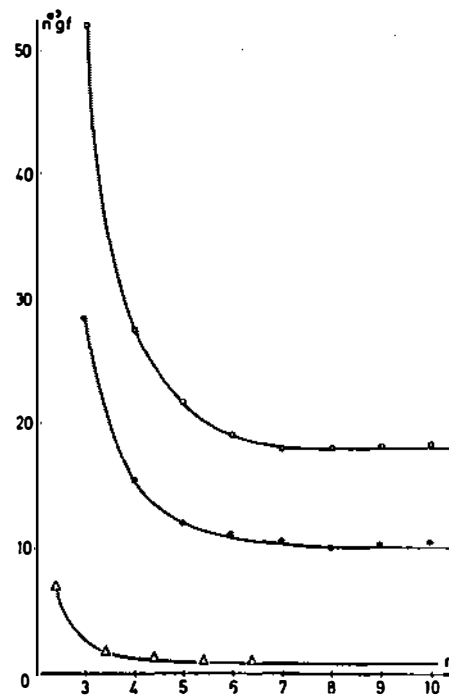

Fig. 5. The quantity gf multiplied by n^{*3} as a function of n^* for the sharp and diffuse series of Cu I:
○ $4p\,^2P^\circ_{3/2} - n\,d\,^2D_{5/2}$, ● $4p\,^2P^\circ_{1/2} - n\,d\,^2D_{3/2}$, △ $4p\,^2P^\circ_{1/2} - n\,s\,^2S_{1/2}$.

by the results of Terpstra and Smit[4]. For copper, there is no direct justification but the extrapolation is plausible because analogous transitions in copper and silver atoms have similar oscillator strengths. Figs. 5 and 6 show that, above well-defined levels, all points lie on the straight lines which are parallel to the n^* axes. This property may be of considerable use in the calculation of the quadratic Stark-constants in which sums over oscillator strengths appear[14]. The dependance of oscillator strengths on the inverse cube of the upper effective main quantum number may be used in order to assess the part of the sum over distant levels.

5. *Summary and conclusion*

The transition probabilities of copper and silver lines were calculated using two approximations. The similarity between the observed Lande factors and the theorctical ones derived from the LS-coupling scheme suggests the applicability of the LS-coupling approximation to the angular part of the

matrix elements of the dipole moment. The radial parts of the same matrix elements were taken from the tabulation of Bates and Damgaard. Their Coulomb approximation can be applied to moderately and highly excited levels in the alkali part of the term diagram of neutral copper and silver

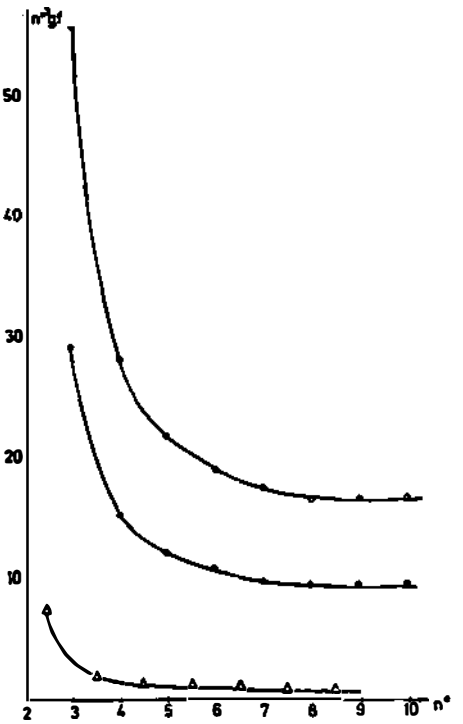

Fig. 6. The quantity gf multiplied by n^{*3} as a function of n^* for the sharp and diffuse series of Ag I:
○ $4p\,^2P^\circ_{1/2} - n\,d\,^2D_{3/2}$, ● $5p\,^2P^\circ_{1/2} - n\,d\,^2D_{3/2}$, △ $5p\,^2P^\circ_{1/2} - n\,s\,^2S_{1/2}$.

atoms. The property that the logarithm of λgf is proportional to $1/n$ is shown to be valid for both copper and silver spectral lines except for the first members in the sharp and diffuse series. Extrapolation to higher members of this linear relation was used in order to show that the oscillator strengths of higher members in each series are proportional to $1/n^{*3}$. All properties derived from the theoretical transition probabilities calculated by the Coulomb approximation are similar between analogous series of spectral lines of copper and silver originating in the alkali part of their term diagram.

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SVOJSTVA JAKOSTI OSCILATORA SPEKTRALNIH LINIJA Cu I i Ag I

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Sadržaj

Koristeći Coulomb-ovu aproksimaciju, izračunate su vjerojatnosti prijelaza za dvadeset linija oštre i difuzne serije bakrenog i srebrnog atoma. Izračunavanja su pokazala da je logaritam jakosti linije proporcionalan inverznom glavnom kvantnom broju gornjeg nivoa. Jakosti oscilatora viših članova u spomenutim serijama, proporcionalne su inverznom kubu efektivnog glavnog kvantnog broja gornjeg nivoa. Niz eksperimentalnih podataka upotrijebljen je za uspoređenje s izračunatim vrijednostima.