Hyperfine Structure and the Polarization of Mercury Resonance Radiation

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The general theory of the calculation of the polarization of resonance radiation is discussed for the case when hyperfine structure has to be considered. The polarization of mercury resonance radiation is computed for various orientations of electric vector and magnetic field, use being made of the hyperfine structure data of Schüler and his collaborators. The polarization of the stepwise radiation of mercury is also calculated and the results compared with the experiments of Richter. Fair agreement between theory and experiment is found. von Keussler's method of calculating the polarization is discussed and it is shown that his method leads to incorrect results.

SINCE the recent analysis of the hyperfine structure of mercury by Schüler and Keyston[1] and Schüler and Jones[2] several writers have made use of these data to calculate the polarization to be expected for the resonance radiation of mercury and for lines excited in stepwise radiation. Thus Larrick and Heydenberg[3] and von Keussler[4] have calculated the polarization to be expected for the resonance line λ2537 of mercury, have compared their results with the experiments of von Keussler[5] and Olson[6], and have found good agreement between theory and experiment. Further von Keussler made the calculation for the separate hyperfine structure components of λ2537, which he found to be in substantial agreement with the experiments of Ellett and McNair[7], and also for the polarization of the stepwise lines in mercury as observed by Richter[8].

Larrick and Heydenberg have carried through the calculation for the case in which the resonance tube is in a zero magnetic field, or in which it is in a magnetic field parallel to the electric vector of the exciting light. The case in which the magnetic field is perpendicular to the electric vector of the exciting light was not considered. von Keussler, on the other hand, did not correctly take into account the relative populations of the upper Zeeman levels of the several hyperfine structure components and was led thereby to erroneous conclusions.

It is the purpose of this paper to review the general method for obtaining theoretically the polarization of any resonance line showing hyperfine structure and to apply it to the problem of mercury resonance radiation and stepwise radiation in mercury.

[1] Schüler and Keyston, Zeits. f. Physik **72**, 423 (1931).
[2] Schüler and Jones, Zeits f. Physik **74**, 631 (1932).
[3] Larrick and Heydenberg, Phys. Rev. **39**, 289 (1932).
[4] v. Keussler, Zeits. f. Physik **73**, 565 (1932).
[5] v. Keussler, Ann. d. Physik **82**, 793 (1927).
[6] Olson, Phys. Rev. **32**, 443 (1928).
[7] Ellett and McNair, Phys. Rev. **31**, 180 (1928).
[8] Richter, Ann. d. Physik **7**, 293 (1930).

General Method

A general method for calculating the polarization of resonance radiation has been given by Van Vleck[9] and applied by the writer[10] to the case of cadmium resonance radiation in which hyperfine structure is involved. To carry out the calculation one usually assumes that the resonance tube is in a magnetic field strong enough to separate the Zeeman levels for each hyperfine structure component but still not strong enough to cause Paschen-Back effect of hyperfine structure. The Zeeman transition diagrams for each hyperfine structure component must then be drawn and the relative transition probabilities for each Zeeman component computed from the usual sum rules. These relative transition probabilities must now be readjusted in such a way that the chance of leaving any magnetic sublevel of any hyperfine structure component will be the same for all such levels. This assumption, equivalent to the statement that the mean life of any upper magnetic sublevel is the same for each such level of any hyperfine structure component, has been justified theoretically. Such a procedure serves to place the absorption coefficients and relative emission intensities of the various Zeeman components of the resonance radiation on a correct scale so that there is no further need for consideration of relative intensities of lines coming from various magnetic states.

Hyperfine structure is ascribed to the spin moment $\boldsymbol{i}$ of the nucleus of a given atom. This nuclear moment vector $\boldsymbol{i}$ then combines with the spin and orbital angular momentum vector of the electrons $\boldsymbol{j}$ to form the total angular momentum of the atom $\boldsymbol{f}$ ($\boldsymbol{f}=\boldsymbol{i}+\boldsymbol{j}$). Thus, for a given electronic state j there may be several hyperfine structure states with different values of f. Each of these states splits into $2f+1$ states in a magnetic field. It is found further that the value of the nuclear moment i is dependent on the isotopic constitution of any given element. Thus, isotopes of even atomic weight usually show no nuclear moment and those of odd atomic weight show some multiple of $\frac{1}{2}$.

If a resonance tube containing a vapor of an element consisting of various isotopes is radiated by a light source containing this element, the intensity distribution of the resonance radiation will depend on the intensity distribution of the light from the source, the relative number of atoms of different isotopic constitution in the resonance lamp, and on the absorption coefficient for the light of a given frequency.

In order to include both resonance radiation, in which an atom goes from a lower level to an upper level under absorption of frequency ν and returns to the same level under emission of light of the same frequency, and other types of radiation, in which it returns to other lower levels with emission of a different frequency, one may consider the following diagram.[11] The atom, originally in one of the hyperfine states (f', j_0), absorbs radiation of intensity I_ν

[9] Van Vleck, Proc. Nat. Acad. Sci. **11**, 612 (1925).

[10] Mitchell, Phys. Rev. **38**, 473 (1931). See however a correction by Ellett and Larrick, ibid. **39**, 294 (1932).

[11] The writer is indebted to Professor G. Breit for this method of presentation.

$[I(f''', j_1; f', j_0)]$, reaches the upper state (f''', j_1), and returns with emission of light to the state (f'', j_2). The number of atoms of isotope A, having a nuclear spin i_A, in the lower state f_A is

$$N = \frac{(2f_A + 1)N_A}{(2j_0 + 1)(2i_A + 1)}.$$

Since to every level f_A there are $2f_A+1$ magnetic levels, the number of atoms of isotope A in any such level is

$$N_{m'} = \frac{N_A}{(2j_0 + 1)(2i_A + 1)}.$$

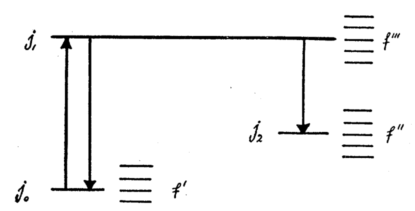

Fig. 1.

Let the transition probability between a magnetic sublevel $m'(f_A', j_0)$ of a hyperfine level f_A' of j_0 to a magnetic sublevel $m'''(f_A''', j_1)$ of a hyperfine level f_A''' of j_1 be for a π component

$$\gamma(m', f_A', j_0; m''', f_A''', j_1),$$

and for a σ component

$$\Gamma(m', f_A', j_0; m''', f_A'''j_1).$$

If the resonance tube be situated in a magnetic field making an angle θ with the electric vector of the exciting light, then the chance of reaching a given upper magnetic level $(m'''f_A'''j_1)$ by the absorption of π and σ components, respectively, is proportional to

$$N_{m'}I(f_A''', j_1; f_A', j_0)\gamma(m'f_A'j_0; m'''f_A'''j_1) \cos^2\theta$$

$$\tfrac{1}{2}N_{m'}I(f_A''', j_1; f_A', j_0)\Gamma(m'f_A'j_0; m'''f_A'''j_1)\sin^2\theta.$$

If the radiation is observed at right angles to the direction of the exciting beam and to the plane of the magnetic field, and if ξ and η are the intensities of radiation polarized along and perpendicular to the direction of the field, respectively, then for the contribution to the intensity from the upper level $(m'''f_A'''j_1)$ we have (omitting the common factor $2j_0+1$)

$$\xi_A = kI(f_A'j_0; f_A'''j_1)\frac{N_A}{2i_A + 1}\gamma(m'''f_A'''j_1; m''f_A''j_2)\left\{\gamma(m'f_A'j_0'; m'''f_A'''j_1)\cos^2\theta + \tfrac{1}{2}\Gamma(m'f_A'j_0; m'''f_A'''j_1)\sin^2\theta\right\}$$

and

$$\eta_A = \tfrac{1}{2}k\frac{N_A}{2i_{A+1}}I(f_A'j_0;\, f_A'''j_1)\Gamma(m'''f_A'''j_1;\, m''f_A''j_2)$$
$$\left\{\gamma(m'f_A'j_0; m'''\, f_A'''j_1)\cos^2\theta + \tfrac{1}{2}\Gamma(m'f_A'j_0; m'''f_A'''j_1)\sin^2\theta\right\}.$$

For the total intensity in each direction one must sum over all magnetic levels, hyperfine levels and isotopes.

$$\xi = k\sum_{ABC\cdots}\ \sum_{f'f''f'''} I(f_A'j_0;\, f_A'''j_1)\frac{N_A}{2i_A+1}\sum_{m''',m'',m'}\left\{\gamma(m'''f_A'''j_1;\, m''f_A''j_2)\right.$$
$$\left.\cdot\left[\gamma(m'f_A'j_0;\, m'''f_A'''j_1)\cos^2\theta + \tfrac{1}{2}\Gamma(m'f_A'j_0;\, m'''f_A'''j_1)\sin^2\theta\right]\right\} \qquad (1)$$

$$\eta = \tfrac{1}{2}k\sum_{A,B,C\cdots}\ \sum_{f',f'',f'''} I(f_A'j_0;\, f_A'''j_1)\frac{N_A}{2i_A+1}\sum_{m''',m'',m'}\left\{\Gamma(m'''\, f_A'''j_1; m''f_A''j_2)\right.$$
$$\left.\cdot\left[\gamma(m'f_A'j_0;\, m'''f_A'''j_1)\cos^2\theta + \tfrac{1}{2}\Gamma(m'f_A'j_0;\, m'''f_A'''j_1)\sin^2\theta\right]\right\}. \qquad (2)$$

The polarization is then given by

$$P = \frac{\xi - \eta}{\xi + \eta}.$$

THE POLARIZATION OF MERCURY RESONANCE RADIATION (λ2537)

In order to explain the hyperfine structure of mercury, Schüler and Keyston assumed that the even atomic weight isotopes ($N_x = 69.88$ percent of an ordinary mixture) show no nuclear moment, the isotope of atomic weight 199 ($N_{199} = 16.45$ percent) shows a moment $i = \frac{1}{2}$, and that of atomic weight 201 ($N_{201} = 13.67$ percent) shows a moment $i = 3/2$. Fig. 2 shows the Zeeman transition diagrams for the various hyperfine structure states. Below each line are given the adjusted transition probabilities and at the right of each upper level is given the population per unit light intensity per atom in each lower level. To conserve space only half of the transitions for the odd atomic weight isotopes are given.

The resonance line of mercury shows five hyperfine structure components. As may be seen from Fig. 3 the lines from the even isotopes do not all come at the same wave-length and furthermore lines from some isotopes may coincide with lines from others. The numbers next each line give the relative intensity of each component as observed by Schüler and Keyston and the wave-length separations in milliangstroms are given below.

In the practical problem of observing the polarization of resonance radiation the exciting light source is usually run at fairly high current density. This means that the vapor pressure in the arc is high enough so that some of the radiation is absorbed by cold atoms near the walls. This tends to make the intensity of all the hyperfine structure components about equal. If the current in the arc is kept very low, the intensity distribution tends more toward the theoretical intensities. These two conditions are usually designated by *broad line* and *narrow line* source respectively.

The calculation has therefore been carried out for these two cases. For the broad line condition formulae (1), (2), and (3) are used and $I(f_A'j_0; f_A'''j_1)$ is made the same for every term of the sum. For the narrow line source, the intensities of the components as given in Fig. 3, together with the number of atoms of a given kind capable of absorbing these frequencies, are used.

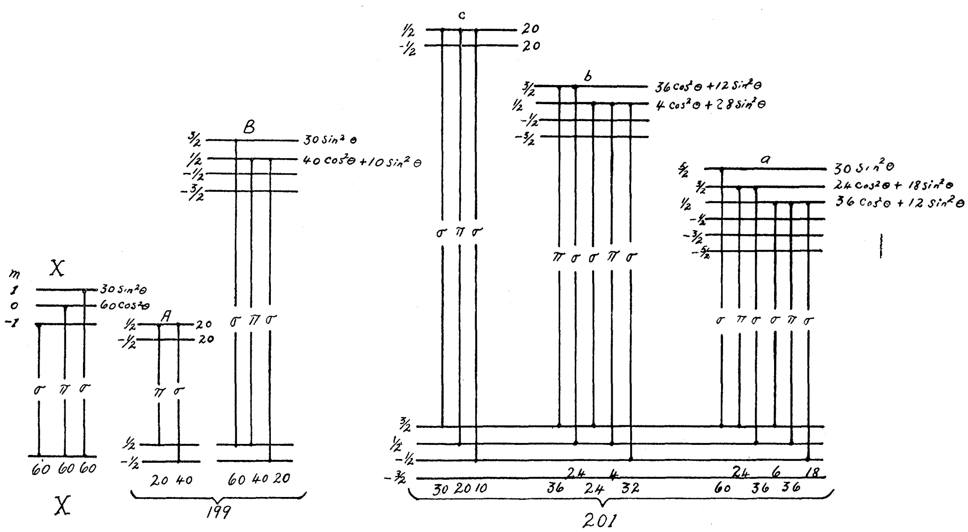

Fig. 2. Hyperfine levels of λ2537.

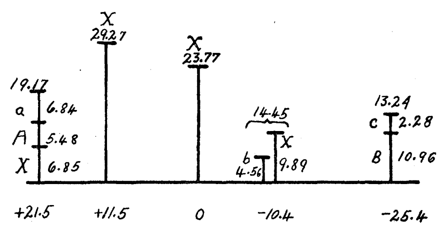

Fig. 3. Hyperfine structure of λ2537.

The results of the calculation are given in Table I for the cases in which the electric vector of the exciting light is parallel ($\theta=0$) or perpendicular

TABLE I. *Polarization of mercury resonance radiation*

Excitation	Polarization (percent) $\theta=0$	$\theta=\pi/2$
Broad line	84.7	73.5
Narrow line	88.7	81.2

($\theta=\pi/2$) to the field. If the experiment is performed in the absence of a magnetic field, spectroscopic stability insures that the correct value will be given by placing $\theta=0$.

The results are in substantial agreement with experiment. von Keussler[5] using a broad line source, found 79.5 percent polarization, while Olson[6] varied the current in his source and found 79 percent with a current of 3.5 amperes, 84 percent at 1 ampere, and 86 percent at 0.4 amperes. Both experiments were performed in a zero magnetic field.

The results of Table I are, of course, in agreement with those of Larrick and Heydenberg who used the same method, but not in agreement with the calculations of von Keussler[4] who obtained 83.4 percent polarization for $\theta=0$. This descrepancy, although not large, is due to a fundamentally incorrect method of calculation as will be shown later.

Polarization of the Separate Hyperfine Structure Components of λ2537

Ellett and McNair[7] measured, by means of a Wollaston prism and a Lummer plate, the polarization of the five hyperfine structure components of the resonance line λ2537 separately. They showed that the three inner components (11.5, 0, −10.4 m.A.) were practically completely polarized, whereas the two outer components showed incomplete polarization. Recently Ellett[12] measured the polarization of resonance radiation containing only the two outer components and found the degree of polarization to be not more than 60 percent.

Table II gives the results of the calculation by the methods outlined above for a case in which the source shows broad lines and when the experiment is carried out in a zero magnetic field.

Table II.

Component	Polarization in percent	
	This method	von Keussler's method
21.5	55.9	54.3
11.5	100	100
0.0	100	100
−10.4	84.8	76.4
−25.4	51.4	51.4

The two components 11.5 and 0.0 show 100 percent polarization as would be expected since they arise from isotopes that show no nuclear spin. As an example of the use of formulae (1) to (3) the calculation of the polarization of the 21.5 m.A. component will be carried out in detail. Fig. 3 shows that this component is made up of the three components I_x, I_A, and I_a of Fig. 2. The polarization will then be given by

$$P=\frac{(450I_xN_x+63I_aN_{201})(3\cos^2\theta-1)}{450I_xN_x(\cos^2\theta+1)+200I_AN_{199}+9I_aN_{201}(7\cos^2\theta+31)}.$$

Substituting $I_x=I_A=I_a$, $N_x=0.0685$, $N_{199}=0.1645$, and $N_{201}=0.1367$, and $\theta=0$, one obtains the result given in the table.

[12] Ellett, Phys. Rev. **37,** 216 (1931).

The results of the calculation are in good agreement with experiment. Owing to the difficulties of the experiment the deviation of the −10.4 m.A. component from 100 percent would not be expected to be observed.

Polarization of Stepwise Radiation

Richter radiated a mixture of mercury vapor and nitrogen with polarized light containing all the lines of the mercury spectrum and observed the radiation given off from the resonance tube in a direction at right angles to the exciting light beam for polarization. He confined his measurements to the visible triplet (λ4047, λ4358, λ5461) from the 7^3S_1 state, and the ultraviolet

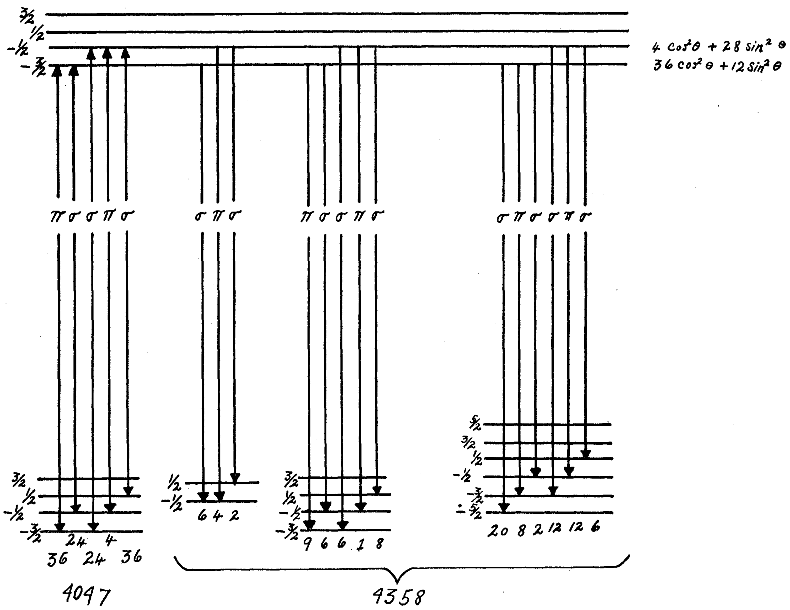

Fig. 4. Excitation of stepwise lines λ4047, λ4358 from isotope 201, upper level $f=3/2$.

triplet (λ2967, λ3131, λ3663) from the 7^3D_1 state, and found these lines to show various degrees of polarization. In order to reach these higher states, normal mercury atoms must absorb λ2537, reach the 6^3P_1 state, be transferred to the 6^3P_0 state by collision with nitrogen, and absorb either λ4047 ($6^3P_0 - 7^3S_1$) or λ2967 ($6^3P_0 - 7^3D_1$) from the arc.

The calculation of the polarization of these lines will be carried out for a broad line source. One must first find the relative number of atoms in any sublevel $(m', f_A'j_0)$ of the 6^3P_0 state at any time. During the excitation to the 6^3P_1 state the relative number of atoms of a given isotopic kind reaching the upper state will be directly proportional to the relative abundance of isotopes in the ground state. Assuming that the mean radiation life for each hyperfine structure component is the same and that the chance of being brought to the 6^3P_0 state by collision with nitrogen is the same for all isotopes, it follows that the relative number of isotopes in the 6^3P_0 state after the process will be the same as that in the ground state. It must be assumed further that collision with nitrogen leads to an equal distribution of atoms among the magnetic sublevels of a given hyperfine state. Since 6^3P_0 has the same structure as the ground state the distribution of atoms among the magnetic sublevels can be taken to be the same as in the ground state.

On account of the many levels involved, the complete level scheme for these transitions can not be given here. As an example, however, the diagram for the excitation of the $f=3/2$ state of the 7^3S_1 state for the isotope 201 is given in Fig. 4. The state is reached by the absorption of one of the hyperfine structure components of 4047 and from it are radiated the three visible lines. The transition[13] probabilities are given at the foot of the diagram and the relative population of each upper level on the right. The transitions for the line λ5461 are not shown.

Richter measured the polarization of the stepwise lines in the two cases $\theta=0$ and $\theta=\pi/2$. A comparison between his experimental results (the mean of all observations for a given orientation of field and electric vector) and calculated values of the polarization is given in Table III. In column 5 of

TABLE III. *Polarization of stepwise radiation*
$7^3S_1-6^3P_{0,1,2}$

Line	Condition	Polarization in percent Observed	Calculated	v. Keussler
λ4047	$\theta=0$	72 ± 6	84.7	83.4
	$\theta=\pi/2$	56 ± 14	73.5	
λ4358	$\theta=0$	49 ± 6	44.6	71.5
	$\theta=\pi/2$	22 ± 4	18.2	
λ5461	$\theta=0$	13 ± 1	3.44	8.7
	$\theta=\pi/2$	8.5 ± 1	3.66	

$7^3D_1-6^3P_{0,1,2}$

Line	Condition	Polarization in percent Observed	Calculated	v. Keussler
λ2967	$\theta=0$	67 ± 7	84.7	83.4
	$\theta=\pi/2$	37 ± 7	73.5	
λ3131	$\theta=0$	29 ± 7	44.6	71.5
	$\theta=\pi/2$	25 ± 1	18.2	
λ3663	$\theta=0$	42 ± 4	3.44	8.7

[13] The adjusted transition probabilities are not given for the hyperfine structure components of λ4358 and λ5461. The adjustment of the figures given (relative transition probabilities) to make the transition probability from any upper magnetic sublevel the same for all such levels is best accomplished during the calculation by using

$$\frac{\gamma(m'''f_A'''j_1;\,m''f_A''j_2)}{\gamma(m'''f_A'''j_1;\,m''f_A''j_2)+\Gamma(m'''f_A'''j_1;\,m''f_A''j_2)}\quad\text{and}\quad\frac{\Gamma(\;\;)}{\gamma(\;\;)+\Gamma(\;\;)}$$

for each Zeeman component in question instead of γ or Γ as given in Eq. (1).

the table are given von Keussler's calculated values. The following observations were obviously not included: (1) When the electric vector of the exciting light was parallel to the observation direction and the magnetic field was zero; and (2) when the magnetic field was in the direction of observation. Only the degree of polarization is given in the table without respect to the direction of the plane of polarization of the fluorescence. One might add that in all cases the calculated and observed direction of polarization are in agreement.

One may see from the table that there is fair agreement between theory and experiment for the visible lines with exception of λ5461. For the two lines λ4047 and λ4358 the decrease in polarization to be expected when the field is perpendicular to the electric vector is observed. For the line λ5461 there seems to be considerable disagreement between theory and experiment. This is probably due to the fact that such a small degree of polarization as that shown by this line is difficult to measure.

For the ultraviolet lines the agreement is not quite so good. The reason may be twofold. In the first place the hyperfine structure of these lines has not been measured, and the calculation was made on the assumption that they follow the same scheme as the visible lines. In the second place the observations are more difficult to make since the lines are weaker. The line λ3663 is seen to be in bad disagreement with theory. This may have its origin in the fact that this line is probably a composite of the three lines λ3663, λ3650, and λ3654.[14]

There still remains one point of divergence between the calculated and observed values. It will be noted that the mean of the observed values of the polarization for λ4047 lies below that calculated while for λ4358 and λ5461 the reverse is true. One would expect that the observed polarization would always lie below the calculated value due to the effect of collisions and imprisoned resonance radiation. Richter has shown, however, that the polarization of λ4047 and λ4358 is practically independent of the nitrogen pressure. The fact that the observed values of the polarization for λ4358 and λ5461 lie above the calculated might be explained if the λ4047 line in the arc were not quite a broad line. In this case one would expect the hyperfine structure components due to the even isotopes to be stronger than those due to the isotopes 199 and 201. This would result in a relative increase in the number of even isotopes in the 7^3S_1 state, and since the polarization of the components due to the even isotopes is higher than that due to the odd there would be a consequent increase in the polarization of all three lines. The effect would be a differential one, however, and would tend to increase the polarization of λ4358 and λ5461 relatively more than that of λ4047. This is due to the fact that the former lines have more hyperfine structure components coming from the upper levels of the odd isotopes than does λ4047, and these components are, in general, weakly polarized.

[14] See Mitchell, Phys. Rev. **36**, 1589 (1930).

Remark on von Keussler's Method

von Keussler calculated the polarization for the mercury lines for the case in which there is no magnetic field, using a method different from the one employed here. He considered first each hyperfine structure component separately and wrote down the relative intensities of each π and σ component of the Zeeman pattern. He then appears to have assumed that those states which are reached by the absorption of σ components alone are not excited and that those which are excited by absorption of π components are all *equally populated*. The degree of polarization for the resonance radiation from this one component would then be

$$P = (J_x - J_y)/(J_x + J_y) \tag{4}$$

where $J_x = \Sigma J_\pi$; $J_y = \Sigma J_\sigma$ (the sum of the intensities of π and σ components, respectively, emanating from upper Zeeman levels). Instead of using the polarization P as written he made use of the notion of spatial polarization defined by

$$P' = (J_x - J_y)/(J_x + 2J_y)$$

where J_x and J_y have the same significance as in (4), and the denominator is the total intensity radiated in all directions of space. Finally he assumed that the spatial polarization of a group of hyperfine structure components would be given by

$$P' = \frac{\sum_k J_k P_k'}{\sum_k J_k},$$

where J_k is the intensity of the kth component and is proportional to $(2f_k+1)/(2i_k+1)N_k$. The observed polarization is given by

$$P = \frac{3}{1 + 2/P'}.$$

The error in the method is, of course, the assumption that all of the upper magnetic levels which are reached by the absorption of π components are equally excited. This may be seen not to be true in general by inspection of Fig. 2. Table III, for the polarization of the five hyperfine structure components of $\lambda 2537$ illustrates this point. The table shows that there is agreement between von Keussler's method and the one used here for all except the two components 21.5 and -10.4 m.A. It is just these two components for which the assumption of equal population of upper magnetic levels does not hold.