ON THE SELF-REVERSAL OF SPECTRAL LINES

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Introductory

The arc spectra of elements sometimes yield lines in which the cores have been absorbed and are replaced by dark lines; this phenomenon, which is common especially in the resonance lines of elements, has been here referred to as the self-reversal of spectral lines. Hyperfine structure study of spectral lines has often been vitiated by this phenomenon, which doubles the main lines and sometimes the satellites also, thereby giving a false pattern for the structure of the lines. Sources giving rise to self-reversal have therefore been carefully avoided in all recent work on hyperfine structure. Apart from an anxiety to avoid sources that introduce complications arising out of self-reversal, I am not aware of any attempt to study the peculiarities of the self-reversed spectral lines. In my study of the hyperfine structure of the arc lines of various elements, such as copper[1], molybdenum,[1] gold,[2] silver,[3] etc., the self-reversed spectral lines have been encountered. Measurements on the reversed lines obtained from cooled hollow cathode sources have led me to infer that the extent of self-reversal in the various lines of a given multiplet is not the same; for instance under the same conditions of discharge the two silver lines ${}^2S_{\frac{1}{2}} - {}^2P_{\frac{1}{2},\frac{3}{2}}$ exhibit different amounts of self-reversal; but the ratio of the reversal separations in the two lines remains constant under all conditions of excitation. The same result has been obtained with the resonance lines of copper. Thus in such line pairs as these, though the individual reversal separations are different and depend on various factors, it is observed that the ratio of the reversal separations in the lines is constant and independent of the physical conditions in the source. There is yet another interesting feature. When each of the gross-multiplet lines is considered for simplicity to consist only of two hyperfine structure components as it is in the resonance lines of copper and gold, the self-reversals in the two components of the same arc lines are observed to be unequal. Here also it

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[1] Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, **1**, 321.

[2] —, *Ibid.*, 1935, **2**, 313.

[3] Not published.

has been found that the reversal ratio between the main line and the satellite is a constant independent of the conditions in the source. An explanation of these observations on the basis of the classical dispersion theory is attempted below; it is followed by a brief discussion of the experimental data in the light of the theoretical conclusions.

Theoretical

Neglecting quantities of the second order, Minkowski[4] and Korff[5] have shown that the classical dispersion theory of Lorentz[6] and Voigt[7] gives for the distribution of energy within a spectral line arising from absorption by a finite thickness of absorbing vapour at moderate temperatures an expression, which according to Korff, is

$$(\Delta\lambda)^2 \log \epsilon \frac{I}{I_0} = -\frac{2\pi e^4 \lambda^2_0}{3m^2c^4} N \tag{i}$$

where I_0 is the intensity of the continuous background,

e, m, charge and mass of the electron respectively,

λ_0, the wavelength of the line under consideration,

$\Delta\lambda$, the wave-length separation of given line from the resonance line λ_0,

I, the intensity of the transmitted light at the given wavelength $\lambda_0 \pm \Delta\lambda$,

c, the velocity of light, and

N, the number of absorbing centres (linear oscillators) per sq. cm. in the line of of sight.

The method of computing N is important. If we should take any element of the alkali group as an example, the number of absorbing centres corresponding to each member of the doublet is taken as $N = n z f$ where n is the number of absorbing atoms per c.c., z the length of the absorbing column, and f the oscillator strength or the proportion of atoms being raised by absorption to the particular doublet state involved. A consideration of the statistical weights of the doublet states $^2P_{\frac{1}{2}}$, $^2P_{\frac{3}{2}}$ gives for f the values $\frac{1}{3}$ and $\frac{2}{3}$; *i.e.*, the ratio of the f values of the two states is equal to the ratio of the quantum weights $(2j+1)$ of the levels.

In the case of a source, the radiation from which is showing self-reversal, the background intensity for absorption is not a constant; it is given by the

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[4] Minkowski, *Z.P.*, 1936, **36**, 839.

[5] Korff, *A.J.*, 1932, **76**, 124.

[6] Lorentz., *Proc. Amst. Acad.*, 1905, **8**, 591.

[7] Voigt, *Münich Ber.*, 1912, p. 603.

radiated line, which by Doppler broadening has, according to Rayleigh,[8] the intensity distribution:

$$I_0 = J\,\epsilon^{-\frac{M}{2R\theta}\frac{c^2}{\lambda^2_0}(\Delta\lambda)^2},$$

where

J is the intensity at the core λ_0,

M, the mass of the radiating centre,

R, Boltzmann constant per atom, and

θ, the absolute temperature.

Assuming that a radiation with the above intensity distribution is subsequently absorbed by the absorbing column, the resulting intensity distribution in the self-reversed line is given by

$$I = J\,\epsilon^{-\frac{Mc^2}{2R\theta}\frac{(\Delta\lambda)^2}{\lambda^2_0}}\;\epsilon^{-\frac{2\pi e^4 N}{3m^2c^4}\frac{\lambda^2_0}{(\Delta\lambda)^2}}.$$

The intensity after absorption, I, will therefore be zero, when $\Delta\lambda = 0$ and again when $\Delta\lambda \to \pm\infty$, *i.e.*, when $\lambda = \lambda_0$ and $\lambda = \pm\infty$ respectively. The wave-length distance of the intensity maximum from λ_0 should now be calculated. Writing $(\lambda_0 - \lambda)$ for $(\Delta\lambda)$, we get

$$\log_\epsilon \frac{I}{J} = -\frac{Mc^2}{2R\theta}\left(1 - \frac{\lambda}{\lambda_0}\right)^2 - \frac{2\pi e^4 N}{3m^2c^4}\left(1 - \frac{\lambda}{\lambda_0}\right)^{-2}.$$

Differentiating,

$$\frac{dI}{d\lambda} = \frac{I}{\lambda_0}\left[\frac{Mc^2}{R\theta}\left(1 - \frac{\lambda}{\lambda_0}\right) - \frac{4\pi e^4 N}{3m^2c^4}\left(1 - \frac{\lambda}{\lambda_0}\right)^{-3}\right].$$

If $\Delta\lambda = \lambda_0 - \lambda$ in the above equation, corresponds to the reversal maximum, then $\frac{dI}{d\lambda} = 0$ whence

$$\Delta\lambda = \lambda_0\left(\frac{4\pi e^4 R\theta}{3M\,m^2\,c^6}\right)^{\frac{1}{4}} N^{\frac{1}{4}}.$$

The wave-number separation $\Delta\nu$ between the two maxima produced by self-reversal is given by

$$\Delta\nu = \left(\frac{64\pi e^4 R\theta}{3M\,m^2\,c^6}\right)^{\frac{1}{4}} \frac{N^{\frac{1}{4}}}{\lambda_0}$$

$$= \left(\frac{64\pi e^4 R}{3m^2\,c^6}\right)^{\frac{1}{4}} \left(\frac{\theta\,n\,z}{M}\right)^{\frac{1}{4}} \frac{f^{\frac{1}{4}}}{\lambda_0}$$

$$= 0\cdot95 \times 10^{-15} \left(\frac{\theta\,n\,z}{M}\right)^{\frac{1}{4}} \frac{f^{\frac{1}{4}}}{\lambda_0}. \qquad \text{(ii)}$$

Thus the reversal separations in wave-numbers in any multiplet group are, under given conditions of excitation which determine the values of θ,

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[8] Rayleigh, *Phil. Mag.*, 1915, **29**, 274–284.

n and z, proportional to $f^{\frac{1}{4}}/\lambda_0$. When we compare the reversals in the two lines λ_1 and λ_2 of the doublet ${}^2S_{\frac{1}{2}} - {}^2P_{\frac{1}{2},\frac{3}{2}}$ where the statistical weights f_1 and f_2 of the upper levels are $\frac{1}{3}$ and $\frac{2}{3}$ respectively, we obtain

$$\frac{\Delta\nu_2}{\Delta\nu_1} = \frac{f_2^{\frac{1}{4}}}{\lambda_2} \bigg/ \frac{f_1^{\frac{1}{4}}}{\lambda_1} = 2^{\frac{1}{4}}\,\frac{\lambda_1}{\lambda_2}. \tag{iii}$$

Generally, however, $\dfrac{f_2}{f_1} = \dfrac{2j_2+1}{2j_1+1}$, the j-values being those of the levels not common to the two lines.

When two hyperfine components having a common upper or lower hyperfine level are reversed, because $\lambda_1 \backsimeq \lambda_2$ we have

$$\frac{\Delta\nu_2}{\Delta\nu_1} = \left(\frac{f_2}{f_1}\right)^{\frac{1}{4}} = \left(\frac{2\mathrm{f}_2+1}{2\mathrm{f}_1+1}\right)^{\frac{1}{4}} \tag{iv}$$

where the f values are the hyperfine quantum numbers of the levels not common to the two components. Since the intensity of a component is proportional to the quantum weight, it follows that the reversal is directly proportional to the fourth root of the intensity.

Comparison with Experimental Results

In support of the theoretical conclusions, a few results of experimental observation will next be given. These results were obtained in the course of the hyperfine structure study of the spectral lines of elements radiated from water-cooled hollow cathode sources carrying 100-200 ma. at about 1000 V in an atmosphere of helium at 2 mms. pressure. It may be pointed out that the assumptions both implied and expressed in deducing the above relations are to a great extent satisfied only in such sources as these and not in open electric arcs. Quartz Lummer-Gehrcke plates were employed in determining the extent of self-reversal, which at no time exceeded 0·3 cm.$^{-1}$ under the conditions of the experiment. In the case of silver, using (iii),

$$\frac{(\Delta\nu)_{2P_{\frac{3}{2}} - 2S_{\frac{1}{2}}}}{(\Delta\nu)_{2P_{\frac{1}{2}} - 2S_{\frac{1}{2}}}} = (2)^{\frac{1}{4}}\,\frac{3383}{3280} = 1{\cdot}23,$$

the mean observed value under two different conditions of discharge is 1·21.

Again in the case of copper,

$$\frac{(\Delta\nu)_{2P_{\frac{3}{2}} - 2S_{\frac{1}{2}}}}{(\Delta\nu)_{2P_{\frac{1}{2}} - 2S_{\frac{1}{2}}}} = (2^{\frac{1}{4}})\,\frac{3274}{3247} = 1{\cdot}20,$$

as against the observed value 1·22.

Considering the case of the hyperfine structure we have in the two components of each of the ${}^2S_{\frac{1}{2}} - {}^2P_{\frac{1}{2},\frac{3}{2}}$ copper lines, where in consequence of the nuclear spin moment $\frac{3}{2}$, the two f values in $^2S_{\frac{1}{2}}$ level are 1 and 2, using (iv),

$$\frac{(\Delta\nu)_{\text{main}}}{(\Delta\nu)_{\text{satellite}}} = \left(\frac{5}{3}\right)^{\frac{1}{4}} = 1\cdot 14,$$

while the observed value is 1·15. The agreement between the observed and the calculated values should be considered good, on account of the difficulty in the accurate determination of reversal separations in practice. The absorption formula (i) has been subjected by Heard,[9] to experimental test by examining the contours of the resonance lines of potassium λ 7665 and λ 7699 in absorption by a method of photographic photometry. His results are in accordance with the classical dispersion theory of line width for a number of atoms per c.c. less than $0\cdot 80 \times 10^{14}$; but even in this region the observed and calculated values show often a deviation of about 10%. A direct verification of (i) is beset with many difficulties; important among them are the accurate determination of the intensities at various points of the absorption line and the correct estimate of N which contains two uncertain factors n and z, the latter being capable of more accurate determination. These difficulties do not arsie in the comparison of reversal separations and a greater measure of agreement is noticed in accord with expectations.

Apart from this agreement between the theoretical and the observed ratio of the self-reversal separations, the absolute value of the reversal separation was computed for copper and silver lines by assuming probable values for θ, n and z, and using the relation (ii). The calculated and the observed values were of the same order. In long column sources where the emitting and absorbing centres coexist, Venkatesachar[10] has shown that the lines are broadened with the intensity distribution given by

$$I_c = J\,\frac{1 - \epsilon^{-A_0 Z \epsilon^{-k(\Delta\lambda)^2}}}{1 - \epsilon^{-A_0 Z}}$$

where A_0 is the absorption coefficient at λ_0 and $k = \frac{M}{2R\theta}\,\frac{c^2}{\lambda^2_0}\cdot$ When $\Delta\lambda = 0$ the intensity at the centre λ_0 becomes $I_0 = J$ thus exhibiting no reversal. It is therefore necessary for self-reversal to consider the emitted lines as passing through the absorbers placed separately after the emitters. In metallic arcs, for instance, the radiation from the luminous core is reversed while passing through the outer envelope of comparatively cooler vapour surrounding the core.

In conclusion, I wish to thank Professor A. Venkat Rao Telang for his valuable guidance.

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[9] Heard, *Month. Not. Roy. Astro. Soc.*, 1934, **94**, 458–466.

[10] Venkatesachar, *Phil. Mag.*, 1925, **49**, 33–59.