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NOTE ON THE INTERPRETATION OF WOOD'S IODINE RESONANCE SPECTRUM[1]

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Abstract

The paper describes a re-analysis of the resonance series described by Mecke, using the formulas developed by Kratzer and Sudholt. The series are correlated with the absorption bands near the exciting mercury line. The recomputed values of the moment of inertia for the normal state ($n=0$) and for the excited electronic level ($n=26$ to 29) are 8.1×10^{-38} gm. cm^2 and 12.5×10^{-38} gm. cm^2 respectively. The origin of these bands is very close to the head, the value of m'' for the head being 1.81.

Introduction

In A valuable recent paper Kratzer and Sudholt[2] have supplied theoretical formulas for the series in Wood's iodine resonance spectrum (as excited by the green mercury line λ5460). These formulas are based on the Lenz[3] theory of the origin of the spectrum. Using the empirical analysis of the series previously published by Mecke[4] they have applied the formulas to the verification of the Lenz theory and the evaluation of the moment of inertia of the iodine molecule. The present paper is an extension and partial revision of their work.

When the exciting mercury line is very narrow, the fluorescent spectrum consists, as is well known, of a series of narrow doublets spaced at approximately equal intervals on a frequency scale and extending from the exciting line down into the red. This series has been designated the "fundamental series" of doublets. When the exciting line is broadened other series of doublets are brought out in most of which the separation of the components of any pair, $\Delta\nu$, is greater than for the fundamental series. One member of the first doublet in each series is covered by the broad exciting line and, as the interval between successive doublets is approximately the same for all the series, the corresponding pairs unite to form definite groups of lines. The "order" of any such group or of any doublet in the group is defined as the number of the group or pair counted from the exciting line as zero. It is designated by the letter p.

According to the Lenz theory, each series is due to the stimulation of

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[1] Cf. abstract of paper No. 37 Washington meeting, American Physical Society, April 23. 1926. [Phys. Rev. **27**, 802, June 1926].

[2] A. Kratzer and E. Sudholt, Zeits. f. Physik **33**, 144 (1925).

[3] W. Lenz. Phys. Zeits. **21**, 991 (1920).

[4] R. Mecke. Zeits. f. Physik **7**, 74 (1921); Ann. d. Phys. **71**, 127 (1923).

a single line in the absorption spectrum and consequent projection of molecules into a definite excited state with a definite vibrational quantum number n' and a definite rotational quantum number j'. The fluorescent spectrum is emitted by the molecules in returning to the various vibrational and rotational sub-levels of the original electronic level. The various orders are due to the various possible values of the final vibrational quantum number n'' and the two components of each doublet are due to the two possible final rotational quantum numbers permitted by the principle of selection

$$j''=j'\pm 1 \tag{1}$$

If we denote the vibrational quantum number of the initial state for the primary absorption process by $\bar{n}$ and the corresponding quantum number for the final state of the secondary emission process by n'', the Lenz theory requires that

$$p=n''-\bar{n}$$

The fact that doublets rather than triplets or single lines are observed is taken to indicate that the absorption bands consist of P and R branches only.

Fig. 1 shows schematically the Fortrat diagrams of absorption bands near the exciting mercury line plotted on the assumption that they are of the same simple type as the cyanogen bands but with the origin very close to the head. This latter assumption will be justified later. The

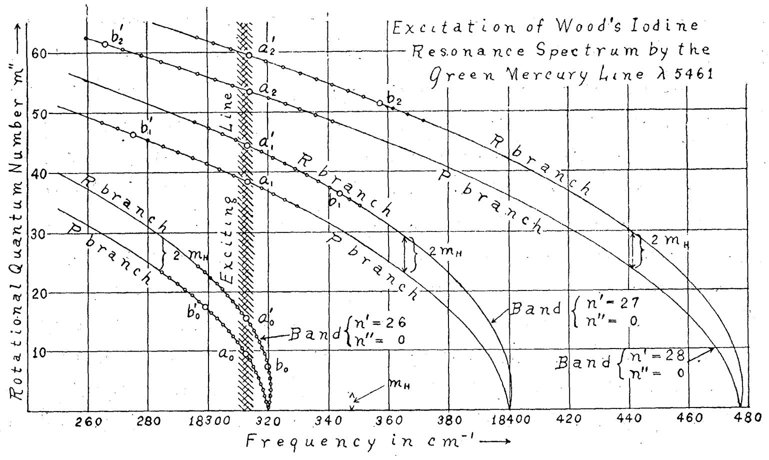

Fig. 1. Schematic Fortrat diagram showing part of the absorption spectrum of iodine in the neighborhood of the green mercury line λ 5461 and its relation to the high and low frequency doublets (indicated by large circles) of order zero in the iodine resonance spectrum excited by λ 5461. The location of the band heads is taken from Mecke's data, but in order to avoid confusion the individual lines are spaced about twice as far apart as in the actual spectrum.

diagram should aid the reader in visualizing the relation of the doublets of order zero to the absorption bands with which they are correlated.

One member of each doublet of order zero coincides with an absorption line and lies under the broad exciting mercury line. The corresponding member of every doublet is called the main line. The other member is called the companion line. If the absorption line is in a P branch, the main lines of all doublets in the given series are also P branch lines, while the companion lines must belong in R branches. In this case each companion line will lie on the high frequency side of the associated main line. Such doublets will be called high frequency doublets. On the other hand, if the primary absorption line lies in an R branch each companion line will lie on the low frequency side of the associated main line, giving what we shall call a low frequency doublet. If the exciting line covers one R branch line and one P branch line in any given absorption band, this band should give rise to two series of doublets with about the same interval between components, but with the companion line in one case on the violet side of the main line, in the other case on the red. Thus the fluorescent series should (and empirically do) occur in pairs. Fig. 1 shows clearly that the doublet interval for any series depends on the distance from the center of gravity of the doublet of order zero to the origin of the corresponding absorption band. Hence doublets originating in bands whose origins are not too close together are easily distinguished. It is therefore convenient to designate the series (usually two) associated with any one band by a common subscript, i, indicating the relative frequencies of the main line and companion line with a prime. Thus $\nu_i'(p)$ in Mecke's notation denotes the frequency of the *low* frequency doublet of order p associated with a band i, the companion line lying on the low frequency side of the main line. $\nu_i(p)$ denotes the frequency of the doublet of order p in a second series associated with the same band i in which the companion line lies on the *high* frequency side of the main line. The necessity of using separate symbols for the frequencies of the two components of a doublet is avoided by adding in brackets the value of the doublet interval to the formula for the frequency of the main line of each series. Thus the empirical frequency formulas published first by Mecke and revised by Kratzer and Sudholt are as shown in Table I. Here $F(p)$ denotes the expression for the frequency of the main line of

TABLE I

$\nu_0 = F(p) \qquad +(3.90-0.0175p)$	$\nu_0' = F(p) \qquad -(5.20-.0231p)$
$\nu_0^* = F(p) \qquad +(4.5 \text{———})$	$\nu_0^{*\prime} = F(p) \qquad -(6.0 \text{———})$
$\nu_1 = F(p)+0.66p+(11.70-0.0386p)$	$\nu_1' = F(p)+0.75p-(12.5 \text{———})$
$\nu_2 = F(p)+1.33p+(16.08-0.0573p)$	$\nu_2' = F(p)+1.5p-(?)$
$\nu_3 = F(p)+1.95p+(19.0 \text{———})$	$\nu_3' = F(p)+2.2p-(19.7 \text{———})$

the fundamental series (also designated as ν_0'). The frequency of the main line is obtained in each case by omitting the terms in parentheses.

The empirical formulas show that the doublet interval decreases linearly with the order p while the main lines of the different series, coincident, or nearly so, in the zero order, spread apart with increasing order. They also indicate that four bands are concerned in the stimulation of these ten series. There are many lines recorded in Wood's observations which are not included in these strongest series.

THE THEORETICAL FORMULAS OF KRATZER AND SUDHOLT

The general form of the above expressions for the resonance spectrum frequencies is

$$\nu_i = F(p) + \gamma_i p + (d_i - \eta_i p) \tag{2}$$

Kratzer and Sudholt find that (2) is in accordance with the Lenz theory and have derived theoretical expressions for $F(p)$ and for the constants γ_i, d_i, η_i. Their work is based on the band spectrum term formula

$$\begin{aligned} T = E/hc &= E^e + n\omega^0 - n^2x + B_n m^2 \\ &= E^e + n\omega^0 - n^2x + (B_0 - \alpha n)m^2 \end{aligned} \tag{3}$$

Here E^e denotes the electronic energy in wave numbers, ω^0 is the vibrational frequency for small amplitudes in wave numbers, and x/ω^0 is to be identified with the vibrational energy constant "x" in the usual band spectrum notation. B_0 is the rotational energy constant $h/8\pi^2Ic$ evaluated for the vibrationless state and expressed in frequency units. α has its usual meaning. m denotes the effective nuclear rotational quantum number, which is related to the true rotational quantum number j and the components of the electronic angular momentum σ and ϵ by the formula

$$m = \sqrt{j^2 - \sigma^2} - \epsilon \tag{4}$$

We shall not concern ourselves here with the theoretical expression for $F(p)$ except to note that the values of ω^0 and x for the lower electronic level may be derived from it.* The formulas for the constants γ_i, d_i, η_i are

$$\gamma_i = 2x''(\bar{n}_i - \bar{n}_0) + \alpha''(\bar{m}_i^2 - \bar{m}_0'^2) \tag{5}$$

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* On the assumption that the initial vibrational quantum number $\bar{n}_0$ for the primary absorption process is 4 for the fundamental series Kratzer and Sudholt get

$$\omega^{0\prime\prime} = 218.304$$
$$x'' = 0.567$$

(Throughout this paper molecular constants associated with the upper electronic level are indicated by a prime while those for the lower electronic level are indicated by a double prime.) They base this assumption on the occurrence of fluorescent lines of order -4 (anti-Stokes terms) in some of Wood's photographs. Professor Loomis has suggested, however (private communication) that none of the anti-Stokes terms belong to the fundamental series as they do not appear in the spectrum obtained with narrow line excitation nor do their frequencies fit the formula for the fundamental series. It seems

$$d_i=(B_0''-\alpha\bar{n}_i)s_i \tag{6}$$

$$\eta_i=\alpha''s_i \tag{7}$$

Here all the constants ω_0'', x'', α'', B_0'' refer to the lower electronic level or normal state of the molecule. $\bar{n}_i$ and $\bar{m}_i$ are the vibrational and rotational quantum numbers for the initial state for the absorption line which stimulates the ith series. s_i is defined in terms of the difference δ between the values of m'' for the final states concerned in the emission of the two components of any doublet.

$$s_i=-(2\delta\bar{m}_i+\delta^2) \tag{8}$$

The quantity δ is treated by Kratzer and Sudholt as an unknown quantity. They eliminate s_i between Eqs. (6) and (7) and taking a value of α determined by Mecke from his partial analysis of some of the absorption bands in the red, evaluate B_0'' from the empirical constants d_i and η_i. Then on the assumption that $\bar{n}_i-\bar{n}_0$ in Eq. (5) is always zero, they compute δ from (5) and (6) and (8). The values for δ obtained in this way are essentially consistent and support the hypothesis that $\bar{n}_i-\bar{n}_0$ is zero. Thus, for those doublets whose main lines belong to P branches, they get the values -2.23; -2.21; -2.19 for δ. For the doublets whose main lines belong to R branches $+2.09$ and $+2.08$.

REEVALUATION OF B_0 AND THE MOMENT OF INERTIA

The starting point of the present revision of the analysis of Kratzer and Sudholt is the observation that theoretically δ should be exactly ± 2. In justification of this statement we note that when bands consist of P and R branches only there is a strong theoretical presumption that σ is zero for both initial and final states. This presumption is borne out by the behavior of such bands near the origin which fits with the simple term formula

$$\frac{E_{rot}}{hc}=B_nm^2=(B_0-\alpha n)(j-\epsilon)^2 \tag{9}$$

In any case the simple term formula (9) is approximately correct for large rotational quantum numbers. Then, if the lower electronic level is single, the value of ϵ for the final state is the same for both branches and

$$|\delta|=(j'+1-\epsilon)-(j'-1-\epsilon)=+2 \tag{10}$$

If the lower electronic level were multiple, we should expect that fact to show itself in a complication of the fluorescent spectrum. Hence the

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likely, therefore, that we should interpret the absence of anti-Stokes terms in this series as proof that $\bar{n}_0$ is equal to zero so that n'' is identical with p. (If half integral vibrational quantum numbers are used, $\bar{n}_0$ is one half and n'' is p plus one half). The corrected values of $\omega^{\circ\prime\prime}$ and x'' are then $\omega^{\circ\prime\prime}=213.667$; $x''=0.592$.

presumption in favor of (10) is strong and we may reasonably attempt to interpret the spectrum on this basis.*

If δ is equal to ± 2, we may redetermine B_0'' by a method more accurate than that of Kratzer and Sudholt, which depends on the poorly known empirical constants η_i. With Kratzer and Sudholt we assume that for the series analyzed by Mecke $\bar{n}_i = \bar{n}_0$. In other words we suppose that the absorption bands whose stimulation is associated with these series all belong to a single n' progression. (In view of the footnote on page 636 we may give $\bar{n}_i$ the value zero, thus identifying the n' progression with that due to absorption by molecules having initially zero vibrational energy.) The assumption that $\bar{n}_i$ is equal to $\bar{n}_0$ is really forced by the fact that the coefficient of $\bar{n}_i - \bar{n}_0$ in (5) is so large that zero is the only value of $\bar{n}_i - \bar{n}_0$ consistent with the observed values of γ_i. Eqs. (5) and (6) then become

$$\gamma_i = \alpha''(\bar{m}_i^2 - \bar{m}_0'^2) \tag{11a}$$

$$d_i = -4B_0''(\pm \bar{m}_i + 1) \tag{11b}$$

(The upper sign is associated with the low frequency doublets (ν_i') and the lower sign with the high frequency doublets ν_i.) (11b) yields the value $-(d_i/4B_0'' + 1)$ for $\bar{m}_0'$. Eliminating $\bar{m}_i$ and $\bar{m}_0'$ from the above equations and solving for B_0'' we obtain

$$B_0'' = \frac{\alpha''(d_i - d_0')}{4\gamma_i}\left\{1 \pm \sqrt{\frac{\gamma_i}{\alpha''}\left(\frac{d_i + d_0'}{d_i - d_0'}\right) + 1}\right\} \tag{12}$$

Table II shows the values of B_0'' calculated from (12). The weighted mean is 0.0343 cm^{-1}.

TABLE II

i	1	1′	2	3	3′
B_0''	.0345	.0342	.0350	.0346	.0334

The values computed by Kratzer and Sudholt from d_i and η_i were 0.0333; 0.0309; 0.0245; 0.0248 with a weighted mean of 0.032 cm^{-1} which is seven percent lower than the result of our calculation. As Kratzer and Sudholt estimate the probable error in the determination of η_i as ± 20 percent, it will be evident that the change of seven percent in the value B_0'' (and hence in η_i) required by the new computation is not inconsistent with the experimental values of η_i.

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* As a matter of fact, we know of no type of band found empirically to date whose fluorescent spectrum would consist of doublets like that of iodine and for which δ would not be ± 2.

CORRELATION OF RESONANCE SERIES WITH ABSORPTION BANDS AND ESTIMATION OF B'

Having evaluated B_0'' we may now compute from (6) and (8) approximate values of $\bar{m}_i$ for each series. Thus setting $\bar{n}_i$ equal to zero as before,

$$\bar{m}_i = \pm\left(\frac{d_i}{4B_0''}+1\right) \tag{13}$$

where the upper sign refers to the high frequency doublets. The difference between the values of $\bar{m}_i$ for the high and low frequency doublets associated with any given band locates approximately the rotational quantum number of the band head which we shall designate as m_H and hence the coefficient of the quadratic term in the frequency formula, $B'-B''$[*]. The frequency formula is

$$\nu=\nu_0\pm 2B'm+(B'-B'')m^2 \tag{14}$$

where m is the rotational quantum number for the lower electronic level.

$$m_H=\frac{B'}{B''-B'} \tag{15}$$

Now $\bar{m}_i$ and $\bar{m}_i'$ are the m-values for two lines (a_i and a_i' in Fig. 1), one in the P branch and the other in the R which lie under the exciting line and hence have approximately the same frequency. Subtracting the corresponding frequency equations from each other, we obtain

$$\bar{m}_i'-\bar{m}_i=2m_H \tag{16}$$

This equation is also easily derived graphically. Table III shows the values of $\bar{m}_i$ and m_H computed from (13) and (16).

TABLE III

i	$\bar{m}'_i$	$\bar{m}_i$	m_H
0	36.9	29.4	3.75
0*	42.7	33.8	4.45
1	90.1	86.3	1.90
2		118.2	
3	142.6	139.5	1.55

In view of the fact that, although the exciting line is quite broad, we are neglecting the differences in frequency between the absorption lines which fall under it, the agreement between the various values of m_H is satisfactory. Discrepancies between ν_i and ν_i' are more serious for the narrow doublets, so that the values of m_H computed from the series 1 and 3 are more accurate than those from series 0 and 0*. The weighted mean value of m_H is 2.26. The corresponding value of $B''-B'$ is .010 cm^{-1}[†]

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[*] Here $B'=B'_0-\alpha'n'$. For the absorption bands under consideration n' is about 26. n'' is zero, however, so that $B''=B''_0$.

[†] Mecke gives the value 0.007 for $B''-B'$ evaluated for a double series of absorption lines associated with the absorption head $n'=26$, $n''=0$ nearest the exciting line. There is apparently an error in this value, however, for it does not check with values of $B''-B'$ measured by him for certain bands of the same system lying in the red.

The small value of m_H shows that in these bands the origin is very close to the head. This partially accounts for the fact that Mecke was led by his partial analysis of the bands in the red to the tentative conclusion that the bands were really single Q branches instead of P and R branches as required by the Lenz theory.

Mecke has made the interesting observation that the observed values of γ_i and γ_i' are approximately integral multiples of γ_1 and γ_1'. Thus $\gamma_i=i\gamma_1$; $\gamma_i'=i\gamma_1'$ very nearly, as is evident on inspection of Table I. This is explicable as a result of the fact that the absorption bands associated with the various values of i form an approximately equidistant series. (We have already given reasons for believing that these bands belong to Mecke's n' progression I for which $n''=0$.)

Let ν_{ex} denote the frequency of the exciting mercury line which is approximately equal to the frequency of the main line of order zero for each series. This frequency is given by (14) if we insert the appropriate value of ν_0 (frequency of band origin) and give m the value $\bar{m}_i$. Let $\nu_0{}^{(i)}$ denote the origin of the band i. Then,

$$\begin{aligned}\nu_{ex}&=\nu_0{}^{(i)}-2B'\bar{m}_i+(B'-B'')\bar{m}_i{}^2,\\ &=\nu_0{}^{(i)}+2B'\bar{m}_i'+(B'-B'')\bar{m}_i'^{\,2}.\end{aligned}\tag{17}$$

Hence

$$\begin{aligned}\nu_0{}^{(i)}-\nu_0{}^{(0)}&=2B'(\bar{m}_i+\bar{m}_0')+(B''-B')(\bar{m}_i{}^2-\bar{m}_0'^{\,2})\\ &=-2B'(\bar{m}_i'-\bar{m}_0')+(B''-B')(\bar{m}_i'^2-\bar{m}_0'^2)\end{aligned}\tag{18}$$

But $\bar{m}_i{}^2-\bar{m}'_0{}^2$ is equal to γ_i/α''. Hence

$$\begin{aligned}\gamma_i&=\frac{\alpha''}{(B''-B')}[\nu_0{}^{(i)}-\nu_0{}^{(0)}-2B'(\bar{m}_i+\bar{m}_0')]\\ \gamma_i'&=\frac{\alpha''}{(B''-B')}[\nu_0{}^{(i)}-\nu_0{}^{(0)}+2B'(\bar{m}_i'-\bar{m}_0')]\end{aligned}\tag{19}$$

Now if the bands form an equidistant series, $\nu_0{}^{(i)}-\nu_0{}^{(0)}$ will be equal to i times the spacing of this series. The terms linear in B' are comparatively small. Hence Eqs. (19) account for the approximate integral relationship noted by Mecke.

These equations may also be used to locate $B''-B'$ and m_H more accurately. For this purpose it is convenient to add them. Then we obtain

$$\gamma_i+\gamma_i'=\frac{2\alpha''}{B''-B'}\left[(\nu_0{}^{(i)}-\nu_0{}^{(0)})+B'\{\bar{m}_i'-\bar{m}_i-2\bar{m}_0'\}\right]$$

Replacing $\bar{m}_i'-\bar{m}_i-2\bar{m}_0'$ by $-(\bar{m}_0+\bar{m}_0')$ (cf. Eq. (16)) and B' by $B''-(B''-B')$ we obtain

$$B''-B'=\frac{2\alpha''[(\nu_0{}^{(i)}-\nu_0{}^{(0)})-B''(\bar{m}_0+\bar{m}_0')]}{\gamma_i+\gamma_i'-2\alpha''(\bar{m}_0+\bar{m}_0')} \tag{20}$$

The frequency difference between the origins $\nu_0{}^{(i)}-\nu_o{}^{(0)}$ may be identified with the frequency differences of the heads which are given by Mecke. The first head in the band series $n''=0$ which lies on the violet side of the green line is that to which Mecke assigns the quantum number $n_a=n'=26$. This is to be correlated with the zero value of i and the succeeding heads for which n' takes on the values 27, 28, 29 are to be correlated with the values 1, 2, 3 for i respectively. Table IV shows the result of the computation of $B''-B'$ from Eq. (20). The agreement between the computed values is excellent, as was to be expected, in view of the fact that the calculation rests primarily on the constants γ_i which are the most accurately determined constants in Mecke's formulas for the resonance series.

TABLE IV

i	$\nu_H{}^{(i)}$	$\nu_H{}^{(i)}-\nu_H{}^{(0)}$	$\gamma_i+\gamma_i{}^1$	$B''-B'$
0	18320.91			
1	18400.19	79.28	1.41	.01214
2	18478.21	197.30	2.83	.01212
3	18553.34	232.43	4.15	.01225
		Weighted	mean =	.0122

Combining the revised value of $B''-B'$ (or $B_0''-B'$) with the value B_0'' previously determined, we obtain

$$B'=.0343-.0122=.0221$$

$$m_H=\frac{B'}{B''-B'}=1.81$$

The agreement between this value of m_H and the values in Table III is quite satisfactory and constitutes a check on our correlation of the resonance series and the absorption heads.

The moments of inertia and internuclear distances characteristic of the two electronic levels of the molecule deduced from our values of B_0'' and B' are

$$I_0''=8.1\times10^{-38}\,\mathrm{g.cm^2}\,; \quad I'=12.5\times10^{-38}\,\mathrm{g.cm^2}$$

$$r_0''=2.78\times10^{-8}\,\mathrm{cm}\,; \quad r_0'=3.5\times10^{-8}\,\mathrm{cm}$$

The quantities B', I', r_0' do not refer to the vibrationless state of the upper electronic level, but are mean values for the vibrational quantum numbers 26 to 29.

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