ANALYSIS OF THE ULTRAVIOLET FLUORESCENCE SPECTRA OF I_2 MOLECULE

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Plates XVA-D

ABSTRACT. New and improved wavelength data on the fluorescence bands of iodine vapour excited by mercury lines is given. Wavelength data on McLennan bands is obtained from thallium spark excitation for the first time. A complete analysis of these fluorescence bands in the region λλ 4738—1959 A. U. is presented for the first time. Four new electronic states in Mulliken's term scheme for I_2 molecule are identified. It is suggested that no resonance series are obtained in ultraviolet on excitation with mercury arc lines.

INTRODUCTION

The fluorescence spectrum of iodine vapour is one of the most extensively studied topics. All the important results have been summarised by Pringsheim in his masterly treatise on "Fluorescence and Phosphorescence" (1949). Dealing with the ultraviolet band systems in fluorescence he says that their analysis is by far less complete than that of the visible bands. Almost all data referring to the upper states are missing. Iodine is one of the few molecules in which we get information about the upper states from fluorescence data, on account of the rich fluorescence spectrum it gives in the ultraviolet. In the absence of a satisfactory analysis of all these bands it is felt worth while to take up an exhaustive investigation of these ultraviolet fluorescence bands.

Oldenberg (1923) discovered this ultraviolet fluorescence giving the resonance spectra on irradiating the vapour with mercury lines 1849 and 1942 A, the bismuth line 1903 A and the zinc line 1900 A. For only the last of these spectra, the wavelengths of the individual members have been published. They were interpreted as forming the resonance series from 5th anti-Stokes member to the 35th Stokes member. The data on the resonance spectrum excited by mercury lines is not available in literature. While no bands were recorded below 2100 A by Oldenberg on excitation with mercury radiations, he claims that the other bands measured by him form two resonance series. He also mentions that some bands in the region below 2310A, are of a doublet or a triplet character with a separation of 7 A. U. He further observes two pairs of bands at 1887 and 1910 A, which have a splitting of 0.9 and 1.1 A. U. respectively. The explanation of the splitting is not clear. In the visible

resonance series the splitting was observed to be about 0.2 A.U. representing the rotational splitting. The splitting observed by Oldenberg is by far greater than the above rotational splitting and so cannot be assigned to the rotational level separations in the vibrational states of the ground state of I_2 molecule. In such a case the nature of the splitting requires close investigation.

The most interesting and complicated bands appear to be those discovered by McLennan and named after him. They extend from 4600 to 2100 A and were obtained on irradiating the vapour with mercury lines 1849 and 1942 A, and Al, Zn, Cd, Mg sparks. Experimentally it was established that these bands were excited only by wavelengths less than 2100 A. They were recorded by him on a low dispersion instrument. They were diffuse and spread out into various groups, the one between 3300 and 3100 A being most conspicuous. McLennan observed that for most of these bands the wavelengths are independent of the exciting radiation. Though qualitative groupings of these bands have been made by Duschinsky and Pringsheim, they admit that they are not of any special significance. An analysis of these bands has not been made till now perhaps due to lack of a complete understanding of the possible electronic states of I_2 molecule.

Mulliken (1935) worked out the complete term scheme in iodine with possible locations of the various configurations with respect to one another. There has been a considerable progress recently on the analysis of the emission and absorption bands of iodine. Venkateswarlu (1946, 1947) analysed the emission bands of iodine and identified a number of electronic states in the scheme given by Mulliken. He observed some coincidences between these Mc bands and those obtained by him and others (Curtis and Evans, 1933) in emission. He suggested therefore that these Mc bands could be explained on the same basis as his interpretation for the emission bands. It was felt that a thorough investigation of this casual suggestion is desirable.

Pringsheim points out a long regular sequence of fluctuations in the region below 2500 A, with a spacing of $\Delta\nu \sim 380$ cm^{-1} appearing simultaneously with the resonance progression. This $\Delta\nu$ of 380 cm^{-1} is claimed to be about twice the ground state frequency (215) and does not find an easy explanation. These points needed clarification. It was also necessary to pick out the resonance series excited by mercury radiation, if any, and separate their wavelength data which do not exist in literature, from that of the Mc bands. Then we might be able to understand the nature of the so called splitting observed by Oldenberg in some bands. Also the various casual suggestions regarding the origin of the Mc bands had to be thoroughly examined and the exact states involved in the emission of these bands are to be identified. Their nature, whether repulsive or non-repulsive has also to be determined.

EXPERIMENTAL

A pyrex glass tube of the special form suggested by Wood, with a strain-free bulb at one end and a Wood's horn at the other has been prepared and used for work in the visible region. Instead of the bulb, a quartz-to-pyrex graded seal tube with a fused-in quartz window is attached to the above tube for work in ultraviolet. A side tube is provided with a constriction to evacuate and seal off with iodine crystals in it. Under such conditions the fluorescence tube contains only iodine crystals and its vapour at a pressure corresponding to the saturated vapour pressure of the substance at a given temperature. For the work in visible region a Fuess spectrograph which has a dispersion of 16A/mm at 4200 A has been used. Hilger small quartz spectrograph having a dispersion of 19A/mm at 2500 A and medium quartz spectrograph having a dispersion of 10A/mm at 2700A and 5A/mm at 2200A, are used for investigations in ultraviolet. Spectra in visible region have been recorded on HP3 and Ilford panchromatic plates, whereas Ilford Selochrome, Special Rapid, Q2 and Q3 plates have been employed in ultraviolet region. A quartz mercury arc run on 220 D. C. at 3.5 amps. and a thallium spark run on a 20,000 volts transformer are the sources of excitation. With thallium spark an exposure of 120 hrs. in ultraviolet region and 150 hrs. in visible region are required with a slit width of about 400 microns, whereas with the mercury arc 48 hrs. in ultraviolet and 24 hrs. in visible were sufficient with a slit width of 230 microns. In the case of the mercury arc special precautions are taken to avoid all extraneous radiation.

RESULTS

With mercury arc excitation the Mc bands could be obtained in the region 4569 to 1942 A and with thallium spark in the region 4738 to 2035 A (figures 1, 4 and 5 in Plates XVA and XVC). As seen from Table I, there is a close agreement between our data and these of McLennan's in the region 2800 to 2100A, whereas there is a considerable deviation in the region 4600 to 2800A. A close band to band examination reveals that our data is more accurate. McLennan bands in the visible region excited by mercury arc and recorded on a Fuess spectrograph (which has a higher dispersion in this region than the medium quartz spectrograph) gave more accurate data and revealed four discrete bands instead of the continuum at 4130 to 4015 A, as reported by McLennan. The other data are also claimed to be accurate within an error of 1 to 2 A.U. as a result of the higher dispersion we could use than McLennan.

ANALYSIS

The starting point of our analysis of the Mc bands was the analysis of the emission bands of iodine in that region by Vankateswarlu. Of all the terms given in Mulliken's term scheme, Venkateswarlu was able to identify fifteen terms and attribute various band groups to transitions between those

terms. The diffuse nature of the bands and the absence of a development as a whole of any system was explained by his suggestion that most of the transitions involved are between a stable state and various repulsive states. His work and that of Mulliken established the fact that in I_2 molecule case *c* type coupling holds good rather than cases *a* and *b*.

TABLE I

McLennan's data λ (A.U.)	Present measurements			
	Mercury arc		Thallium spark	
	Intensity	λ (A.U.)	Intensity	λ (A.U.)
			8	4738
			6	4703
			6	4641
			6	4605
4608				
4550	1	4569	1	4570
			2	4532
4505	0	4512		
4452	1	4458	4	4454
	1	4408		
			2	4358
			1	4339
4290			2	4303
	1	4269		
4250	2	4238	2	4246
4210	2	4196	2	4200
4170	1	4152	4	4156
4130	0	4118	4	4130
	2	4090	4	4099
			3	4055
4015	2	4005		
			2	3979
3925	3	3926	2	3922
3870	4	3857	2	3852

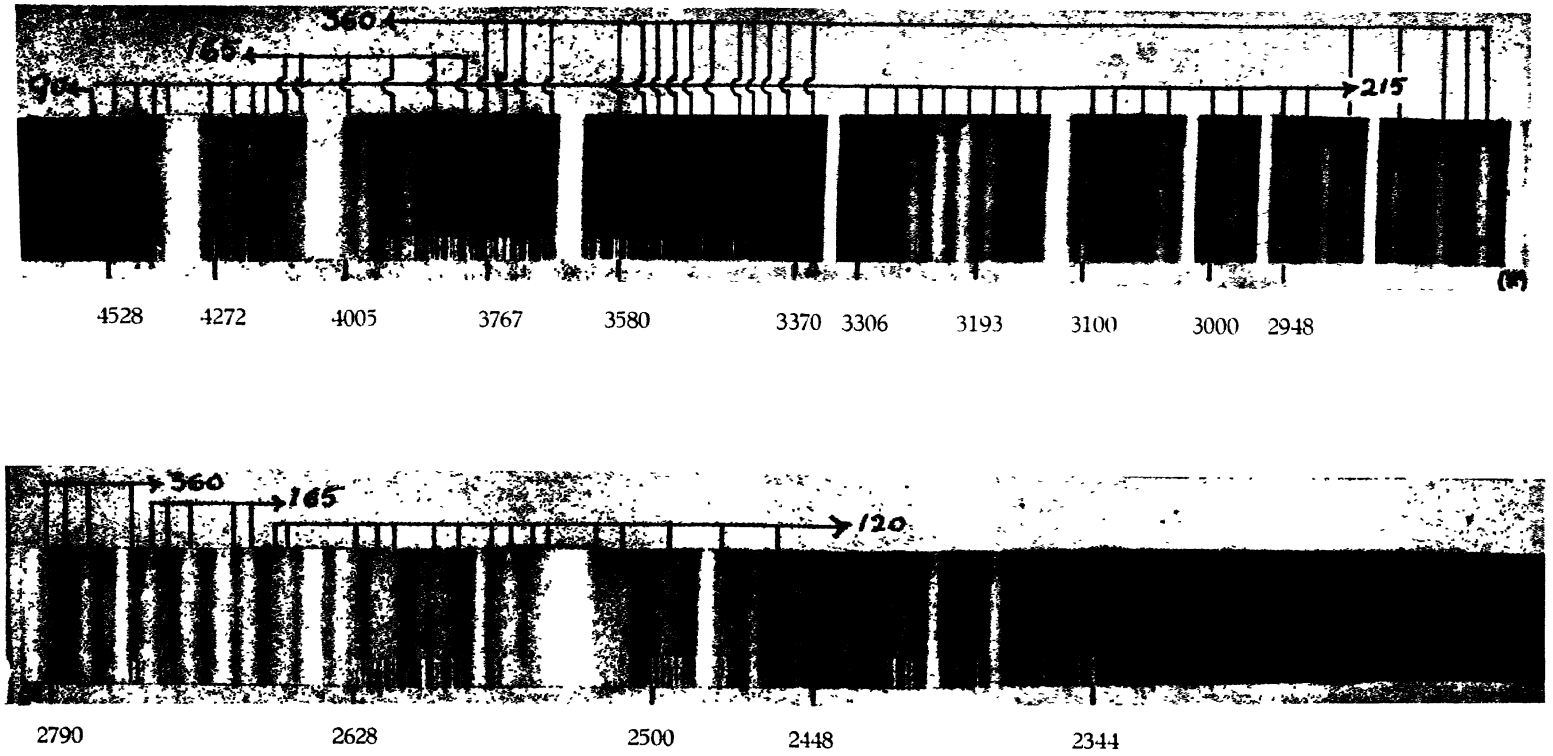


Fig. 1. Mclennan bands of I_2 vapour exited by Hg arc, on medium quartz spectrograph. They are marked as different groups, into which they have been analysed. The numbers 90, 120 etc. are the values of ω_e, in units of cm^{-1}, of the upper states from which the groups arise, due to transitions to lower repulsive states. The wavelengths of standard iron lines are marked in A U.

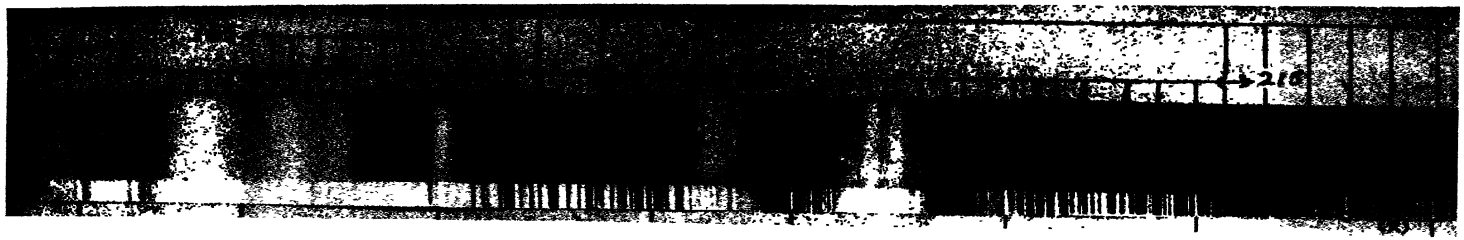
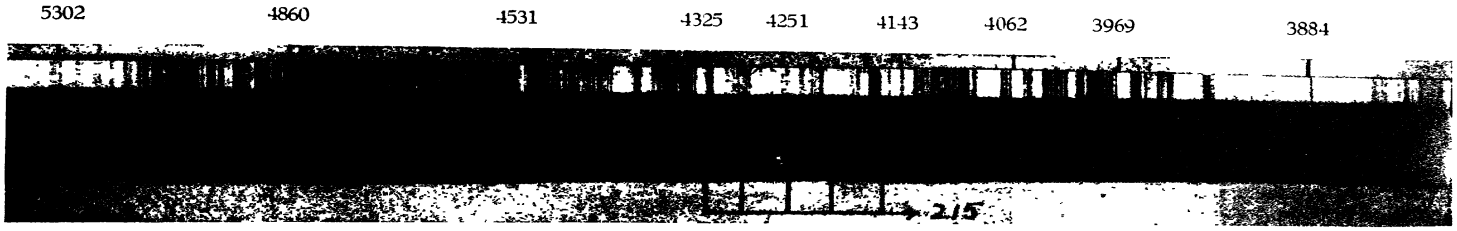


Fig. 2. Mc bands excited by a thallium spark. The analysis, analogous to the above is indicated.



Thallium green line 5350·8A

Fig 3 Mc bands in visible excited by thallium spark and recorded on Fuess spectrograph.

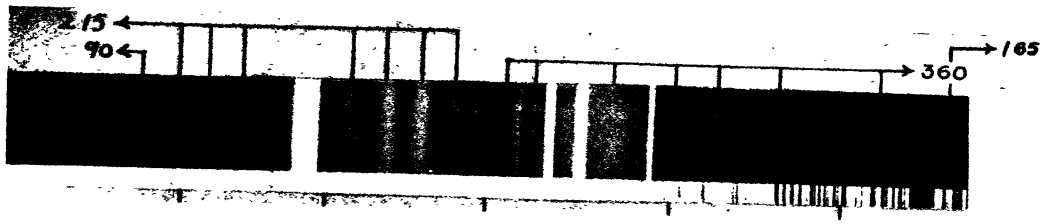


Fig 4 Similar to Fig. 3, but excited by a mercury arc and reveal greater number of bands. On analysis they are grouped as indicated

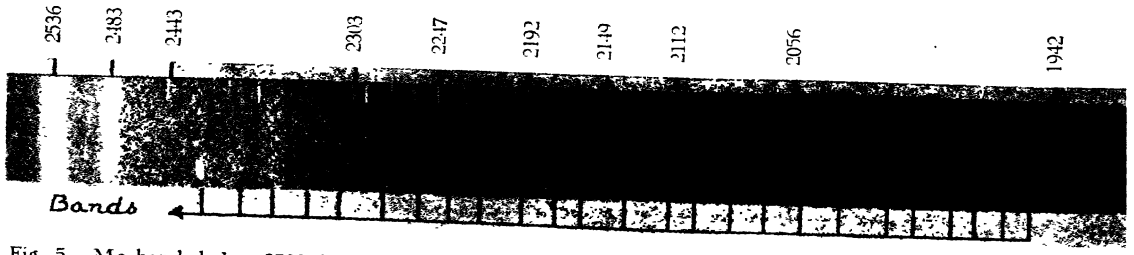


Fig. 5. Mc bands below 2500 A.U. recorded on a small quartz spectrograph, showing the extension upto 1942 A.U., the exciting mercury line

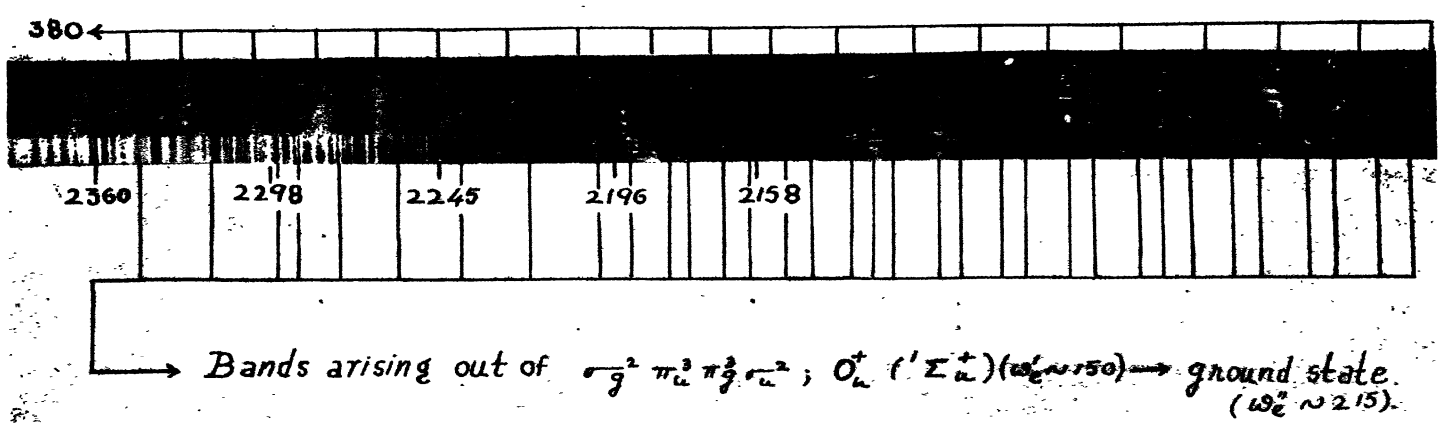


Fig. 6

Fig. 6. Bands below 2400 A U. recorded on Ilford Q3 plate with a medium quartz spectrograph, excited by mercury lines. Bands with 380 cm^{-1} successive differences arise out of a transition from an upper repulsive state to a lower state ($\omega''e = 380$). Other bands represent a system involving the ground state ($\omega''e = 215$) and a stable upper state ($\omega'e = 150$).

TABLE I (contd).

McLennan's data λ (A U.)	Present measurements			
	Mercury arc		Thallium spark	
	Intensity	λ (A.U.)	Intensity	λ (A U.)
3800	2	3805	2	3795
	2	3777		
	0	3750		
3725	0	3739	3	3732
	1	3699		
	2	3673	2	3668
3625			2	3640
			2	3607
3585	4	3585		
3555	1	3554		
	1	3539	2	3543
3520	1	3512		
	0	3501	2	3495
3475	2	3468	3	3175
3445	1	3436	2	3446
3420	1	3414	4	3415
3395	3	3383	4	3392
3365	0	3355	4	3364
			4	3353
3315			3	3318
3290	4	3301	3	3302
3268	8	3276	3	3282
3245	10	3252	4	3253
3220	10	3229	6	3230
3195	10	3205	3	3202
3175	9	3182	4	3178
	4	3162	4	3157
	3	3135	4	3141
	3	3123	4	3121

TABLE I (contd,)

McLennan's data λ (A U.)	Present measurements			
	Mercury arc		Thallium spark	
	Intensity	λ (A.U.)	Intensity	λ (A.U.)
3107				
3090	6	3097	4	3096
3065	1	3077	2	3076
	6	3057	4	3058
3047	6	3038	4	3038
3009	4	3000	3	3003
2993	5	2984	4	2984
2960				
2946	4	2951	2	2954
2930	3	2935	3	2929
2915				
2900	5	2904	2	2899
2883	6	2874	3	2871
2853	6	2845	3	2857
2825	1	2832		
	4	2819	2	2815
2799	4	2793	2	2790
	1	2780		
2774	4	2771	2	2766
2760				
	2	2745	2	2740
2737	4	2735		
2727	2	2725	4	2725
2715	6	2714	4	2709
2697	4	2701		
2685	8	2683	4	2684
	4	2671		
2667	6	2662	4	2656
2638				

TABLE I (contd.)

McLennan's data λ (A.U.)	Present measurements			
	Mercury arc		Thallium sparks	
	Intensity	λ (A.U.)	Intensity	λ (A.U.)
2628	4	2629	3	2632
2622	4	2621		
2617				
2612	1	2612	2	2610
2594	3	2591		
2580	2	2582	2	2581
	2	2568		
2560	6	2561	2	2556
	1	2554		
2545	2	2545		
			2	2534
	1	2520		
2515	1	2516		
	2	2512	2	2512
2495	8	2495	2	2491
2476	6	2470	2	2474
2450	6	2453	2	2458
			2	2444
2426	8	2427	2	2425
2408	8	2408	2	2407
2382	8	2386	2	2381
2360	7	2363	2	2361
2340	6	2345	2	2340
	4	2329		
2320	6	2322	2	2322
	2	2308		
2300	5	2300		
	3	2287	2	2292

TABLE I (contd.)

McLennan's data λ (A.U.)	Present measurements			
	Mercury arc		Thallium spark	
	Intensity	λ (A.U.)	Intensity	λ (A.U.)
2277	5	2279		
	4	2263	2	2266
2254	4	2257		
2237	3	2246	2	2239
2218	3	2226	2	2220
2195	3	2205	1	2196
2179	2	2182	1	2176
2162	2	2161		
2148	2	2142	1	2148
2129	1	2122	1	2121
	1	2103	1	2103
	1	2084	1	2081
	1	2066	1	2066
	1	2052	1	2057
			1	2047
	1	2034	1	2035
	1	2020		
	1	2005		
	1	1989		
	1	1971		
	1	1959		
	2	1942		

Tables II, III, IV, V, VI include all Mc bands extending from the visible region down to 40754 cm^{-1}. Table II contains five groups of bands arising out of a transition from the stable state $\sigma_g\pi^4_u\pi^3_g\pi^2_u$. $1_g(^3\Pi_{1g})$ with $\omega \sim 215$ to various repulsive states as identified by Venkateswarlu. A few bands excited by mercury arc radiations do not appear among those excited by thallium spark and vice versa. The bands given in our data do not always agree with those in the data due to Venkateswarlu. But the differences of the order of 215 cm^{-1} appear to be genuine. The transition being between a

TABLE II

Bands arising out of transition from a stable state $\sigma_g\pi^4_u\pi^3_g\sigma^2_u$. $I_g(^3\Pi_{1g})$ with $\omega \sim 215$ to various repulsive states (figures 1 and 2).

Mercury arc		Transition	Thallium spark	
ν(cm^{-1})	$\Delta\nu$		ν (cm^{-1})	$\Delta\nu$
22157			22445	
	268			3×198
22425		$I_g \rightarrow \sigma_g{}^2\pi_u{}^3\pi_g{}^3\sigma_u{}^2$. $I_u(^3\Sigma_u{}^+)$	23040	
	255			193
22680			23233	
23418			22940	
	171			3×198
23589			23545	
	237	$I_g \rightarrow \sigma_g{}^2\pi_u{}^3\pi_g{}^2\sigma_u{}^2$. $0_u{}^-(^3\Sigma_u{}^+)$		258
23826			23803	
	252			252
24078			24055	
30285			30281	
	231			179
30516			30460	
	225	$I_g \rightarrow \sigma_g{}^2\pi_u{}^3\pi_g{}^3\sigma_u{}^2$. $I_u{}^-(^3\Delta_{1u})$		272
30741			30732	
	219			219
30960			30951	
	232			270
31192			31221	
31418			31457	
	198	$I_g \rightarrow \sigma_g{}^2\pi_u{}^3\pi_g{}^3\sigma_u{}^2$. $I_u{}^-(^3\Delta_{1u})$		210
31616			31667	
31889			31828	
	2×196			204
32080		$I_g \rightarrow \sigma_g{}^2\pi_u{}^3\pi_g{}^3\sigma_u{}^2$. $2_u(^3\Delta_{2u})$	32032	
	210			258
32490			32292	
				210
			32500	
32702			32692	
	205			215
32907			32907	
	2×209			2×192
33324			33290	
	178	$I_g \rightarrow \sigma_g{}^2\pi_u{}^4\pi_g{}^3\sigma_u$. $I_u(^1\Pi_u)$		212
33502			33502	
	2×178			3×210
33877			34131	
	185			
34062				

TABLE III.

Bands arising out of transition from a stable state $\sigma_g\pi^4_u\pi^4_g\sigma_u \quad o^+_u(^1\Sigma^+_u)$ with $\omega \sim 165$ to various repulsive states (figures 1 and 2).

Mercury arc		Transition	Thallium spark	
$\nu(cm^{-1})$	$\Delta\nu$		$\nu(cm^{-1})$	$\Delta\nu$
24277			24055	
	166			151
24443		$o_u^+ \rightarrow \sigma_u^2\pi_u^4\pi_g^3\sigma_u^2$. $o_g^+(^1\Sigma_g^+)$	24206	
	3×173			183
24962			24389	
				2×133
			24654	
				3×157
			25125	
25464		$o_u^+ \rightarrow \sigma_u^2\pi_u^4\pi_g^3\sigma_u^2$ $o_g^+(^3\Sigma_g^-)$	25490	
25920		$o_u^+ \rightarrow \sigma_g^2\pi_u^4\pi_g^2\sigma_u^2$. $1_g(^3\Sigma_g^-)$	25953	
26274		$o_u^+ \rightarrow \sigma_g^2\pi_u^3\pi_g^4\sigma_u$. $1_g(^1\Pi_g)$	26343	
36552			36903	
	134			2×172
36686			37247	
	149			
36835		$o_u^+ \rightarrow \sigma_g^2\pi_u^3\pi_g^4\sigma_u$. $o_g^+(^3\Pi_{ug})$		
	177			
37012				
	2×130			
37261				

stable upper state and a repulsive lower state, the band system corresponds only to a single progression containing the upper state frequencies. If different sets of vibrational levels in this state are responsible for the emission and fluorescence bands, then the wavelength positions need not be the same in both cases. This might possibly explain any discrepancy between the emission and fluorescence data. For instance, two progressions excited by mercury arc start at 23418 and 30285 cm^{-1}, whereas 22948 and 30006 cm^{-1} are the starting points for similar progressions in emission data. These transitions given in Table II from 1_g to five repulsive lower states are able to account for 23 bands (figures 1 and 2).

The upper state 1_g ($^3\Pi_{1g}$) is located at 51528 cm^{-1} by Venkateswarlu from the data on the dissociation limits and products and the first bands of three of the groups given by him. The first bands in our groupings are systematically of a higher frequency than those given by Venkateswarlu to a maximum of 500 cm^{-1}. In the light of the above explanation we can consider that at least two higher vibrational quanta are involved in the transition giving rise to fluorescence spectrum. If this interpretation is valid

then the approximate value of the height of the 1_g state may be confirmed to be 51528 cm^{-1}. The five lower states $1_u(^3\Sigma^+_u)$, $0^-_u(^3\Sigma^+_u)$, $1^-_u(^3\Delta_{1u})$, $2_u(^3\Delta_{2u})$, $1_u(^1\Pi_u)$ may be confirmed at 29399, 28580, 21522, 19712, 18878 cm^{-1} respectively as located by Venkateswarlu.

A similar procedure and explanation led us to the identification of five groups of bands arising out of transitions from a stable upper state $\sigma_g\pi^4_u\pi^4_g\sigma_u$ $0^+_u(^1\Sigma^+_u)$ with $\omega \sim 165$ to various repulsive states. The groups and transitions are set out in Table III. In three transitions $0^+_u \rightarrow {}^3\Sigma^-_g$, $1_g(^3\Sigma^-_g)$, $^1\Pi_g$ we find only one band each. The assignment of these single bands has been made possible by comparison with the emission data. Venkateswarlu obtained only pairs of bands with separation of about 165 cm^{-1} and assigned these transitions. We obtained one component each in these pairs and hence the assignment. 11 bands excited by mercury lines and 10 bands excited by thallium lines are assigned to these transitions.

The determination of the heights of these levels is more reliable than in the earlier case. The upper state $0^+_u(^1\Sigma^+_u)$ was located at 51683 cm^{-1} from an analysis of the Cordes bands in the region 1950 to 1794 A. The lower states $0^+_g(^1\Sigma^+_g)$, $0^+_g(^3\Sigma^-_g)$, $1_g(^3\Sigma^-_g)$, $1_g(^1\Pi_g)$, $0^+_g(^3\Pi_g)$ may be considered to be at 27619, 26345, 25916, 25525, 14821 cm^{-1} respectively.

There are three groups of bands with separations of the order of 120 cm^{-1} assigned to three transitions from a stable upper state $1_g(^1\Pi_g)$ with the configuration $\sigma_g\pi^4_u\pi^3_g\sigma^2_u$ to three repulsive states (Table IV) (figures 1 and 2). In the first two transitions more bands are obtained in the mercury source while there is an equal number of bands in mercury and thallium sources in the third group. A maximum number of 17 bands are assigned to these transitions. The state $1_g(^1\Pi_g)$ is fixed up at 58572 cm^{-1} and the lower states $1_u(^3\Delta_{1u})$, $2_u(^3\Delta_{2u})$, $1_u(^1\Pi_u)$ at 21522, 19712, 18878 cm^{-1}. The process of identification of these states was the same as that adopted in the case of the states giving rise to the bands with separations of 215 cm^{-1} (Table II).

Table V contains five groups of bands with separations of about 360 cm^{-1}. The transitions were suggested to be from the stable state $\{(\sigma^2_g\pi^4_u\pi^3_g;\ ^3\Pi_g 1\tfrac{1}{2})\sigma^x_g\}^3\Pi_{2,1g}$ to five different repulsive states. As could be seen from the table there is better consistency in the values of $\Delta\nu$ in these transitions than in previous cases. The progression with 34062 cm^{-1} as its first band started with 34432 cm^{-1} in case of emission bands. But this agrees with the second band 34425 cm^{-1} in our data. So the actual location of the repulsive state 1_u $(^3\Delta 1_u)$ has to be fixed at 21892 cm^{-1} instead of at 21522 cm^{-1} as given by Venkateswarlu. The stable state $^3\Pi_{2,1g}$ has been identified at 56000 cm^{-1}, and the other repulsive states 1_u $(^3\Sigma_u{}^+)$, $0_u{}^-$ $(^3\Sigma_u{}^+)$, 2_u $(^3\Delta_{2u})$, 1_u $(^1\Pi_u)$ may be identified at 29399, 28580, 19712, 18878 cm^{-1} respectively.

There are about 6 bands (in mercury arc source) and 3 bands (in thallium source) in the region 3750 to 3383 A not fitting into any one of these transitions. They have a mean separation of about 360 cm^{-1}. These bands are not contained in the list of emission bands given by Venkateswarlu. They

could not be connected with any of the bands given in the earlier tables. The value of the separations is the same as that to be found in Table V. This suggests that these bands may arise out of the same upper state as those contained in Table V. The lower state may be likewise identified as a repulsive state $\sigma^2_g\ \pi_u^3\ \pi_g^3\ \sigma_u^2$; o_u^- ($^1\Sigma_u^-$). This newly identified transition is tabulated as a continuation of Table V because of the common upper state. It is interesting to note that this transition occurs only in fluorescence but not in emission. It may be added, however, that the lower state o_u^- ($^1\Sigma_u^-$) was suggested to be involved in another transition with $\sigma_g\ \pi_u^4\ \pi_g^3\ \sigma_u^2$; 1_g ($^3\Pi_{1g}$) resulting in a continuum at 3416 A. The height of the state o_u^- ($^1\Sigma_u^-$) is located by us at 29341 cm^{-1}.

TABLE IV

Bands arising out of transition from a stable state $\sigma_g\pi^4_u\pi^3_g\sigma^2_u$. $1_g(^1\Pi_g)$ with $\omega\sim$ 120 to various repulsive states (figures 1 and 2).

Mercury arc		Transition	Thallium spark	
$\nu(cm^{-1})$	$\Delta\nu$		$\nu(cm^{-1})$	$\Delta\nu$
37428			37639	
	127			3×115
37555			37983	
	4×118			3×107
38026		$1_g\rightarrow\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$. $1_u(^3\Delta_{1u})$	38303	
	116			
38142				
	131			
38273				
			38738	
38584				3×126
	134		39112	
38718				3×113
	2×106			
38929				
	107		39451	
39036		$1_g\rightarrow\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$. $2_u(^3\Delta_{2u})$		
	134			
39170				
	111			
39281				
	4×113			
39734				
39671			39797	
	126			3×112
39797			40132	
	2×135			2×138
40068		$1_g\rightarrow\sigma_g^2\pi_u^4\pi_g^2\sigma_u$. $1_u(^1\Pi_u)$	40408	
	3×135			2×131
40474			40671	
	2×140			2×116
40754			40904	

TABLE V

Bands arising out of transition from a stable state $\{(\sigma_g^2\ \pi_u^4\ \pi_g^3,\ ^2\Pi_{g1/2}\ \sigma^x_g)\}$ $^3\Pi_{2,\ 1g}$ with $\omega \sim 160$ to various repulsive states.

Mercury arc ν	Mercury arc $\Delta\nu$	Transition	Thallium spark ν	Thallium spark $\Delta\nu$
26469			27259	
	2×374			4×379
27218			28777	
	2×334			2×348
27886			29473	
	363	$^3\Pi_{2,\ 1g} > \sigma^2_g\ \pi^3_u\ \pi^3_g\ \sigma^2_u.\ ^1\Sigma^-_u\ (^3\Sigma^+_u)$		338
28249			29811	
	306			
28555				
	2×362			
29283				
26738			26798	
	3×383			2×334
27886			27465	
	363			2×376
28249		$^3\Pi_{2,\ 1g} \rightarrow \sigma^2_g\ \pi^3_u\ \pi^3_g\ \sigma^2_u.\ \sigma^-_u\ (^3\Sigma^+_u)$	28217	
	...			387
29095			28604	
	2×352			2×335
29798			29274	
34062			34485	
	363			336
34425			34821	
	360			
34785				
	354			
35139		$^3\Pi_{2,\ 1g} \rightarrow \sigma^2_g\ \pi^3_u\ \pi^3_g\ \sigma^2_u.\ ^1\Delta_u\ (^3\Delta_{1u})$		
	324			
35463				
	330			
35793				
	...			
36077				
	342			
36419				
35300			35514	
	2×331			318
35961		$^3\Pi_{2,1g} \rightarrow \sigma_g^2\ \pi_u^1\ \pi_g^3\ \sigma_u^2.\ ^2\Delta_u\ (^3\Delta_{2u})$	35832	
				311
			36143	
				343
			36486	
...	...	$^3\Pi_{2,\ 1g} \rightarrow \sigma_g^2\ \pi_u^4\ \pi_g^3\ \sigma_u.\ ^1\Pi_u\ (^1\Pi_u)$	36686	...
26659			27716	
	368			4×324
27027			29011	
	3×367			2×356
28129			29722	
	337	$^3\Pi_{2,1g} \rightarrow \sigma^2_g\ \pi_u^3\ \pi_g^3\ \sigma_u^2.\ \sigma^-_u\ (^1\Sigma^-_u)$		
28466				
	361			
28827				
	2×362	(This transition is newly identified).		
29551				

TABLE VI

Bands arising out of transition from a stable state $\sigma_g \pi_u^4 \pi_g^4 \sigma_u$. 1_u $(^3\Sigma_u^-)$ with $\omega \sim 90$ to various repulsive states.

ν(cm^{-1}) Mercury arc	$\Delta\nu$	Transition	ν(cm^{-1}) Thallium spark	$\Delta\nu$
...	...	1_u $(^3\Sigma_u^+) \rightarrow \sigma_u^2 \pi_u^4 \pi_g^2 \sigma_g^2$. $0_g^+(^3\Sigma_g^-)$	21100	2×79
			21257	
...	...	1_u $(^3\Sigma_u^+) \rightarrow \sigma_g^2 \pi_u^4 \pi_g^2 \sigma^1_u$ $1_g(^3\Sigma_g^-)$	21541	2×84
			21709	
21881	...	1_u $(^3\Sigma_u^+) \rightarrow \sigma^2_g \pi_u^3 \pi_g^4 \sigma_u$. 1_g $(^1\Pi_g)$	21876	2×91
			22059	

Another set of transitions where we can give better information than available from earlier work is the pairs of bands with a separation of 90 cm^{-1} (Table VI). Venkateswarlu identified three bands at 4747.2, 4662.1 and 4575.2 A as due to the three transitions given in Table VI. As remarked by us earlier the data of Mc bands in this region as given by Mc Lennan are not quite reliable. In the excitation by mercury lines we obtain only one band 4569 A corresponding to 4575.2 A in emission. We, however, obtain six bands with the thallium spark source which could be easily paired off with separations of 2×84 cm^{-1} (figures 1 and 2). The upper state 1_u $(^3\Sigma_u^+)$ at 44900 cm^{-1} is also involved in the transition resulting in Pringsheim-Rosen, Kimura-Miyanishi (P.R. K.M.) bands in the region 2700 to 2000 A. It has an ω-value = 90 cm^{-1} obtained from the analysis of the above bands. This could be identified with the mean value 84 cm^{-1} suggested above by us. This observation confirms with definite evidence the identification of the above transitions, 1_u $(^3\Sigma_u^+)$ to the repulsive states 0_g^+ $(^3\Sigma_g^-)$, 1_g $(^3\Sigma_g^-)$ 1_g $(^1\Pi_g)$. The heights of these repulsive states are 26345, 25916, 25525 cm^{-1}.

The band 2444 A is the least wavelength involved in all the above tables, Below this wavelength there are in all 64 bands in the region. 2427 to 1959 A recorded on Ilford Q3 plates. This whole region was obtained by excitation with mercury lines. Excitation with thallium spark gave bands upto 2035 A only (Table I). The original data of Mc Lennan extends upto 2129 A (Table I). Venkateswarlu published no emission bands in this region. The P.R. K.M. bands extend from 2700 to 2000 A. There is a close agreement between some of these fluorescence bands and the P.R.K.M. bands in this region.

According to earlier workers some of these bands may form the resonance series excited to vibrational quanta of large values. As already pointed out the successive difference of 380 cm^{-1} in some bands is difficult to explain as

two times the ground state difference. Also the magnitude of the splitting of some bands into doublets is not of the proper value corresponding to the rotational separation in the resonance series. Besides some bands show actually a triplet structure with peculiar intensity distribution. A close examination of the bands and their successive differences led us to doubt whether there is any genuineness about the so called doublet and triplet structure. We are more inclined to consider these doublets and triplets as accidental groupings of two and three bands. The higher dispersion used by us led to a more reliable data both on the magnitude of the separations and the relative intensities of the bands under consideration.

We ultimately rejected the theory of attributing the doublet structure to the resonance series. If we accept the existing suggestion that some of these bands form the resonance series the following peculiarities are conspicuous. Low values of the vibrational quanta are not evidently excited. Only high values of the vibrational quanta appear in the analysis. If we accept 380 cm^{-1} as 2×215 (which is in itself a questionable approximation) only alternate vibrational quanta seem to be excited. While the presence or absence of some bands in a resonance progression is not in itself a serious draw back on the analysis (for instance, the 2nd, 5th etc., members in the visible resonance series are recorded as missing), it must be noted that these missing bands are too regular to believe. It appeared plausible to us that the systematic difference of 380 cm^{-1} covering the whole region 2427 to 1959 A may be a genuine difference not connected with 215 in the ground state. The bands involved in these differences are marked in figures 5 and 6. It is evident from these two that there is a gradual decrease in intensity as we go down to the short wavelength side of this progression. This series of bands includes besides others some components of the so called doublets and triplets. It appears reasonable to consider that these bands result out of a transition between two states neither of which is the ground state. Considering the diffuse nature of the bands we can conclude that one of the two states is a repulsive state while the other one is a stable state with $\omega \sim 380$ cm^{-1}. These two states have to be identified in the term scheme given by Mulliken. The upper state may be reasonably identified with the repulsive state proposed by Pringsheim (1949) at an approximate height of 55000 to 60000 cm^{-1}. In the term scheme due to Mulliken there is one state 2_g ($^3\Pi_{2g}$) in the configuration $\sigma_g\pi_u^4\pi_g^3\sigma_u^2$. The overall height of this configuration was suggested by him to be 8.1 e.v. In the same configuration two other states 1_g ($^3\Pi_{1g}$) and 1_g ($^1\Pi_g$) with $\omega \sim 215$ and 120 cm^{-1} respectively were identified earlier, at heights of 6.39 and 7.26 e.v. If we consider this new state 2_g ($^3\Pi_{2g}$) to be at about 7.5 e.v. the lower state may be fixed up at about 1.0 to 1.5 e.v. The right type of state can be identified as 2_u($^3\Pi_{2u}$) in the configuration $\sigma_g^2\pi_u^4\pi_g^3\sigma_u$

TABLE VII

Bands arising out of transition from a repulsive state $\sigma_g\pi_u^4\pi_g^3\sigma_u^2$; $2_g(^3\Pi_{2g})$ to a stable state $\sigma_g^2\pi^4{}_u\pi^3{}_g\sigma_u$; $2_u(^3\Pi_{2u})$ with $\omega \sim 380$ (figures 5 and 6). (These two states are newly identified.)

Intensity	λ(Å.U)	ν(cm^{-1})	Δν
8	2427	41191	
			325
8	2408	41516	
			382
8	2386	41898	
			408
7	2363	42306	
			345
4	2344	42651	
			389
6	2323	43040	
			400
4	2301	43440	
			377
6	2282	43817	
			335
6	2264	44152	
			386
4	2245	44538	
			388
6	2225	44926	
			387
4	2206	45313	
			418
6	2186	45731	
			310
4	2171	46041	
			357
3	2155	46398	
			360
4	2138	46758	
			426
3	2119	47184	
			384
3	2102	47568	
			328
4	2087	47896	
			388
4	2070	48284	
			433
2	2052	48717	
			383
5	2036	49100	
			389
4	2020	49489	
			385
2	2004	49874	
			377
1	1989	50251	
			382
1	1974	50633	
			387
1	1959	51020	

This state is a stable state with $\omega \sim 380$ cm^{-1}. In the same configuration two other states 1_u ($^3\Pi_{1u}$) and 0_u^+ ($^3\Pi_{0u}$) which are also stable,

were identified from an analysis of the near infrared and visible bands. There is also one repulsive state (1_u ($^1\Pi_u$), involved in a transition giving rise to the Mc bands with 120 cm^{-1} separation (Table IV). The upper state for these 120 cm^{-1} bands results out of the same configuration as the repulsive state $2_g(^3\Pi_{2g})$ suggested by us for the 380 cm^{-1} bands. As case c type of coupling holds good in I_2 molecule both repulsive and stable states can occur in the same configuration. It appears therefore plausible that the above group of bands may arise out of a transition between a repulsive upper state $\sigma_g\pi_u^4\pi_g^3\sigma_u^2$; $2_g(^3\Pi_{2g})$ and a stable lower state $\sigma_g^2\pi_u^4\pi_g^3\sigma_u$; $2_u(^1\Pi_{2u})$. (Table VII).

We are finally left with 38 bands in the region 2353 to 2010 A. The most intense bands appear to be in the region below 2150 A. In general these bands are more intense than the earlier group of 380 cm^{-1} separation. It can be seen from Table IX that the successive differences of these bands alternate between 150 and 215 cm^{-1} (average values) systematically. There appeared no other way of connecting these bands with other groups or treating them as two independent groups. They could be arranged into a Deslander's scheme as given in Table VIII. The scheme is built up starting with the highest frequency band and treating 150 cm^{-1} as the upper state vibrational frequency. Then 215 cm^{-1} will readily fit in as the lower state frequency developing a peculiar Deslander's scheme. Each band can be seen to be characterised by a (v', v'') value. The exact numbering of these v', v'' values is however not possible as no band could be definitely ascribed to a particular (v', v'') value. So an arbitrary start with v' and v'' is made and successive positions are marked as $v'+1$, $v'+2$, $v'+3$,...etc., 24 successive v' levels and 19 successive v'' levels could definitely be identified. No bands corresponding to low v', v'' values are obtained. From Table VIII it appears again that only bands corresponding to high v' and v'' values are observed. This is rather peculiar, but yet consistent with the systems discussed earlier. In the band system with 380 cm^{-1} it was pointed out how the intensity of bands was observed to increase with the higher v'' values. Likewise it may be possible that in the present system bands with low (v', v'') values may altogether vanish.

Of the two states the one with a mean separation of 215 cm^{-1} may be identified with the ground state itself. The upper state is also a stable state with a number of quantized vibrational levels. Its exact height cannot be fixed up as the exact (v', v'') numbering is not known for this system. However, from the region of bands it may be fixed up at about 45000 to 50000 cm^{-1} above the ground state o_g^+ ($^1\Sigma_g^+$). A suitable state at about this height and satisfying all the requirements of the selection rules may be found in the configuration $\sigma_g^2\pi_u^3\pi_g^3\sigma_u^2$ and designated as o_u^+ ($^1\Sigma_u^-$). The fact that it is a $^1\Sigma_u^+$ may support the idea of a stable state. This interpretation of these bands as a transition between two stable states one of which is the ground level will explain (1) the difficulties about the doublet and triplet

TABLE IX

Bands arising out of transition from a stable state $\sigma^2_g\pi^3_u\pi^3_g\sigma^2_u$. $o^+_u(^1\Sigma^+_u)$ with $\omega\sim150$ to the ground state $\sigma^2_g\pi^4_u\pi^4_g$. $o^+_g(^1\Sigma^+_g)$ with $\omega\sim215$ (The first stable state is newly identified).

Intensity	λ(A.U.)	ν(cm^{-1})	Δν
2	2353	42491	
			422
2	2330	42913	
			386
2	2309	43299	
			240
2	2296	43539	
			148
4	2288	43687	
			236
3	2276	43926	
			134
4	2269	44057	
			203
2	2259	44260	
			155
3	2251	44415	
			240
3	2239	44655	
			174
4	2230	44829	
			222
2	2219	45051	
			178
3	2210	45229	
			207
4	2200	45436	
			164
3	2192	45600	
			278
3	2179	45878	
			297
6	2165	46175	
			139
4	2159	46314	
			179
4	2150	46493	
			149
8	2143	46642	
			204
6	2134	46846	
			127
8	2128	46973	
			325
6	2114	47298	
			145
4	2107	47443	
			211
4	2098	47654	
			123
8	2092	47777	
			220
4	2083	47997	
			139
12	2077	48136	

TABLE IX (contd.)

Intensity	λ (A U.)	ν (cm^{-1})	Δν
12	2077	48136	
			246
4	2066	48382	
			104
10	2062	48486	
			155
6	2055	48641	
			229
8	2046	48870	
			141
8	2040	49011	
			212
6	2031	49223	
			149
8	2025	49372	
			222
3	2016	49594	
			147
8	2010	49741	

structure, (2) the reason why the resonance series are not obtained even though a transition to the ground state is obtained, and (3) the relative intensity anomalies of the doublets and triplets.

Our final conclusion is that when iodine vapour is excited by mercury lines below 2000A, no resonance series in the rigorous sense of the word is obtained. All the bands form one system or another of the McLennan type of bands. A transition to the ground state is involved in some bands but only from various vibrational levels of a stable upper state, resulting in the development of a band system involving the vibrational differences in both the states.

With this interpretation we are able to explain all the bands obtained in fluorescence spectrum of iodine excited by mercury and thallium lines. Finally we may add the explanation given by Pringsheim as to how a molecule in the ground state could be raised to a level possibly higher than the exciting radiation. It was suggested that the exciting radiation might take up the molecule to a stable state, lower than the exciting radiation, from which it is transferred to any higher state possibly by some process of collisions (Pringsheim, 1949).

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REFERENCES

Curtis, W. E. and Evans S. F., 1933, *Proc. Roy. Soc.*, **141A**, 603.
Duschinsky, F., Hirschlaff E. and Pringsheim P., 1935, *Physica.* **2**, 439

Duschinsky, F. and Pringsheim P., 1935, *Ibid.*, **2**, 633 and 923.
Hirschlaff, E., 1932, *Z. f. Physik.* **75**, 325.
Loomis, F, W , 1926, *Phys. Rev.*, **27**, 802,
,, 1927, *Ibid*, **29**, 112, 355.
McLennan, J C., 1913, *Proc. Roy., Soc.* **88A**, 289.
,, 1915, *Ibid.* **91A**, 23.
Mulliken, R. S., 1934, *Phys. Rev.*, **46**, 549.
Oldenberg, O., 1923, *Z. f. Physik.* **18**, 1.
,, 1924, *Ibid.*, **25**, 136.
Pringsheim, P., 1921, *Ibid.* **8**, 126.
,, 1921, *Ibid* , **5**, 130.
,, 1949, "Fluorescence and Phosphorescence" p. 162, 165,
Venkateswarlu, P., 1946, *Proc. Ind. Acad. Sci.*, **24A**, 473, 480.
,, 1947, *Ibid.* **25A**, 119, 133.