

## IODINE RESONANCE SPECTRA EXCITED BY THE YELLOW MERCURY LINES

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## ABSTRACT

The resonance spectra of iodine vapor in vacuum excited by the two yellow mercury lines from the Cooper-Hewitt glass lamp have been analyzed. The spectra excited by the yellow line at 5771.2Å is found to consist of a series of doublets the main lines of which conform closely to the formula set up by Mecke from Wood's experimental data. No anti-Stoke's lines were observed to be excited by this excitation.

The excitation by the yellow line at 5792.3Å was found to be much more complicated, consisting of three series of doublets one of which shows two anti-Stoke's members; and another shows one anti-Stoke's member. The remaining series did not show any anti-Stoke's members; however the zero order of this series is also missing on the photographic plates.

It is calculated that the molecules giving rise to the series having two, one, and no anti-Stoke's members must have vibrational energy in the unexcited state as represented by the quantum numbers  $\bar{n} \geq 2, 1, \text{ and } 1$  respectively. Then by further calculating the positions of the heads of the bands of which the excited lines are members, it is seen that there are band heads sufficiently close to these calculated values, having values of 2, 1, and 1 respectively for  $\bar{n}$ , but none sufficiently close having other possible values for  $\bar{n}$  greater than these.

## INTRODUCTION

THE resonance spectrum of iodine vapor is of great theoretical interest because of its aid in perfecting the modern quantum theory as applied to complicated band spectra. The reason for this is that the absorption spectrum of iodine is very complicated, consisting of many overlapping bands, the individual lines of which appear crowded together to the extent of about 20 lines to the Angstrom unit throughout the region from about 5000Å to about 7700Å; whereas the resonance spectrum excited by monochromatic light is very simple, consisting of a series of doublets of approximately constant doublet width and doublet separation, when expressed in frequencies. In addition to the Stokes members of the doublet series (i. e. doublets of greater wave-length than that of the exciting light), there have been observed by Wood,<sup>1</sup> Pringsheim<sup>2</sup> and the writer various anti-Stokes members, i. e. members of shorter wave-length than that of the exciting light. Wood and Pringsheim used for monochromatic excitation the green mercury line, and it was found by Loomis<sup>3</sup> that none of the anti-Stoke's members thus excited belonged to any of the doublet series formulated by Mecke from the work of

<sup>1</sup> R. W. Wood, *Phil. Mag.* **26**, 828-848 (1913); *Phil. Mag.* **35**, 236-252 (1918); *Researches in physical Optics*, Part 2, 1919. R. W. Wood and M. Kimura, *Phil. Mag.* **35**, 252-261 (1918).

<sup>2</sup> P. Pringsheim, *Zeits. f. Physik.* **7**, 206-216 (1921); **8**, 126-131 (1921).

<sup>3</sup> F. W. Loomis, *Bulletin of the National Research Council*, No. 57, Chap. VI, "Fluorescent Band Spectra," Dec. 1926.

Wood and Pringsheim. More recently, however, Loomis<sup>4</sup> has shown that these anti-Stoke's members, together with a few previously unassigned Stoke's members, appear to form the skeleton of three other plausible series not formulated by Mecke. However, since these three new series of Loomis' are too short and incomplete to allow accurate analysis to be made of them, and accurate deductions drawn as to the origin of anti-Stoke's lines, it was the purpose of this work to find series of sufficient length and completeness containing both Stoke's and anti-Stoke's doublet members.

#### EXPERIMENTAL METHOD

The experimental method consisted in photographing the fluorescent light of iodine vapor when excited by various monochromatic radiations. The resonance tube consisted of a glass tube about 3 cm in diameter and about 50 cm long, one end of which was blown out as an optically clear bulb, care being taken to have no part of this bulb acting as a lens when the fluorescent light was observed end-on through this bulb. The other end of the tube was drawn off to a point and was then painted black on the outside so as to give a black background for observations. A side tube was added near the bulb so that the density of the iodine vapor could be controlled independently of the temperature of the larger resonating portion of the tube. This tube was then pumped to a high vacuum while being heated continuously in a Bunsen flame while the iodine crystals were stored away in the cool side tube attached to the resonance tube. After being sufficiently evacuated and baked, the resonance tube was sealed off from the vacuum system, whereupon the vapor from the iodine crystals in the side tube diffused throughout the tube. Since relatively high dispersion was necessary in order to resolve the fluorescence spectra and since the fluorescence light of iodine, even under the best circumstances, is relatively weak, though readily discernible by the eye, it was desirable to select as a source of monochromatic excitation some source which could be run as long as desired without attention. To fulfill this requirement the commercial mercury arc in glass was chosen and in order to obtain as intense an excitation as possible the resonance tube was surrounded closely by a battery of four of these mercury lamps. The lamps used were the Cooper-Hewitt vertical type with automatic starting band and auxiliary apparatus (i.e. the lamps are started without tilting as was necessary in the old type lamps). The glass lamp was chosen instead of the quartz one because the former operates at a lower temperature than the latter and hence emits the sharper lines. But the mercury arc contains three lines sufficiently strong to excite fluorescence, these three lines being the green one at 5462.23A, and the two yellow ones at 5771.2A and at 5792.3A (all wave-lengths reduced to vacuum). Since, then, three doublet series would be excited simultaneously by direct excitation with the mercury arc, it was desirable to filter out by a suitable absorption screen, the series not of current interest. To screen out the green light, which as will be seen later is not of current interest, without cutting out the yellow lines

<sup>4</sup> F. W. Loomis, *Phys. Rev.* **29**, 112-134 (1927).

also, the resonance tube was wrapped completely (with the exception of the bulb through which the resonance spectra was observed) in sheets of gelatin impregnated with eosin.

The complete set-up then consists of a battery of four Cooper-Hewitt 20-inch glass lamps of the vertical type, mounted upon a permanent stand and placed at the corners of a square, at the center of which was placed vertically the resonance tube wrapped with the eosin-gelatin sheets, thereby receiving its excitation through its cylindrical wall. Just above the resonance tube and on its vertical axis, was a right-angled prism so placed as to reflect the fluorescence light from the resonance tube into a horizontal direction on to the slit of the spectrograph. Between this right angled prism and the slit was placed a lens in such a position as to focus the fluorescence light upon the slit. In order to minimize the amount of scattered mercury light from the lamps reaching the slit, the prism and the bulb were kept clean and two black screens with circular apertures were placed, one over the upper ends of the mercury lamps, its aperture being over the resonance bulb, the other one vertically in front of the vertical face of the prism. The aperture in the latter screen was much the smaller of the two. The spectrograph had a dispersion of about 16.5Å per mm of photographic plate, the plate being 5 inches long. A comparison spectrum of the iron arc was put on each exposed plate. The density of the iodine vapor was regulated by keeping the end of the side arm of the resonance tube in a thermos bottle containing water at the desired temperature.

The resonance spectra by excitation with the green mercury line has already been intensively investigated, the experimental work having been done by Wood, using both glass and quartz mercury arcs for excitation. All of the series excited by the broad green mercury line from the quartz arc operating at high voltages, as well as the series excited by the sharp line emitted by the relatively cold glass mercury arc have been formulated by Wood,<sup>1</sup> Mecke,<sup>5,6</sup> Kratzer and Sudholt<sup>7</sup> and Loomis.<sup>3,4</sup> It has been found that all of these series of Stokes members originally formulated by Mecke are characterized by having the same value for the vibration quantum numbers in the unexcited state (the common quantum number being probably zero) and that none of the anti-Stokes members fit into any of these formulated series of Stokes members. Loomis, more recently, has found fragments of three more plausible series to which the anti-Stokes members apparently belong. Since the green mercury line excitation has already been intensively investigated without showing with sufficient completeness series containing both Stokes and anti-Stokes lines, the writer then studied the excitation by the yellow mercury lines.

A reproduction of the resonance spectra excited by the glass mercury arc with the green line screened from the exciting light by the eosin gelatin filter is shown in Fig. 1. Every line appearing on this plate was measured

<sup>1</sup> R. Mecke, *Zeits. f. Physik* **7**, 33-35 (1921).

<sup>6</sup> R. Mecke, *Ann. d. Physik* **71**, 104-134 (1923).

<sup>7</sup> Kratzer and Sudholt *Zeits. f. Physik* **33**, 144-152 (1925).

in Angstrom units and these were then reduced to wave-lengths in vacuum, then converted to frequencies ( $\nu_0$ ) in terms of the reciprocal of the wave-

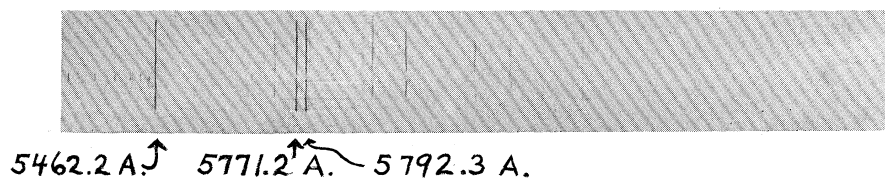


Fig. 1. Resonance spectra excited by the glass mercury arc with the green line excluded by an eosin gelatin filter.

length in vacuum in  $\text{cm}^{-1}$  units. Mecke<sup>6</sup> has already formulated the main lines of the doublet series excited by the 5771.2 line as follows:

$$\nu_M = 17327.4 - 212.82p + 0.592p^2 + 0.0021p^3 \quad (1)$$

where  $p$  is the order of the doublet, specifying the line in coincidence with the exciting line at 17327.4 as the zero order (i.e.  $p=0$ ) and Stokes members

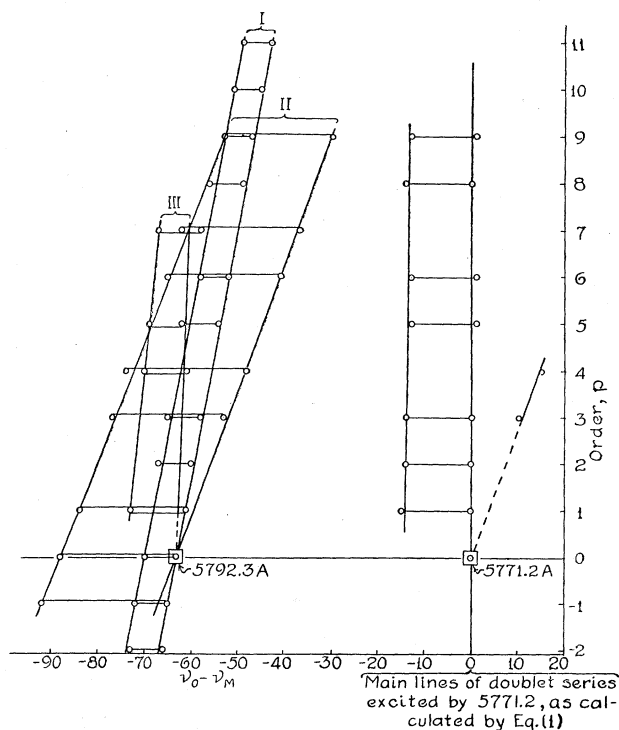


Fig. 2. The frequency difference  $\nu_0 - \nu_M$  as a function of the order number  $p$  for the observed lines in the resonance spectra of iodine.

being positive, anti-Stokes members being negative, and all orders being assigned integral numbers counting successively from  $p=0$ . From this

formula the values of  $\nu_M$  were calculated for every order from  $p = -2$  to  $p = +11$  inclusive. The results are recorded in Table I, along with the difference between these observed  $\nu_0$ 's and the calculated  $\nu_M$ 's for the same order, from Mecke's formula. With this table as a guide, every observed line was plotted as shown in Fig. 2, where the order  $p$  is plotted as ordinate and the difference  $\nu_0 - \nu_M$  is plotted as abscissa. By an inspection of the points as plotted in Fig. 2 it was found that every line observed could be assigned to one of four doublet series with the exception of two lines, one in

TABLE I  
Values of  $\nu_0$  (observed) and of  $\nu_M$  (calculated from Mecke's formula).

Order ( $p$ )	$\nu_M$ (calc. from Mecke's Form.)	$\nu_0$ (Observed)	$\nu_0 - \nu_M$	Order ( $p$ )	$\nu_M$ (calc. from Mecke's Form.)	$\nu_0$ (Observed)	$\nu_0 - \nu_M$
-2	17755.4	17689 17682	-66 -73	+5	16278.3	16279 16265 16224 16216 16209	+1 -13 -54 -62 -69
-1	17540.8	17476 17469 17449	-65 -72 -92	+6	16072.2	16073 16059 16031 16020 16014 16007	+1 -13 -41 -52 -58 -65
0	17327.4	17327 17264 17257 17239	0 -63 -70 -88	+7	15867.3	15830 15809 15805 15800	-37 -58 -62 -67
+1	17115.2	17115 17100 17054 17042 17031	0 -15 -61 -73 -84	+8	15663.7	15664 15650 15615 15608	0 -14 -49 -56
+2	16904.2	16904 16890 16844 16837	0 -14 -60 -67	+9	15461.4	15462 15448 15431 15414 15408	+1 -13 -30 -47 -53
+3	16694.3	16704 16694 16680 16641 16636 16629 16617	+10 0 -14 -53 -58 -65 -77	+10	15260.5	15216 15210	-45 -51
+4	16485.6	16501 16437 16425 16416 16412	+15 -48 -61 -70 -74	+11	15060.8	15018 15012	-43 -49

the 3rd order, the other in the 4th order, both on the high frequency side of  $\nu_M$ , and these two lines appear to be main line fragments of another doublet series excited by 5771.2. From this it is seen that excitation with 5771.2 gives rise to one series of doublets, the main lines of which conform quite accurately to Mecke's formula, and that excitation with 5792.3 gives rise to three series of doublets, one of which, Series I appears to embrace two anti-Stokes doublet members, whereas another one, Series II appears to embrace one anti-Stokes doublet member. The remaining series is much less complete

than the other two, only four members being observed, none of these being anti-Stokes doublet members. It is worthy of mention that in no case was only one-half of a doublet observed except in the case of the zero order of 5771.2, where, however, the companion line may be masked by the scattered light of the exciting line from the mercury lamps. Having thus assigned by the graphical method every line which appears to one of four doublet

TABLE II  
Series of doublets excited by 5771.2.

Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )	Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )
0	5771.2	17327		5	6142.9	16279	14
		missing			6148.0	16265	
1	5842.7	17115	15	6	6221.8	16073	14
	5847.6	17100			6227.0	16059	
2	5915.8	16904	14	7		missing	
	5920.7	16890					
3	5990.1	16694	14	8	6384.0	15664	14
	5995.1	16680			6389.7	15650	
4		missing		9	6467.5	15462	14
					6473.1	15448	

series, these lines were then tabulated as in Tables II, III, IV and V, for comparison with the series of doublets previously reported by Wood to have been excited by the yellow mercury lines. These two series are repro-

TABLE III  
Series I of doublets excited by 5792.3.

Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )	Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )
-2	5653.1	17689	7	5	6163.6	16224	8
	5655.3	17682			6166.8	16216	
-1	5722.1	17476	7	6	6242.2	16020	6
	5724.3	17469			6244.6	16014	
0	5792.3	17264	7	7		missing	
	5794.6	17257					
1		missing		8	6404.2	15615	7
					6406.8	15608	
2	5936.8	16844	7	9	6487.4	15414	6
	5939.1	16837			6490.1	15408	
3	6011.0	16636	7	10	6571.8	15216	6
	6013.3	16629			6574.5	15210	
4		missing		11	6658.6	15018	6
					6661.5	15012	

duced in Tables VI and VII. Comparing Tables II and VI for excitation by 5771.2, it is seen that the present work reports three lines not previously noted, and fails to show any line in the tenth order, whereas the main line

TABLE IV  
Series II of doublets excited by 5792.3.

Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )	Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )
-1	5722.1 5730.9	17476 17449	27	4	6083.9 6093.1	16436 16412	24
0	5792.3 5800.7	17264 17239	25	5	missing		
1	5863.5 5871.8	17054 17031	23	6	6237.9 6247.3	16031 16007	24
2	missing			7	6317.0 6327.0	15830 15805	25
3	6009.2 6017.7	16641 16617	24	8	missing		
				9	6480.4 6490.1	15431 15408	23

TABLE V  
Series III of doublets excited by 5792.3.

Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )	Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )
-1	missing			5	6166.1 6169.3	16218 16209	9
0	missing			6	missing		
1	5863.5 5867.7	17054 17042	12	7	6325.4 6329.1	15809 15800	9
2	missing						
3	missing						
4	6088.3 6091.7	16425 16416	9				

TABLE VI  
Series of doublets excited by 5771.2 (Wood's values)

Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )	Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )
0	5771.2	17327.4	—	5	6143.1	16283.9	—
	missing				missing		
1	5842.5 5847.2	17115.9 17102.2	13.7	6	6222.1 6227.1	16071.7 16058.8	12.9
2	5915.8 5920.2	16903.9 16889.6	14.3	7	6303.5	15864.1	—
					missing		
3	5990.0 5995.1	16694.5 16680.3	14.2	8	missing		
4	missing			9	6467.9 6473.2	15460.9 15448.3	12.6
				10	6553.0	15260.2	—
					missing		

of the doublet in this order was previously reported and is found to be properly located in this series. Since no anti-Stokes members were found to

be excited in either case by 5771.2, this excitation is of no further interest here. Concerning the series excited by 5792.3 it is seen that series Number I most nearly corresponds to the series previously reported. This previously reported series, however, showed such lack of regularity that it was remarked at the time that though "the doublets are present in all order, the difference

TABLE VII  
Series of doublets excited by 5792.3 (Wood's values).

Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )	Order ( $p$ )	$\lambda$	$\nu$	Doublet Width ( $\Delta\nu$ )
-2	5658.6	17672.2	5.3	4	6084.3	16435.7	10.8
	5660.3	17666.9			6088.3	16424.9	
-1	5722.1	17476.1	3.4	5	6163.9	16223.5	5.8
	5723.2	17472.7			6166.1	16217.7	
0	5792.3	17264.4	16.8	6	6242.3	16019.7	6.9
	5797.9	17247.6			6245.0	16012.8	
1	5871.3	17032.0	6.1	7	6325.8	15808.3	8.6
	5873.4	17025.9			6329.2	15799.7	
2	5936.8	16844.1	6.1	8	6404.0	15615.2	6.6
	5938.9	16838.0			6406.7	15608.6	
3	6010.8	16636.7	6.9				
	6013.3	16629.8					

between their components vary in a very irregular manner from a minimum of 3.4 to a maximum of 16.8." The present series, however, shows the 1st, 4th, and 7th orders to be missing, those previously reported not belonging to this series but being doublets or fragments of the other two series which are here shown to be excited simultaneously. Furthermore, the 9th, 10th and 11th orders of doublets are observed here, whereas no lines were previously reported in these orders. It will be noted that Series I includes two anti-Stokes doublet members, that Series II includes one anti-Stokes doublet member, and that Series III shows no anti-Stokes member. So it is of interest to determine by theoretical deductions the values of the vibration quantum numbers of the molecules in the unexcited state, which give rise to these three series, and to note how these deductions compare with the observed number of anti-Stokes members in each of these series.

#### THEORETICAL DEDUCTIONS

(a) *Introductory.* The band spectra have been long known to be emitted by the molecule and not by the atom. The energy in the molecule is due to three things, namely: (1) its electrons, (2) the vibration of its nuclei, and (3) the rotation of the entire molecule as a single unit. Letting  $E$  represent energy, and letting  $e$ ,  $n$ , and  $m$  represent the electronic, vibrational, and rotational quantum numbers respectively, it has been deduced by Kratzer that

$$E = E_e + E_n + E_m = E_e + h\omega_0 n(1 - xn) + h(B - \alpha n)m^2, \quad (1)$$



where  $x$  is a function of the binding of the nuclei and would be zero if the vibrations of the nuclei were harmonic; and  $\alpha$  is a function of the deformation of the molecule as a whole due to its rotation and is very small relative to  $B$  which is defined as  $h/8\pi^2J$ , where  $h$  and  $J$  are Planck's constant and the moment of inertia of the molecule about its axis of rotation, respectively.

It has been observed that for the series excited by the green mercury line, which have no anti-Stokes members, the main line of the doublet of zero order of each series coincides with some portion of the exciting line, which therefore shows that the final electronic state of the molecule for every series observed is the same as that of the unexcited molecule. Furthermore, in the case of the series excited by the yellow mercury lines the same is true (the anti-Stokes members are accounted for by an initial vibrational energy other than zero). So hereafter use will be made of the fact that the electronic energy is the same in the final state after emission as in the unexcited molecule. The complicated absorption spectrum indicates that in the unexcited state molecules must exist having various values of vibrational and rotational energy, but when excited to fluorescence by strictly monochromatic light, only those molecules can be excited which have definite values of  $e$ ,  $n$  and  $m$  of such magnitude that the absorption line due to these molecules is in coincidence with the exciting line. So every molecule in the unexcited state which later becomes excited by the monochromatic light has common values of  $e$ ,  $n$ , and  $m$ , and since each of these molecules is excited by the same light, then each molecule will undergo a like change in  $e$ ,  $n$ , and  $m$  in the process of excitation, and so every molecule in the excited state also will have the same values of  $e'$ ,  $n'$  and  $m'$ . But on emission, the changes which take place are limited by the selection principle to  $m' \rightarrow m' + 1$  and  $m' - 1$ . Further, because of the non-harmonic vibrations of the nuclei,  $n'$  can change to any lesser value of  $n$  down to and including  $n'' = 0$ . (The  $(-)$ ,  $(')$  and  $('')$  denote the unexcited, the excited and the final state in the emission of the molecule, respectively.)

(b) *Deductions.* It has been shown by Kemble and Witmer that according to the modern quantum theory of band spectra

$$\bar{m}_i = \mp (d_i/4B_0'' + 1) \quad (2)$$

where  $\bar{m}_i$  is the rotational quantum number in the unexcited state of the molecule giving rise to the series denoted by  $i$ .  $B_0''$  has been calculated by Loomis to be very nearly 0.0373. The width of the doublet in  $\text{cm}^{-1}$  units in the zero order of the  $i$ th series is represented by  $d_i$ . To determine  $d_i$  with the maximum accuracy, use is made of the previously found theoretical expression of Kratzer and Sudhott,  $\Delta\nu_i = d_i - \eta_i p$ , where  $\Delta\nu_i$  is the doublet width in  $\text{cm}^{-1}$  units in the  $p$ th order of the  $i$ th series, and  $d_i$  and  $\eta_i$  are empirically determined constants for any one series. So by measuring the width of each doublet as recorded in Tables III, IV and V and plotting these doublet widths against  $p$ , a straight line is drawn as determined by these plotted points (see Fig. 3) and the ordinate at  $p = 0$  where this straight line intersects it is noted, and is the most correct value for  $d_i$  (see Table VIII,

TABLE VIII  
Values of constants for Series I, II and III.

Series	I	II	III
(1) $d_i$ (from Fig. 3)	-6.8	-24.9	-9.3
(2) $\bar{m}_i$ (calc. by Eq. 2)	48	177	66
(3) $(\nu_k - \nu_i)_p$		$(\nu_I - \nu_{II})_9 = -17$ $(\nu_{II} - \nu_{III})_7 = +21$ $(\nu_{III} - \nu_I)_7 = -7.5$	
(4) $\bar{n}_k - \bar{n}_i$		$\bar{n}_I - \bar{n}_{II} = 1.09$ $\bar{n}_{II} - \bar{n}_{III} = -0.002$ $\bar{n}_{III} - \bar{n}_I = -1.09$	
(5) $(\nu_H - \nu)_i$	25	368	49
(6) $(\nu_H)_i$	17290	17632	17313
(7) $\nu_H$ (from Table IX)	17284	17589 17680	17303
(8) $(n_1, n_2)$ of $\nu_H$ in 7)	(2.7	(1.6) (1.5)	(1.9)

row 1). Since  $B_0''$  is known and  $d_i$  can be measured for each series, we are able to calculate  $\bar{m}_i$  for each series of doublets (see Table VIII, row 2). In each of the series it is seen by Fig. 2 that the component line has a lesser frequency than the main line of the same doublet, i.e., that the separation of the component from the main line  $\Delta\nu$ , is negative, which means according to the selection principle for band spectra that the excited absorption line lies on an  $R$  branch. The values for  $d_i$  were obtained directly by the above

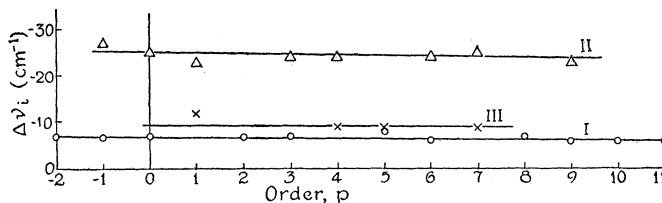


Fig. 3. Doublet width  $\Delta\nu_i$  of the series I, II, and III excited by 5792.3 as a function of the order number  $p$ .

method for the Series I and II, but since Series III consists of but four observable doublets which vary irregularly in width precautions were taken to draw the straight line through the four points for Series III as correctly as possible. In order to do this, use was made of the fact that  $B_0'' = \alpha''(d_i/\eta_i)$ , as deduced by Loomis, which means that since  $B_0''$  and  $\alpha''$  are constants for iodine, that for every doublet series in the iodine spectrum  $(d_i/\eta_i)$  will be a constant. So  $\eta_i$  was determined as well as  $d_i$  for series I and II and the average values for  $(d_i/\eta_i)$  were thus found from these two series. Then knowing the value that  $(d_i/\eta_i)$  should have for series III,  $d_i$  was then measured to a first approximation for Series III by simply drawing in the straight line in the position denoted by the four plotted points. Having thus determined  $(d_i/\eta_i)$ , and  $d_i$  approximately for Series III, the approximate value of  $\eta_i$  for this series was then calculated from the former two quantities, and then a line drawn in Fig. 3, having the slope as fixed by  $\eta_i$  and placed as accurately as possible relative to the four plotted points. The intersection of this revised

line with  $p=0$  was taken as  $d_i$  for Series III. Table VIII gives in the first row the values of  $d_i$  so determined, and in row 2 the values of  $\bar{m}_i$  so deduced from Eq. (2).

Furthermore, Loomis has calculated, making use of constants deduced by Mecke from absorption spectra of iodine, that the separation of the main lines in the  $p$ th order of two doublets series excited by the same narrow line, say the  $i$ th and  $k$ th series is:

$$(\nu_k - \nu_i)_p = (\epsilon_k - \epsilon_i) + p[1.192(\bar{n}_k - \bar{n}_i) + 0.00012(\bar{m}_k^2 - \bar{m}_i^2)] \quad (3)$$

where  $\epsilon_k$  and  $\epsilon_i$  are separations of the main lines of the zero order doublets of these two series from the corresponding line of some other series excited by the same line. Actually the difference  $(\epsilon_k - \epsilon_i)$  is so small compared to the separation of the higher ordered doublets that  $(\epsilon_k - \epsilon_i)$  may be neglected without noticeable error. Now  $(\nu_k - \nu_i)_p$  may be measured directly from Fig. 2 for any order of  $p$  (preferably, of course, the highest order of  $p$  common to both series). And  $\bar{m}_k$  and  $\bar{m}_i$  have already been calculated for these series as recorded in Table VIII, row 2. Hence everything is known excepting  $\bar{n}_k - \bar{n}_i$  which may then be calculated from Eq. (3). In Table VIII is recorded in row 3 the values of  $(\nu_k - \nu_i)$ , and in the fourth row the values of  $\bar{n}_k - \bar{n}_i$  calculated from Eq. (3). It will be observed that within the limits of experimental error  $\bar{n}_I - \bar{n}_{II} = 1$ ,  $\bar{n}_{II} - \bar{n}_{III} = 0$ , and  $\bar{n}_{III} - \bar{n}_I = -1$ . Now from Fig. 2, since Series I has two anti-Stokes members, it appears that this series is emitted by molecules having initially at least two quanta of vibrational energy, i.e.,  $\bar{n}_I \geq 2$ , whence according to the above  $\bar{n}_{II} = \bar{n}_{III} \geq 2 - 1 \geq 1$ . Since inspection of Fig. 2 also shows that Series II has one anti-Stokes member, it indicates that the deduced value of  $\bar{n}_{II} \geq 1$  and the assumed value of  $\bar{n}_I \geq 2$  may, at least, be correct. The correctness of  $\bar{n}_{III} \geq 1$  can not be checked by Fig. 2 because of the missing low ordered doublets of this series.

TABLE IX  
Position of iodine absorption band heads (by Mecke).

$n_1$	$n_2$	$\nu$	$n_1$	$n_2$	$\nu$	$n_1$	$n_2$	$\nu$
1	-3	18340.4	1	2	17942.3	0	9	17515.5*
0	0	18320.9	0	5	17892.8	1	7	17495.1
1	-2	18266.2	1	3	17857.3	2	5	17467.7*
0	+1	18239.1	0	6	17801.6	0	10	17416.5*
1	-1	18187.7	1	4	17769.2	1	8	17399.7
0	+2	18155.1	0	7	17708.2	2	6	17377.1
1	0	18107.5	1	5	17679.7	0	11	17315.7*
0	+3	18070.1	0	8	17612.1	1	9	17302.5
1	+1	18025.9	1	6	17589.0	2	7	17284.0
0	4	17982.4	2	4	17557.2*	1	10	17203.5

\* Values calculated from Equation (5); all other values are observed.

These estimates of  $\bar{n}$  are of course not absolute, all that is accomplished definitely is to calculate differences in the  $\bar{n}$ 's between the three series under consideration. However, the following method has been devised by the writer to determine the absolute values of  $\bar{n}$ , and not simply differences in their values.

To do this, use is made of the position of the heads of the absorption bands of iodine vapor as found experimentally by Mecke and of the values of the rotation quantum numbers in the unexcited state of the molecules associated with the heads of the bands as calculated by Loomis. A portion of Mecke's table of absorption band heads is reproduced in Table IX. The first two columns give the values of  $n_1$  and  $n_2$  assigned by Mecke in the general formula for band heads:

$$\nu(n_1, n_2) = \nu_0 + (an_2 + bn_2^2 + cn_2^3) - (a'n_1 + b'n_1^2 + c'n_1^3) \quad (4)$$

which, for the particular case of iodine, according to Mecke, takes the definite form of:

$$\begin{aligned} \nu(n_1, n_2) = & 18320.97 - 80.66n_2 - 1.012n_2^2 + 0.0033n_2^3 \\ & - 213.76n_1 + 0.596n_1^2 + 0.0021n_1^3 \end{aligned} \quad (5)$$

where the maximum value of  $n_2$  appears to be about 26, and  $n_1$  ranges from 0 to 9, both inclusive. From the behavior of the band heads under certain experimental variations, Mecke concluded that  $n_1$  represents the initial state in absorption, i.e., is identical with  $\bar{n}$  of the notation hitherto used in this paper. Furthermore, Loomis concludes that  $n_2$  is identical with  $26 - n'$ . So, if we can assign each resonance spectrum series to the excitation of a line in a definite absorption band of Mecke's, we have immediately the absolute values of  $n_1$  or, what is the same thing, of  $\bar{n}$ .

The total energy of a molecule is:

$$E = E_e + h\omega_0n(1 - xn) + h(B_0 - \alpha n)m^2 \quad (6)$$

so, by the quantum theory:

$$\begin{aligned} \nu = (E' - E'')/h = & (E_e' - E_e'')/h + \omega_0'n'(1 - x'n') + (B_0' - \alpha'n')m'^2 \\ & - \omega_0''n''(1 - x''n'') - (B_0'' - \alpha''n'')m''^2. \end{aligned}$$

But what is here wanted is the difference in frequency of the absorption line coinciding with the exciting line, and the head of the band of which this excited line is a member. For the same band all of the terms in Eq. (6) excepting those involving  $m$  are constant. Loomis has calculated  $B_0'$  and  $B_0''$  to be 0.023 and 0.0373, respectively, whereas Mecke has calculated  $\alpha'$  and  $\alpha''$  to be 0.00015 and 0.00012 respectively. And since  $n'$  and  $n''$  will never be large,  $\alpha'n'$  and  $\alpha''n''$  will be neglected in these calculations since they will be small relatively to  $B_0'$  and  $B_0''$  if the magnitude of experimental errors be considered.

It has been observed that all of the series excited by the yellow mercury line 5792.3 belong to the  $R$  branch. Hence from Eq. (6):

$$\begin{aligned} (\nu_H - \nu)_i = & [B_0'(\bar{m}_{H_i} + 1)^2 - B_0''\bar{m}_{H_i}^2] - [B_0'(\bar{m}_i + 1)^2 - B_0''\bar{m}_i^2] \\ = & B_0'[(\bar{m}_{H_i} + 1)^2 - (\bar{m}_i + 1)^2] - B_0''[\bar{m}_{H_i}^2 - \bar{m}_i^2]. \end{aligned}$$

$\bar{m}_{H_i}$  as calculated by Loomis was found to be approximately 2 for every band calculated in the iodine absorption spectrum. So using Loomis' values of

$B_0'$  and  $B_0''$  and  $\bar{n}_H$  and the values of  $\bar{m}_i$  herein calculated, the values of  $(\nu_H - \nu)_i$  are calculated and recorded in Table VIII, row 5. But  $\nu$  is in every case 17264.4, so  $\bar{\nu}_H$  was so calculated and recorded in row 6. Referring to Table IX which is a portion of Mecke's table of absorption band heads, it is seen that the band heads, having values of  $n_1$  here found possible, lying closest to the calculated heads, are as given in row 7, of Table VIII along with the values of  $n_1$  and  $n_2$  assigned to them by Mecke. Within the limits of experimental error the agreement between the calculated and the closest possible absorption band heads for each series is sufficiently close, though no band head could be definitely decided upon by this method alone as being the correct one. But, when it is recalled that the appearance of two anti-Stokes members in Series I and of one anti-Stokes member in Series II as shown in Fig. 2 makes it necessary that  $\bar{n}_I \geq 2$  and that  $\bar{n}_{II} \geq 1$ , it follows immediately that the band heads recorded in Table VIII, rows 7 and 8, are the only possible ones in Mecke's table, because all other band heads of Mecke sufficiently close to the calculated heads have values of  $n_1$  less than the values restricted by Fig. 2.

A similar calculation has been made by the writer for the series excited by 5462.23. In this case, using Loomis' values again from Wood's more accurate wave-length measurements than were possible with the spectrograph here used, it follows definitely that the band head involved is Mecke's (0,0) which checks Loomis' assumption based on the equality of  $n$  for every series excited by the broad green mercury line from the quartz arc at high voltages.

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5462.2 A. ↗ 5771.2 A. ↗ 5792.3 A.

Fig. 1. Resonance spectra excited by the glass mercury arc with the green line excluded by an eosin gelatin filter.