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CORRELATION OF THE FLUORESCENT AND ABSORPTION SPECTRA OF IODINE

By F. W. Loomis

Abstract

The lines near Hg5460 in Wood's fluorescent spectrum of iodine excited by the quartz mercury arc are identified with definite lines in the absorption spectrum. This identification furnishes the key to the *analysis of the absorption spectrum*. Values of the *constants of the iodine spectrum*, based on new measurements, are as follows: for the unexcited state $B_0''=0.037300\pm0.000003$, $I_0''=7.42\times10^{-38}$ g.cm^2, $r_0''=2.66\times10^{-8}$ cm; for the excited state $B'(26)=0.023368\pm0.000005$, $I'(29)=11.83\times10^{-38}$ g.cm^2, $r'(29)=3.37\times10^{-8}$ cm; $C(29,0)=-0.013932$, $m_H''(29,0)=1.677$. The identification, in the absorption bands, of both components of the fluorescent doublets makes possible the calculation of *absolute rotation quantum numbers*; and these furnish direct evidence for the hypothesis of half quantum numbers. Lines in Wood's magnetic rotation spectrum which show the "normal" direction of rotation are found to belong to P branches; those which show the opposite direction, to R branches.

Three *new series of fluorescent doublets*, $\nu(29,45\frac{1}{2})$, $\nu(29,50\frac{1}{2})$ and $\nu(29,51\frac{1}{2})$, extending to the -1 order, are found and formulated, and their relationship to bands (29,1) and (29,0) demonstrated.

Revised versions of Mecke's *equations for band heads*, based on corrected numbering, and of the constants of four red bands, based on new computations, are given; and the apparent occurrence of Q branches in the red bands is shown to be due to the fact that the values of these constants are such as to cause the lines of the P and R branches to coincide.

Calculated values of the *constants of the fluorescent series*, based on the results of the new absorption measurements, agree well with the values of these constants determined empirically from the fluorescent spectrum. Every detail is in agreement with the theory advanced by Lenz to account for the simple fundamental series of doublets excited by the narrow green mercury line.

ONE of the notable successes of the modern theory of band spectra is the explanation by Lenz[1] of the striking experiments of R. W. Wood[2] on the fluorescence of iodine vapor excited by monochromatic light. The spectrum reported by Wood was a series of approximately equally spaced doublets, of nearly constant frequency interval, extending from the doublet of "order" zero, whose short-wave component coincides with the exciting green mercury line, to the doublet of order 27, well down in the red. The simplicity of this spectrum offers a marked contrast to the very complex absorption spectrum, or to the fluorescent spectrum excited by white light. Nevertheless no explanation of it was put forward

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[1] Lenz, Phys. Zeits. **21,** 691 (1920).

[2] R. W. Wood, Researches in Physical Optics, II (1919); Phil. Mag. **35,** 236 and 252 (1918).

until Lenz showed that it constitutes a clear example of the working of the Bohr selection principle for rotational quantum numbers. For, if only one absorption line is excited, all the excited molecules must be in the same state, having the same values of the vibrational quantum number n' and of the rotational quantum number j'. In the return transitions which accompany the emission of the fluorescent light the final value of j (i.e., j'') is limited, according to the Bohr selection principle, to $j''=j'\mp 1$; while, if the vibration is anharmonic, all values of n'' are possible. The result is a series of lower energy levels arranged in fairly close pairs approximately evenly spaced; and a spectrum like that reported by Wood.

When the exciting green mercury line was broadened by using a quartz lamp run at a high temperature it covered seven apparent iodine lines and the resulting spectrum was more complex. It then consisted of groups of lines close to the original (the so-called "fundamental") doublets, tending toward the violet side of them in the groups of higher order, but having no apparent uniformity of pattern. Several new doublet series have, however, been found among these lines and empirically formulated by Mecke.[3,4] The form of Mecke's empirical expression has been accounted for theoretically by Kratzer and Sudholt,[5] in harmony with Lenz's theory of the fundamental doublet series; and they have been able to make a rough calculation of the moment of inertia of the iodine molecule from the numerical values of some of the constants in Mecke's series. Kemble and Witmer[6] have extended and revised the work of Kratzer and Sudholt, have identified the bands in the absorption spectrum to which the excited lines of most of Mecke's series belong, and have made a more accurate computation of the moment of inertia.

An important objection to Lenz's theory, and one which holds equally aganist those of Kratzer and Sudholt, and Kemble and Witmer, has, however, been put forward by Mecke.[4] He has studied the absorption spectrum, choosing four bands in the red region to avoid the complexity of the numerous overlapping bands in the green, and has found that these bands apparently consist only of Q (null) branches, corresponding in band spectrum theory to transitions with $j''=j'$, whereas it is a necessary assumption of the Lenz theory that only transitions to $j''=j'\mp 1$ should occur, and hence that the absorption bands should consist of R and P (positive and negative) branches.

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[3] Mecke, Zeits. f. Physik **7**, 73–85 (1921).

[4] Mecke, Ann. d. Physik **71**, 104–134 (1923).

[5] Kratzer and Sudholt, Zeits. f. Physik **33**, 144–152 (1925).

[6] Kemble and Witmer, Phys. Rev. **28**, 633 (1926).

In the present paper the fluorescent lines in the zero order have been identified with definite lines in the absorption spectrum, and this identification has served as a clue to the unravelling of the complex overlapping absorption bands in the green. It is shown that they consist of *R* and *P* branches as required by the Lenz theory. Precise calculations of the absolute rotation quantum numbers, based on this identification, agree closely with the hypothesis of "half-quantum numbers." Accurate values of the moment of inertia and other constants of the iodine spectrum have been computed and an extrapolation into Mecke's red region has shown that his apparent finding of *Q* branches was due to an unfortunate accident in the selection of four bands in which the lines of the *R* and *P* branches overlapped so closely as to be inseparable with his resolution. Three new fluorescent series of a slightly different type are also reported and assigned to their place in the absorption spectrum. And the assignment of absorption lines to their *R* and *P* branches has made it possible to demonstrate the regularity in Wood's magnetic rotation spectrum.

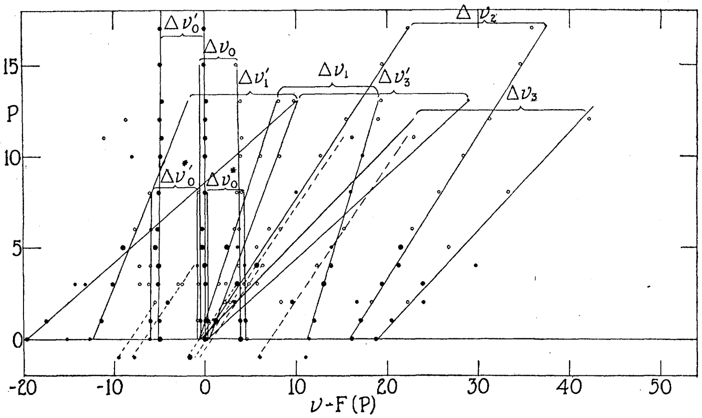

Fig. 1. Fluorescent series. The blackness of the points roughly indicate the intensities.

MECKE'S FLUORESCENT SERIES

The series in the fluorescent spectrum excited by the broad green line are exhibited in Fig. 1, which is like one made, but not published, by Mecke.[7] Here the ordinate is p, the order[8] of a group, and the abscissa is $\nu - F(p)$ where ν is the frequency of any line and

$$F(p) = 18307.5 - 213.667p + 0.592p^2 + 0.00207p^3 \qquad (1)$$

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[7] L.c. page 75. R. W. Wood, Researches in Physical Optics, II, p. 33, published a similar diagram, but in terms of wave-length, in which the doublet series lie on curved lines and are consequently more difficult to pick out.

[8] It is convenient to follow Wood's nomenclature in which a fluorescent line which coincides with some part of the exciting mercury line is called a "resonance line," the

is Mecke's formula for the series of main lines of the fundamental doublets. In this arrangement the main line of each fundamental doublet is brought to the axis of ordinates, and each doublet series is represented by a pair of nearly parallel straight lines. Nine of the ten doublet series which Mecke reported, slightly modified by Kratzer and Sudholt and by the writer, as explained below (see Table V), are indicated in Fig. 1 by continuous lines. The tenth, ν_2', is omitted, because the writer has found it to be illusory. The broken lines represent new series to be described below.

Mecke's empirical formulas[4] for his series are as follows:

$$\begin{array}{llll}
\nu_0 = F(p) & +(3.8) & \nu_0' = F(p) & +(-5.0) \\
\nu_0^* = F(p) & +(4.5) & \nu_0^{*\prime} = F(p) & +(-6.0) \\
\nu_1 = F(p)+0.66p & +(11.6) & \nu_1' = F(p)+0.75p & +(-12.5) \\
\nu_2 = F(p)+1.33p & +(16.0) & \nu_2' = F(p)+1.5p & +(-?) \\
\nu_3 = F(p)+1.95p & +(19.0) & \nu_3' = F(p)+2.2p & +(-19.7)
\end{array} \tag{2}$$

where the quantities in parentheses are the doublet intervals and if omitted leave the expressions for the main lines, but if included give the companion lines. The constant terms in the parentheses will be denoted by d_i and the coefficients of p by γ_i. The "fundamental series" of doublets is ν_0'.

RECALCULATION OF MECKE'S ABSORPTION DATA

Mecke[4] has measured the iodine absorption band heads in the region 5000–7000A and has shown that they all belong to the same band system, for which he publishes a formula in terms of two arbitrary parameters, n_1 and n_2. For several reasons he concludes, correctly, that n_2 corresponds to n', the upper level vibrational quantum number, but increases as n' decreases. As $n_2 = 26$ seems to be a limiting value he concludes that it is the zero of n' and sets $n' = 26 - n_2$. An inspection of Fig. 2 will show that this is only an approximation and that some future investigation may necessitate changing all the values of n' by a few units or half units. Since, however, only relative values of n' are needed in this paper, it is simplest to retain Mecke's assignments of n' for the present. Similarly, he concludes that n_1 corresponds to, and increases with, n'', the lower level vibrational quantum number. And, since the coefficients of n_1, n_1^2, and n_1^3 are sensibly the same as those of p, p^2 and p^3 in the expression (1) for Wood's fluorescent doublets he

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component of any doublet which is on the same side as the resonance line of the series to which it belongs is called the "main line," and the other component the "companion line." The "order," p, is the ordinal number of a group, counted from the "group of zero order" which contains the resonance line.

justifiably identifies n_1 with p. He is, however, mistaken in concluding from Pringsheim's[9] observation of antistokes groups as far as the -4 order, that the zero of n'' must be at least $n_1 = p = -4$. For, while it is true that the zero of a series having antistokes members must be at least as low as the lowest member, the fundamental series, for which $p = n_1$, does not contain any antistokes members; nor do any of the series (2)

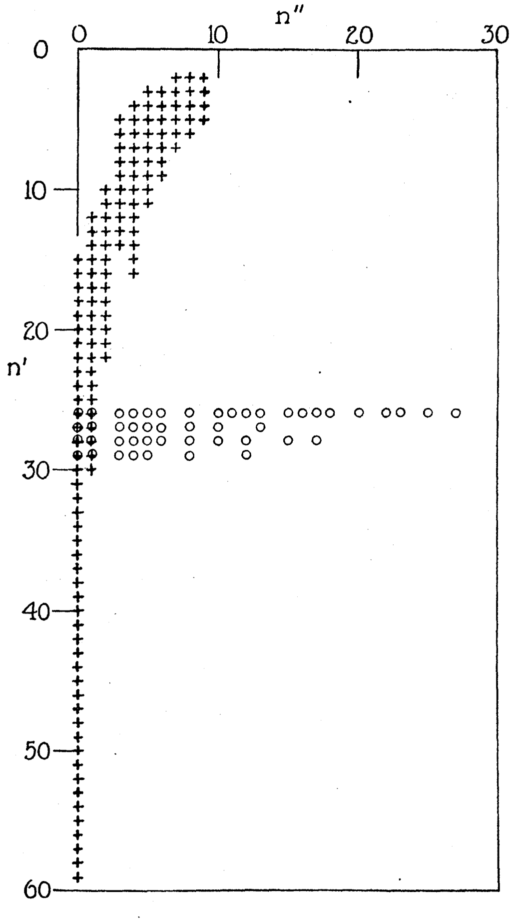

Fig. 2. Numbering of absorption bands.

which Mecke has found in the fluorescent spectrum, as can be seen from an inspection of Fig. 1, and as is evident from their γ's, which, according to the theory of Kratzer and Sudholt, are so small that they must belong to series with the same $\bar{n}$, i.e., having the same number of vibrational quanta before excitation, as the fundamental series. It is a safe assertion

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[9] Pringsheim, Zeits. f. Physik **7**, 206 (1921).

that the bands to which the zero order fluorescent lines of the fundamental series and of Mecke's series belong have the least possible value of n''. There is at present no way to ascertain whether or not this minimum value is zero. Quite probably, in the light of the new quantum mechanics[10] and by an analogy with the findings from isotope effect measurements by Mulliken[11] and Watson[12] in the spectra of BO and MgH, the minimum value will be $\frac{1}{2}$. However, we shall, in this paper, for simplicity, assume it to be zero and set $n''=n_1=p$ for the fundamental series and others having no antistokes members. For any series having $\tilde{n}$ antistokes members, $n''=n_1=p+\tilde{n}$. No errors introduced in this way will be serious enough to affect our arguments. Using this numbering, the expression which represents Mecke's band heads becomes:

$$\begin{aligned}\nu(n', n'') = 15597.70 &+ (126.59n' - 0.755n'^2 - 0.0033n'^3) \\ &- (213.76n'' - 0.596n''^2 - 0.0021n''^3)\end{aligned} \tag{3}$$

Mecke's measurements of band heads are good only to about 0.5 cm^{-1} and Kemble and Witmer have shown that the heads lie within a few lines (2 in the green, or about 0.05 cm^{-1}) of the origin, so that Eq. (3) is equally valid for band origins, and can be compared with the usual theoretical expression

$$\begin{aligned}{}_0\nu(n', n'') = \nu^e + (\omega^{0\prime}n' - 2\omega^{0\prime}x'n'^2 \cdots) \\ - (\omega^{0\prime\prime}n'' - 2\omega_0{}''x''n''^2 \cdots)\end{aligned} \tag{4}$$

Mecke[13] mentions that Eq. (3) does not adequately represent the bands with large n''s, and probably terms in higher powers are required. It is the writer's intention to attempt to improve it when he has completed the accurate measurement of certain absorption bands on which he is now engaged.

The crosses in Fig. 2[13] show all the absorption bands found by Mecke, plotted according to the assignment of n' and n'' numbering just explained. The circles show the bands to which the doublets in Mecke's fluorescent series belong, the values of n' being those assigned by Kemble and Witmer.

Mecke has also measured the individual lines of the four bands (4,7), (4,8), (5,7) and (5,8), which lie in the red, where the lines are less numerous and resolution easier than in the neighborhood of the green mercury line. He has found, as has been stated, that they appear to consist of Q branches and has represented them in the form

$$\nu = \nu_H + CM^2 \tag{5}$$

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[10] Heisenberg, Zeits. f. Physik **33**, 879–893 (1925).

[11] Mulliken, Phys. Rev. **25**, 259–294 (1925).

[12] Watson, Nature, May (1926).

[13] Cf. Mecke's Fig. 4, l.c., p. 133.

where M represents the ordinal number, starting from the head, and C is approximately -0.008. He states that, since he was unable to resolve the bands within about 30 lines of the heads, his numbering, M, may be wrong by a few units. The error in numbering is, however, a constant throughout the four bands; i.e., his relative numbering is correct. For, although a change of, say, $+1$ in the M's of any of the pairs of bands in (7) would not result in a detectable combination defect, it would introduce into (7) a linear term of the order of $0.016M$ which is not admissible, since (7) is the difference of two equations like (5).

He has also found that C varies from band to band, as indeed it should, since[14]

$$C = B' - B'' = (B_0' - \alpha' n') - (B_0'' - \alpha'' n''), \tag{6}$$

and he has represented the differences between corresponding lines of the four bands as follows:

$$\left.\begin{aligned} \nu(4,7,M) - \nu(4,8,M) &= \nu(5,7,M) - \nu(5,8,M) = \text{const.} + 0.00011M^2 \\ \nu(4,7,M) - \nu(5,7,M) &= \nu(4,8,M) - \nu(5,8,M) = \text{const.} - 0.00015M^2 \end{aligned}\right\} \tag{7}$$

which means that $\alpha'' = 0.00011$ and $\alpha' = 0.00015$. Since the quantities C, α' and α'' are of fundamental importance in all the theories of the fluorescent series, and were only roughly evaluated, the writer has recomputed them from Mecke's data, in the following manner. M was determined for some of the first resolved lines in each band from Eq. (5) using both measured and extrapolated values of ν_H and approximate values of C. In this way it was found that all his M's were approximately 4 units too large. If one is to assume that Mecke's apparent Q branches are really P and R branches whose lines coincide, the head must have an m either coincident with that of some line or midway between two lines;

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[14] This paper follows the notation usual in treating of band spectra; specifically that in the recent report on "Molecular Spectra in Gases" by a committee of the National Research Council. Primed letters refer to the upper energy level, double primed letters to the lower level, letters with a bar over them refer to the state of the molecule before absorption. n, j and m are the quantum numbers corresponding to vibration, total angular momentum and nuclear angular momentum respectively. The rotational energy is expressed as hBm^2, where $B = B_0 - \alpha n$, and $B_0 = h/8\pi^2 cI$, $I = mr^2/2$ being the moment of inertia; and α depends on the law of force between the nuclei. Since $j' - j'' = \pm 1$ it follows, if one sets $m' = j' - \rho'$ and $m'' = j'' - \rho''$, that $m' - m'' = \pm 1 - (\rho' - \rho'')$. The resulting expressions for the frequencies of band lines are:

$$\begin{aligned} \nu(n',n'',m',m'') &= {}_0\nu(n',n'') + B'm'^2 - B''m''^2 \\ &= {}_0\nu(n',n'') - B''[1 \mp 2(\rho' - \rho'') + (\rho' - \rho'')^2] + 2B''[\pm 1 - (\rho' - \rho'')]m' + Cm'^2 \\ &= {}_0\nu(n',n'') + B'[1 \mp 2(\rho' - \rho'') + (\rho' - \rho'')^2] + 2B'[\pm 1 - (\rho' - \rho'')]m'' + Cm''^2 \end{aligned} \tag{a}$$

where $C = B' - B''$ and the upper sign of each double sign refers to the R branch. ${}_0\nu(n',n'')$ is the band origin and is given by Eq. (4). These expressions are simplified, if one sets $\rho' = \rho''$ to $\nu = {}_0\nu - B'' \pm 2B''m' + Cm'^2 = {}_0\nu + B' \pm 2B'm'' + Cm''^2$, which is very probably correct in the light of results below.

i.e., the M's must be either nearly integral or nearly half-integral. Much the best values which satisfy this condition are obtained by subtracting 4 from Mecke's M's, leaving the corrected M's integers and signifying that the head coincides with a line. The corrected M's were then used in Eq. (5) to calculate, by least squares, the constants ν_H and C for band (5,8). The results were:

$$\nu_H(5,8) = 14540.44, \qquad C(5,8) = -0.00808$$

The frequency differences between corresponding lines of different bands were then formulated, as in (7), by least squares, using the corrected M's, with the following results:

$$\begin{aligned} \nu(4,7,M)-\nu(4,8,M) &= 204.51+0.000119M^2 \\ \nu(5,7,M)-\nu(5,8,M) &= 204.54+0.000118M^2 \\ \nu(5,7,M)-\nu(4,7,M) &= 119.54-0.000175M^2 \\ \nu(5,8,M)-\nu(4,8,M) &= 119.46-0.000156M^2 \end{aligned} \tag{8}$$

yielding the weighted mean values $\alpha'' = 0.00012$, $\alpha' = 0.00017$. The changes from Mecke's values of α' and α'' are largely due to the correction of the M's. As Mecke's C needs only very slight correction, he presumably calculated it by the method of second differences, which is independent of the absolute numbering.

If we anticipate a little by taking $B''(0) = 0.0373$ from (11), we can combine it with the data just obtained to calculate, on the justifiable assumption that $\rho' - \rho'' = 0$ in Eq. (a), footnote 14, the line numbers of the band heads,

$$m_H'' = B'/(B''-B') = B'/-C \tag{9}$$

and the frequencies of the origins,

$$_0\nu = \nu_H - B'B''/(B''-B') \tag{10}$$

For

$$\begin{aligned} B''(8) &= B''(0) - 8\alpha'' = 0.03634 \\ B''(7) &= B''(0) - 7\alpha'' = 0.03646 \\ B'(5) &= B''(8) + C(5,8) = 0.02826 \\ B'(4) &= B'(5) + \alpha' = 0.02843 \\ B'(0) &= B'(5) + 5\alpha' = 0.02911 \end{aligned} \tag{11}$$

The results are exhibited in Table I.

TABLE I

Constants of the red bands

Band	B'	B''	C	m''_H	$\nu_H - {}_0\nu$
(5,7)	.02826	.03646	−.00820	3.45	0.126
(5,8)	.02826	.03634	−.00808	3.50	0.127
(4,7)	.02843	.03646	−.00803	3.54	0.129
(4,8)	.02843	.03634	−.00791	3.59	0.131

Now it will be shown below that the *m*'s of the iodine bands are half-integers, so that the numbers in the fifth column of Table I indicate that the heads of all four of these bands very nearly coincide with lines, and that consequently the lines of the *P* and *R* branches nearly cover each other. It is because of his unfortunate selection of these particular bands, coupled with the smallness of m_H'', which brings the origins far within the unresolved region near the heads, that Mecke appeared to find *Q* branches. These values of m_H'' also check the correction of exactly -4 which was applied, above, to Mecke's *M*'s; for, if the heads closely coincide with lines, the *M*'s, which are line numbers counted from the heads, must be nearly integral.

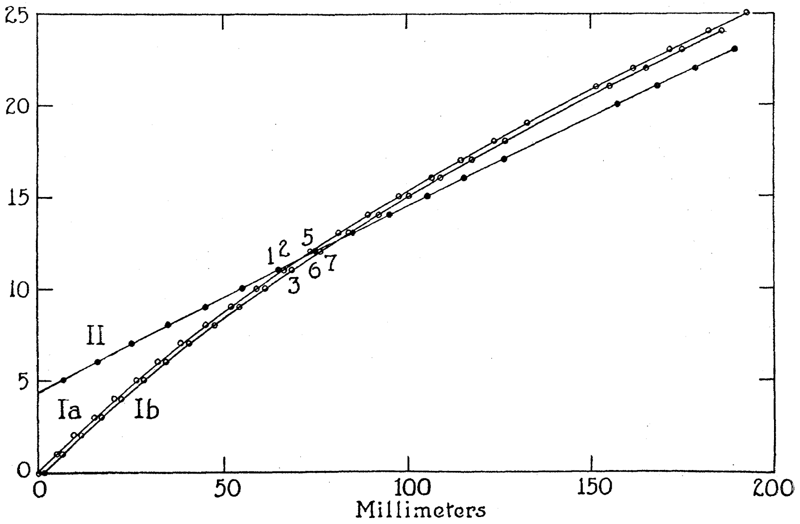

Fig. 3. Mecke's green series.

It would have been more pertinent to the problem had Mecke been able to measure the absorption spectrum in the neighborhood of the green mercury line which excites the fluorescence, but the density of lines was there too great for the resolution of his instrument. Wood photographed this region with his 40 foot spectrograph, but gives only the wave-lengths of the seven absorption lines which are covered by the wide green mercury line. He publishes a reproduction[15] of a part of this spectrum, but it contains only one comparison line (Hg5460) and the scale can be only roughly determined as about 30 mm/A. Mecke has found three series of regularly spaced lines in this reproduction which he calls Ia, Ib and II. They are shown in Fig. 3[16] in which the abscissas

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[15] Wood, Researches in Physical Optics II, plate Ia. Phil. Mag. **35**, 236–252 (1918) plate VIa.

[16] Mecke, l.c. Fig. 3, page 128.

are positions of lines on Wood's reproduction, in mm; and the ordinates are arbitrary parameters assigned by Mecke. The absorption lines which Wood has numbered 2 and 5 belong to series Ia, 3 and 7 to Ib, and 1 and 6 to II. Line 4 does not belong to any of them. Mecke mentions that series Ia and Ib, which are very similar, may be positive and negative branches, but considers them more probably electronic doublets.

IDENTIFICATION OF FLUORESCENT LINES IN THE ABSORPTION SPECTRUM

It has occurred to the writer, however, that there are good reasons for identifying these series Ia and Ib with the R and P branches which are required by the Lenz theory in the band which excites the fluorescent series ν_0, ν_0^*, ν_0' and $\nu_0^{*\prime}$. These series, which all have $\gamma=0$, must according to Kratzer and Sudholt's equation[17, 18]

$$\begin{aligned}\gamma_i&=2\omega^{0\prime\prime}x''(\bar{n}_i-\bar{n}_0')+\alpha''(\bar{m}_i^2-\bar{m}_0'^2)\\&=1.192(\bar{n}_i-\bar{n}_0')+0.00012(\bar{m}_i^2-\bar{m}_0'^2)\end{aligned}\qquad(12)$$

all be excited by lines in the same band, which must therefore contain four lines within the broad green mercury line. This is corroborated by calculation of the spacing, near Hg5460, between successive lines of the branch which excites the series ν_0', from the values of B, C and $\bar{m}$ of this band published by Kemble and Witmer or from the writer's revised values in this paper. The calculated spacing is[14]:

$$d\nu/dm=\pm 2B'+2C\bar{m}=-0.82\ cm^{-1}\qquad(13)$$

whereas the width of the mercury line is about 1.3 cm^{-1}. Now series Ia and Ib supply the four lines needed, and their spacing is about 7.45 mm on the reproduction, which corresponds to $d\nu/dm=-0.83$ cm^{-1} and agrees well with that just found from data on fluorescence. Moreover the position of the head of the band which excites ν_0', calculated from fluorescent data, using Eq. (a), footnote 14, and Eq. (10) and the approximation $\rho'-\rho''=0$, is 18323, while the head of the series Ia and Ib is, according to Mecke's extrapolation[19] at 18320.9, and by Eq. (3) $\nu_H(26,0)$

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[17] l.c., pp. 147 and 150.

[18] Detailed proofs of this equation and of most of the others in this paper are to be found in the writer's Chap. VI of the recent report on "Molecular Spectra in Gases" by a committee of the National Research Council.

[19] L.c., p. 128. Mecke also states that the fluorescent series ν_0, ν_0^*, ν_0' and $\nu_0^{*\prime}$ are surely excited by the absorption series to which lines 2, 3, 5 and 7 belong; ν_1 and ν_1' by the series containing lines 1 and 6; ν_2 and ν_2' by that containing line 4; and ν_3 and ν_3' by the series containing line 0, which coincides with a satellite of Hg5460. Except for ν_3 and ν_3' these assignments agree with the conclusions of the present paper. But Mecke does not arrive at any assignment of the individual fluorescent series to individual absorption lines.

$=18320.97$. Moreover line 11 of series Ib is Wood's absorption line 3 which nearly coincides with the narrow green mercury line and certainly excites the fundamental series ν_0'.

Wood has made a number of tentative suggestions, based on experiments in which the exciting light was varied by filtering with bromine vapor, etc., as to which absorption lines account for which fluorescent lines, but neither he nor others[20] have considered them conclusive, and as it turns out, many of them are wrong. The ascription of series ν_0' to absorption line 3, about which there can be no doubt, together with Mecke's arrangement of absorption spectrum lines into series Ia, Ib and II, is, however, enough of a start to permit the identification of the lines which excite the other fluorescent series with some certainty.

Series ν_0' and $\nu_0{}^{*\prime}$ have a negative doublet interval and their main lines must therefore belong to the *R* branch. It follows that series Ib is the *R* branch and that line Ib 12, the other line in this series within the green mercury line, excites $\nu_0{}^{*\prime}$. Lines Ia 11 and Ia 12 must excite series ν_0 and $\nu_0{}^*$. Since the companion lines of series ν_0 have lower frequency than those of $\nu_0{}^*$, its exciting line must also be the one with lower frequency, or Ia 12; and Ia 11 must excite $\nu_0{}^*$. These assignments are checked by the corrected doublet intervals which they yield. The doublet intervals originally reported by Mecke, necessarily based on subtraction of the frequency of the center of the unresolved main line group from those of the observed companion lines, were as follows:

$$\Delta\nu_0=+3.8 \quad \Delta\nu_0{}^*=+4.5 \quad \Delta\nu_0'=-5.0 \quad \Delta\nu_0{}^{*\prime}=-6.0$$

They should, since they are due to excitation of adjacent lines in the two branches of a single band, be equal in pairs. Now that we have identified the individual main lines of the several series we can use their measured frequencies (see Table II) to find much better values of the zero order $\Delta\nu$'s which are as follows:

$$\Delta\nu_0=+4.4, \quad \Delta\nu_0{}^*=+4.3, \quad \Delta\nu_0'=-5.0, \quad \Delta\nu_0{}^{*\prime}=-5.2$$

It will be seen that they are very nearly equal in pairs, as they should be.

It is natural to expect that the next strongest absorption series in the λ5460 region will be the *R* and *P* branches of the band (27,0) which excites the fluorescent series ν_1' and ν_1. The spacing between successive lines in either branch of this series, calculated as above, should be 2.11 cm^{-1}, whereas Mecke finds the single series, II, with a spacing of 10.0 mm corresponding to 1.12 cm^{-1}, or about half what one should expect. The natural conclusion is that alternate lines of this series II belong to the *R*, the others to the *P*, branch. Lines II 12 and II 11,

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[20] Mecke, l.c., p. 127.

TABLE II

Identification of the zero order fluorescent lines on Wood's absorption spectrum reproduction

Series	Exciting (main) line						Companion line				
	Branch	Wood's number	Mecke's number	position on reproduction	$\nu-F(0)$	magnetic rotation	Branch	Wood's number	$\nu-F(0)$	Mecke's number	position on reproduction
ν_0	*P*	5	Ia 12	73.5	−0.53	+	*R*	5	+ 3.9	Ib 6	34.5
ν_0^*	*P*	2	Ia 11	66.4	+0.26	+	*R*	4	+ 4.6	Ib 5	28.3
ν_1	*P*	6	II 12	74.9	−0.68	+	*R*	3	+11.4		off
ν_2	*P*	4		70.4	−0.18	+	*R*	2	+16.1		off
ν_3	*P*	5		73.5	−0.53	+	*R*	1	+18.8		off
ν_0'	*R*	3	Ib 11	68.7	0.00	−	*P*	7	− 5.0	Ia 17	114.5
$\nu_0^{*\prime}$	*R*	7	Ib 12	76.2	−0.83		*P*	8	− 6.1	Ia 18	123.5
ν_1'	*R*	1	II 11	64.9	+0.45		*P*	9	−12.2	II 22	178.6
ν_2'	*R*	–		——	——		*P*				
ν_3'	*R*	2		66.4	+0.26	+	*P*		−19.6		off

which are the two lines of this series within the green mercury line, should be assigned to series ν_1 and ν_1' respectively (and not vice-versa), because this gives corrected doublet intervals in the zero order, $\Delta\nu_1=12.0$ and $\Delta\nu_1'=-12.7$, which agree well with those in higher orders (see Fig. 7), while the alternative assignment gives $\Delta\nu_1=10.9$ and $\Delta\nu_1'=11.6$, which do not.

Series ν_2 is assigned by Wood to absorption line 4 because it is the first new series to come out when the narrow mercury line, which lies between absorption lines 3 and 4, is broadened, either by raising the potential from 30 volts, which excites only the fundamental series, to 60 volts, or by using end-on emission. We can now be sure of this point because line 4 is the only absorption line shown on the reproduction, which has not been assigned by Mecke to his series Ia, Ib or II. Line 4 consequently belongs to the *P* branch of band (28,0) since ν_2 has a positive doublet interval. Mecke's series ν_2' is probably illusory. It is based on only 5 main lines and no companion lines, although the intensity of the two companions of a doublet should be equal unless they happen to be unequally reabsorbed. Moreover all the supposed main lines fit about equally well into other series. This point is confirmed by the writer's work on absorption bands in this region, described below, wherein it is found that no line of the *R* branch of band (28,0) lies within the broad green mercury line.

No more lines within Hg5460 are left to account for series ν_3 and ν_3' but the writer's absorption measurements on band (29,0) show that a line on its *R* branch coincides with line 2 and one on its *P* branch with line 5. See Fig. 6. The above assignments are summarized in Table II.

Having identified the main lines in the absorption spectrum it is easy to pick out the corresponding companion lines by adding or subtracting the known doublet interval. The resulting correspondence is also shown in Table II. The fact that both main lines in the Ib series turn out to have companion lines in the Ia series, and vice versa, and that the companion line of II 11, an odd numbered line, is II 22, an even numbered line, is a good check on our interpretation of these three series.

Wood[21] has investigated the rotation of the plane of polarization of mercury arc light passed through iodine vapor parallel to a strong magnetic field, and has reported that, for five of the absorption lines 1–7, the rotation is as shown in the seventh column of Table II. Here a + sign indicates the normal direction of rotation, the same as for the *D* lines of sodium. It will be seen that we have been forced to assign to a *P* branch every line which shows + magnetic rotation and to an *R* branch the line which shows − magnetic rotation. The apparent partial exception in line 2, which shows a + rotation and has been assigned to the *P* branch of band (26,0) and to the *R* branch of band (29,0), is accounted for by the faintness of the (29,0) lines this far from the origin. This result, by its regularity, tends to confirm our assignment of absorption lines. It may also be of value as a check on any proposed theory of the Zeeman effect in band spectra.

NEW ABSORPTION MEASUREMENTS: HALF QUANTUM NUMBERS

Having identified in the absorption spectrum both lines of the fluorescent doublets, we know which lines in the *R* and *P* branches of bands (26,0), (27,0), (28,0) and (29,0) have the same m', and can easily deduce which have the same m''. That is, we know the values of m' except for a single additive constant for each band; and similarly we know the values of m'' except for a possibly slightly different additive constant in each band. Thus (see Table II), lines Ia 17 and Ib 11 are the *P* and *R* branch components of the fundamental doublet of zero order, and must

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[21] Wood, Researches II, pp. 85–94; Wood and Ribaud, Phil. Mag. **27**, 1009–1018 (1914). The magnetic rotation spectrum was made with vapor of high density and disclosed the existence of a new absorption line, 4′, which does not show on the reproduction.[15] This line has not yet been assigned to any band.

have the same m'. If one denotes m' in the P branch by $m'=a+A'$, where a is Mecke's arbitrary numbering, it then follows that in the R branch $m'=b+6+A'$. Similarly lines Ia 16 and Ib 12 must have the same m'' and if in the P branch $m''=a+A''$ then in the R branch $m''=b+4+A''$. It can easily be verified, by reference to Table II, that these equations also assign equal values of m' to both components of the doublets $\Delta\nu_0, \Delta\nu_0{}^*$ and $\Delta\nu_0{}^{*\prime}$. We are now in a position to plot the frequency differences,[14]

$$\nu_R(m')-\nu_P(m')=4B''(m_R''+1)=\nu_b(b)-\nu_a(b+6)=4B''(b+5+A'')$$

and

$$\nu_R(m'')-\nu_P(m'')=4B'(m_R'-1)=\nu_b(b)-\nu_a(b+4)=4B'(b+5+A'), \tag{14}$$

against Mecke's arbitrary R branch numbering, b; to find $4B''$ and $4B'$ from the slopes of the graphs; and to determine A'' and A' and hence the absolute numbering of the lines from the points at which the frequency differences extrapolate to zero.

The writer did this at first using the wave-lengths of the fluorescent lines as reported by Wood to determine the scale of his absorption spectrum reproduction, on which companion lines are lacking. The values of B'' and B' so obtained, while they agreed satisfactorily with those calculated, as explained below, from the constants of the fluorescent series, could hardly be trusted to more than a few percent, since they depended on measurements made on a printed reproduction, which may have become distorted, which covered a very short region of the spectrum, and whose scale had to be found from fluorescent data of only moderate precision.

Much better results have, however, been obtained by analyzing some new plates of the iodine absorption spectrum taken with a 20 foot spectrograph by Wood and Klingaman for a forthcoming paper[22] and kindly made available to the author in advance of publication. Starting from the lines picked out by fluorescence it has already proved possible to identify with certainty some 100 or 200 lines in each of seven bands overlapping the green mercury line. The complete results of the analysis, which is still in progress, will be published later. But Fig. 4 represents the frequency differences (14), for band (26,0) plotted against b; and their linear extrapolation to locate the origin of absolute numbering. It is apparent from the graph that the lines cannot intersect the axis at integral values of b. The equations of these graphs have been determined by least squares from the frequencies of many more lines than are plotted

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[22] Wood and Klingaman, Phil. Mag. (in press).

in Fig. 4; including those of several other bands, some of which were followed to values of m as high as 150. For these bands m^3 terms had to be added to Eqs. (14). The constants of interest here are:

$$\begin{array}{ll} B'(29)=0.023368\pm0.000005 & A'=17.5 \\ B''(0)=0.037300\pm0.000003 & A''=18.551\pm0.055 \\ C(29,0)=-0.013932 & m''_H(Eq.\ 10)=1.677 \\ I'(29)=11.83\times10^{-38}\ \mathrm{g.\ cm}^2 & r'(29)=3.37\times10^{-8}\ \mathrm{cm} \\ I_0''=7.42\times10^{-38}\ \mathrm{g.\ cm}^2 & r_0''=2.66\times10^{-8}\ \mathrm{cm} \\ I_0'=9.51\times10^{-38}\mathrm{g.\ cm}^2 & r_0'=3.01\times10^{-8}\ \mathrm{cm} \end{array} \tag{15}$$

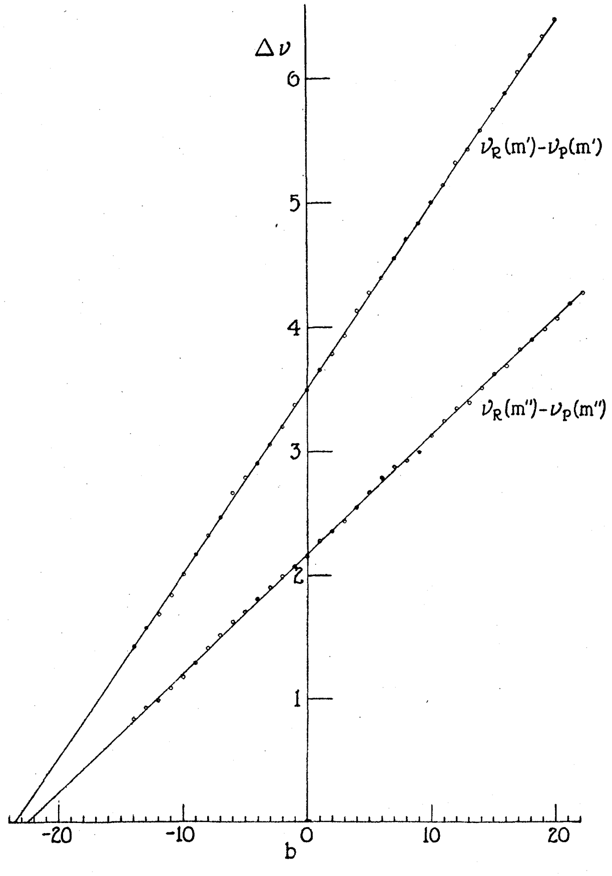

Fig. 4. Determination of the m''s, m'''s, B' and B'' for band (26,0).

These values of A' and A'', or those of m' and m'' which are deduced from them and which are given in Table III together with those similarly deduced from other bands, are evidence for the doctrine of half quantum numbers; or at least definitely disprove the earlier hypothesis of integral numbers, and are consistent with that of half-integral ones. They may perhaps be considered as direct evidence as any yet available on this point, since the assignment of the same m' to both members of a fluorescent doublet is indisputable. Because the computed m's are half integers within their probable error, they have for simplicity been taken as exact half-integers in the writer's further analysis of the absorption bands, though slight deviations from half integers have been found in the bands of other substances.

TABLE III

Results of new absorption measurements

Band	i	m'	$\bar{m}$	frequency of companion line	
				in absorption	in fluorescence
(26,0)	0	$29\frac{1}{2}$	$30\frac{1}{2}$	18311.37	18311.4
	0*	$28\frac{1}{2}$	$29\frac{1}{2}$	18312.04	18312.1
	0′	$34\frac{1}{2}$	$33\frac{1}{2}$	18302.36	18302.5
	0*′	$35\frac{1}{2}$	$34\frac{1}{2}$	18301.36	18301.4
(27,0)	1	$80\frac{1}{2}$	$81\frac{1}{2}$	18318.82	18318.9
	1′	$85\frac{1}{2}$	$84\frac{1}{2}$	18295.22	18295.3*
(28,0)	2	$108\frac{1}{2}$	$109\frac{1}{2}$	18323.45	18323.6
	2′	——	——	none	none
(29,0)	3	$129\frac{1}{2}$	$130\frac{1}{2}$	18326.23	18326.3
	3′	$134\frac{1}{2}$	$133\frac{1}{2}$	off plate	18287.9

*Wood gives 18294.8. The value in the table is from a remeasurement of his reproduction.

The measured frequencies, in the region covered by the zero order fluorescent group, of the absorption lines of the four bands, (26,0), (27,0), (28,0) and (29,0), which account for Mecke's fluorescent series, are plotted in Fig. 5 against the computed values of m'. The observed fluorescent doublets are also indicated, so that this figure serves to show the relationship between these doublets and the absorption spectrum. It will be seen that the requisite lines within Hg5460 have been found in these bands to account for all Mecke's fluorescent series except ν_2'; and reasons have been given for believing that this one is illusory. Band (30,0) is also plotted in Fig. 5 and it is evident that it contains no line within the wide green mercury line; which explains why there are no series ν_4 and ν_4'. It is perhaps worthy of note that the characteristic of band (27,0) which led Mecke to assign the lines of both branches to the single series II, i.e., the falling of the lines of one branch midway between those of the other, is part of the general picture. This can be seen by finding the vertical distance between the R and P branches of each band in Fig. 5. This quantity which might be written $m_R'(\nu) - m_P'(\nu)$ is 5.64, 5.50, 5.35, 5.20 and 5.07 for the bands (26,0) to (30,0) respectively. It changes regularly from band to band but happens to be exactly a half integer for band (27,0), giving rise to the misleading appearance of this particular band. In fact, the analyses of bands (29,0), (30.0) and others in which fluorescent lines had not been identified, were started by making approximate extrapolations for $m_R'(\nu) - m_P'(\nu)$.

New Fluorescent Series with Antistokes Members

The fundamental series of doublets definitely does not extend into the antistokes region, since prolonged exposures made by R. W. Wood with Cooper Hewitt excitation, though they brought out the positive orders with great intensity, failed to show any trace of the fundamental doublet series in the negative orders. It follows that the $\bar{n}$ of the fundamental series, i.e., the number of vibrational quanta which the molecules concerned in its emission possessed before excitation, must be the minimum possible value of n, presumably 0 or $\frac{1}{2}$. And, since Kratzer and Sudholt have proved that all Mecke's fluorescent series have the same $\bar{n}$, it follows that none of them can have antistokes members. The question then arises as to the origin of the group of five lines in the -1 order of the spectrum excited by the quartz lamp; and whether there are any lines in other orders which belong to the same fluorescent series. Wood does not record the wave-lengths of these lines, but they appear clearly on his reproduction.[23] The writer has measured them from the repro-

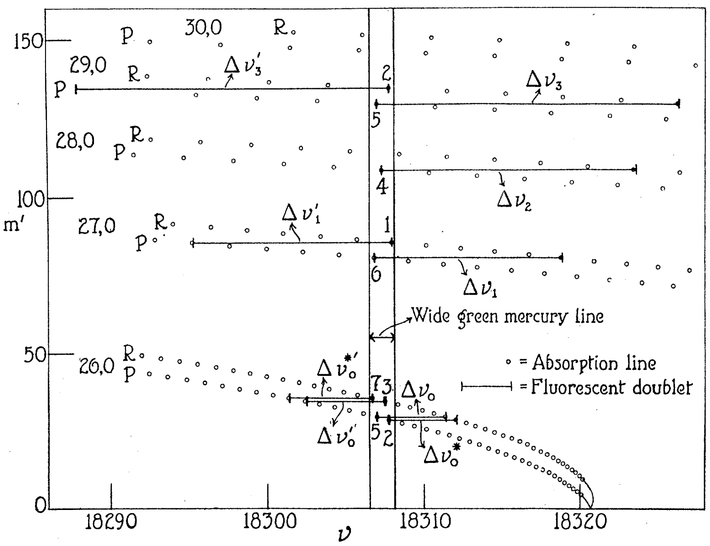

Fig. 5. Relation of the fluorescent doublets in the zero order of Mecke's series to their absorption bands.

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[23] R. W. Wood, Researches in Physical Optics II, Plates II*m* and *y*; Phil. Mag. **35**, 236–252 (1918), Plate VII*m*.

TABLE IV

Lines of new fluorescent series, and corresponding absorption lines

Order		Fluorescent Lines −1	0	2	3	Absorption Lines Band		(29,0)	(29,1)
Doublet	Component	$\nu-F(-1)$	$\nu-F(0)$	$\nu-F(2)$	$\nu-F(3)$	m'	branch	$\nu-F(-1)$	$\nu-F(0)$
high	main		+0.25	+2.75	+ 4.2	$45\frac{1}{2}$	*P*	−1.01	+0.26 #2
1st low	main	− 1.7	+0.75	+3.25	+ 4.8	$50\frac{1}{2}$	*R*	−0.57	+0.70 #0
2nd low	main		−0.35	+2.15	+ 3.5	$51\frac{1}{2}$	*R*	−1.90	−0.68 #6
high	companion	+6.0	+7.2	+9.55		$45\frac{1}{2}$	*R*	+5.77	+7.04
1st low	companion	−7.8	−6.6	−4.15	− 2.5	$50\frac{1}{2}$	*P*	−8.08	−6.80
2nd low	companion	−9.6	−8.25	−5.55		$51\frac{1}{2}$	*P*	−9.60	−8.31
unidentified high	companion	+11.0	+12.9?	+16.65?	+19.4?	?	*R*	———	———

ductions and they are given in the third column of Table IV and plotted in Fig. 1. The accuracy is less than for the positive order lines which Wood measured on his plates. It is obvious from Fig. 1 that they do not, as they should not, belong to any of Mecke's series, which are indicated by continuous lines. On the reproduction the similarity of this group to the +2 group is striking; and also significant because the fundamental doublets are too faint to appear in the +2 order, and it is therefore likely that no lines belonging to Mecke's series will be found there, and that all the +2 lines belong to series containing antistokes members. On drawing straight lines, in Fig. 1, through the corresponding lines of groups −1 and +2 it is evident that several of them hit previously unassigned lines in higher orders, and very probably represent new fluorescent series. Three plausible new series of doublets can be identified, their main lines being resolved in the 2nd and 3rd orders, though appearing as a single strong hazy line in the reproduction of the −1 group. They are represented by approximately parallel lines with a γ of about 1.38. Computing $\bar{m}$ roughly from the doublet interval and the constants which have been found for bands in this region by Eq. (14) and substituting in (12) it is evident that $\bar{n}-\bar{n}_0{}'=1$, and that these series are excited by a band whose $n''=1$, and end in the −1 order. One can also use these $\bar{m}$'s in Eq. (a), footnote 14, and Eq. (10) to find the frequency of the head of the band to which they belong. The results identify it as band (29,1) whose head calculated by (3) is at 18340.6 cm^{-1}. This identification is amply confirmed by the writer's measurements of the line frequencies of bands (29,1) and (29,0) on Wood and Klingaman's plates. One line in the P branch of (29,1) and one in its R branch are covered by the mercury line itself, and another R branch line is Wood's absorption line 0 which coincides with a satellite. These correspond to the one doublet with companion line on the high frequency side and the two with the companion lines on the low side. The frequencies of the lines in this band which have the same m' as the three lines which coincide with the green mercury line and its satellite, are given in Table IV, column 10. It will be seen that they are sensibly equal to the frequencies, in column 4, of the zero order lines in these new fluorescent series. The latter, which are apparently too faint to appear in fluorescence, were interpolated; in the case of the companion lines, by drawing straight lines in Fig. 1 between the corresponding points in the -1 and $+2$ orders; in the case of the main lines, by drawing lines through the 3 points representing the main lines of the $+2$ order, parallel to those just drawn through the companion lines. Moreover, the absorption lines of band (29,0) which have the same m's as those tabulated from band (29,1) agree with the fluorescent lines in the -1 order, as will be seen on comparing columns 9 and 3. These new series can consequently be safely identified as $\nu(n',m')=\nu(29,45\frac{1}{2})$, $\nu(29,50\frac{1}{2})$ and $\nu(29,51\frac{1}{2})$.

Fig. 6, which is similar to Fig. 5, shows the relation of these (interpolated) zero order fluorescent doublets to the absorption spectrum. The constants of the new series are included in Table V. They are represented by the broken lines in Fig. 1.

The lines of band (29,1), which are rather faint near Hg5460, coincide with two of the six lines for which Wood has observed the magnetic rotation. A line on the P branch coincides with line 2, whose magnetic rotation is normal, and this agrees with the rule stated above. A line on the R branch, however, coincides with line 6, whose magnetic rotation is also normal, and this would constitute an exception to the rule were it not that line 6 has also been assigned to the P branch of band (27,0) which is much stronger.

New Equations for the Fluorescent Series

The identification of the zero order fluorescent lines of Mecke's series in the absorption spectrum which can be much more accurately measured makes possible a considerably improved version of the Eqs. (2); for it precisely fixes one point on each line in Fig. 1. This is of particular importance in the case of the main lines, all of which Mecke of necessity put through the origin, i.e., the center of the unresolved group, but which can now be sent through their appropriate absorption lines. It is also of assistance in the unresolved main line group of higher orders in the ν_0, $\nu_0{}^*$ and $\nu_0{}^{*\prime}$ series, which can be assumed to be arranged in about the same manner in the first few orders as in the zero order. The revised equations are of the form

$$\nu = F(p)+\epsilon+\gamma p+(d-\eta p) \tag{16}$$

where, as in (2), the quantities in parentheses are the doublet intervals, and if omitted or included give the main or companion lines series respectively. The constants of these equations are given in Table V. They are represented by the lines in Fig. 1. The terms ϵ_i are the frequencies of the absorption lines which excite the various series, relative to $F(0)=18307.50$. The terms d_i are the doublet intervals in the zero order, taken from the absorption measurements. Mecke's γ_i's have been retained as they are large enough to have been determined with accuracy. Kratzer and Sudholt published values of η_i, which represents the decrease of the doublet separation in higher orders, and computed the constant B_0'' from them, though only to perhaps 20 percent. But, because it is

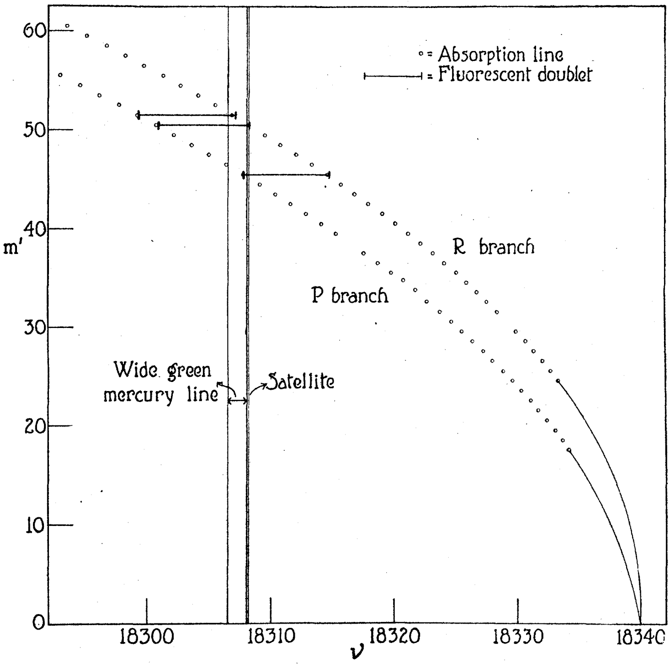

Fig. 6. Relation of the interpolated zero order fluorescent doublets of the three new series to band (29,1).

TABLE V

Constants of the fluorescent series

	From fluorescence		From absorption			
	Empirical		Empirical		Theoretical	
Series	γ	η	ϵ	d	γ(Eq. 12)	$\eta = d\alpha''/B_0''$
ν_0	0.00	.025 ± ?	−0.53	+ 4.40	−0.02	.014
$\nu_0{}^*$	0.00		+0.26	+ 4.28	−0.03	.013
ν_1	0.66	.062 ± .015	−0.68	+12.00	0.66	.039
ν_2	1.33	.052 ± .006	−0.18	+16.13	1.30	.052
ν_3	1.95		−0.53	+19.26	1.91	.062
$\nu_0{}'$	0.00	.021 ± .003	0.00	− 5.14	0.00	.017
$\nu_0{}^{*\prime}$	0.00		−0.83	− 5.31	0.01	.017
$\nu_1{}'$	0.75		+0.45	−12.73	0.72	.041
$\nu_3{}'$	2.2		+0.26	−19.9*	2.00	.064
$\nu(29{,}45\frac{1}{2})$	1.39		+0.26	+ 6.78	1.32	.022
$\nu(29{,}50\frac{1}{2})$	1.38		+0.70	− 7.50	1.35	.024
$\nu(29{,}51\frac{1}{2})$	1.35		−0.68	− 7.63	1.36	.025

*from fluorescence.

possible to make somewhat better estimations of the variation in the doublet interval, now that the doublet interval of zero order is precisely known, the writer has thought it worth while to repeat their calculations. The intervals of all fluorescent doublets, of which both members can be assigned to series without ambiguity, are plotted against p in Fig. 7. The lines which represent them have been put through the zero order $\Delta\nu$'s as measured in absorption and their slopes, η, determined by least squares. Nevertheless the mean value of $B_0'' = \alpha'' d_i/\eta_i$ calculated from

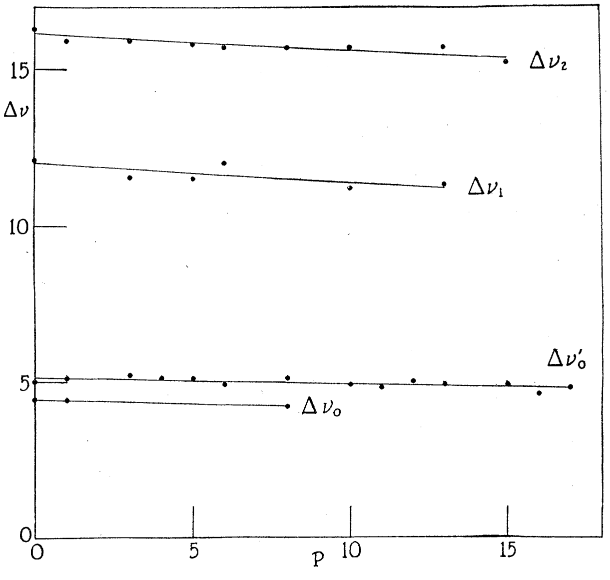

Fig. 7. Revised determination of η.

them, using the revised $\alpha''=0.00012$, is 0.031 ± 0.003 and differs by twice its probable error from that in (15).

The results of the absorption measurements may now be used to calculate theoretically the constants of the fluorescent series. The d's and ϵ's have, of course, already been taken from absorption data. The γ's can be calculated from Eq. (12), taking the $\bar{m}$'s from column 4 of Table III, using the revised $\alpha''=0.00012$, and setting $\bar{n}_i-\bar{n}_0'=0$ for all Mecke's series. For the new series extending to the -1 order, $\bar{n}-\bar{n}_0'=1$; and $2\omega_0''x''$ can be taken from comparison of (4) with (3) as 1.19. The γ's so calculated are given in column 6 of Table V, and are in excellent agreement with the observed values in column 2. The η's calculated from the equation[17,18]

$$\eta = d\alpha''/B_0'' \tag{17}$$

are given in column 7 and the agreement with observation is about as good as could be expected in a quantity so difficult to measure.

The first published estimate of the important constant B_0'', which yields the moment of inertia of the unexcited iodine molecule, was Kratzer and Sudholt's value 0.032, based on the inaccurately determined quantities η_i. This was bettered by Kemble and Witmer who showed that it could be calculated from the quantities d_i, γ_i and α'' which are more accurately known. They published a weighted mean value of $B_0''=0.0343$, computed from Mecke's original d_i's (2) and α''. The writer[24] has also calculated this quantity with essentially the same equations as Kemble and Witmer, but using the revised α'' and values of d_i, which had been revised in accordance with the identification, on Wood's absorption spectrum reproduction, of the main lines of the zero order fluorescent group. The values calculated from the various fluorescent series agree well among themselves and the mean value, $B_0''=0.0367$ is probably as good a one as can be extracted from the data already published by Wood and Mecke.

Of course the value $B_0''=0.037300$ found from the writer's measurements of Wood and Klingaman's new absorption plates is very much more precise, but this also depends on the fluorescent spectrum, which furnished the clues without which the absorption spectrum could not have been unravelled.

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[24] For the equations and details of this calculation the reader is referred to the writer's Chap. VI of the National Research Council Committee report on "Molecular Spectra in Gases." The precision gained by using the revised d_i's is particularly apparent on comparing the discordant values of m''_H calculated by Kemble and Witmer and given in their Table III, with those in Table III of Chap. VI.

The most important conclusion of this paper is that the complex fluorescent spectrum excited by the quartz arc confirms, in every detail, the theory advanced by Lenz to account for the simple spectrum excited by the Cooper Hewitt arc.

New York University,
Sept. 18, 1926.