Physics. — *"Bands in the secondary spectrum of hydrogen"*. By G. H. Dieke. (Communicated by Prof. P. Ehrenfest).

(Communicated at the meeting of May 31, 1924).

Among all the molecular spectra the secondary or many-lined spectrum of hydrogen occupies a special place. Owing to the small moment of inertia of the hydrogen molecule the distance between the lines in one band must be much greater than in any other band spectrum and for the same reason every band can contain but few lines in this case. This is the reason why the aspect of the many-lined spectrum is totally different from an ordinary band spectrum. It is impossible to recognize the bands at a glance, as is possible in most molecular spectra, and between the series of lines in one band generally lie many lines of a different origin.

In 1912 G. S. Fulcher[1]) found certain groups of lines with a constant difference of wavelength, and he demonstrated that these lines are strongest with low voltage discharges. He further pointed out that according to the measurements of Dufour[2]) they do not show the Zeemaneffect. F. Croze[3]) arranged a number of lines without the Zeemaneffect in series, in which the second differences of the frequencies were nearly constant. The Fulcher bands form part of his series. Lenz[4]) explained this regularity on the principle of the quantum theory of band spectra. In this paper we shall try to arrange further lines in bands and explain the origin of these bands. The results however lead to an interpretation differing from the one given by Lenz.

The secondary spectrum of hydrogen has in recent times been measured by Watson[5]), Porlezza and Norzi[6]), Croze[3]), and most

[1]) G. S. Fulcher Phys. ZS. 13 p. 1137, 1912.
   Astrophys. J. 37 p. 60, 1913.
[2]) Dufour Ann. Chim. et Phys. 9 p. 361, 1906.
       Journ. de Phys. 8 p. 258, 1909.
[3]) F. Croze Ann. de phys 1 p. 35, 1914.
[4]) W. Lenz, Verh. D. Phys. Ges. 21. p. 632, 1919.
   A. Sommerfeld, Atombau u. Spektrallinien, 3. Aufl. p. 534.
[5]) H. E. Watson Proc. Roy. Soc. A 82 p. 189, 1909.
[6]) C. Porlezza e G. Norzi Atti Accad. Lincei 20 (1) p. 819, 1911.
   C. Porlezza; ibid. 20 (2) p. 176, 1911.

exhaustively by MERTON and BARRATT[1]). The two last-named scientists also investigated the change of intensity at different conditions of discharge. The regularities found by FULCHER can easily be extended with the table given by them. We shall first mention the results found, and then discuss the admissibility of the conclusions given here.

Three groups of bands could be found, one in the red, one in the green, and one in the blue part of the spectrum. The red group is the most complete, and will therefore be taken as an example. The structure of it can be seen from the figure in which the number m is plotted as ordinate against the frequency as abscissa. The branches A, B, C, etc. are zero branches, that is to say, they are due to the transition $m \rightarrow m$ of the rotational quantum-number m, and the lines of these branches satisfy the equation

$$v = A + Cm'^2 \qquad (m' = 1.5 , 2.5 \ldots) \quad \ldots \quad \ldots \quad (1)$$
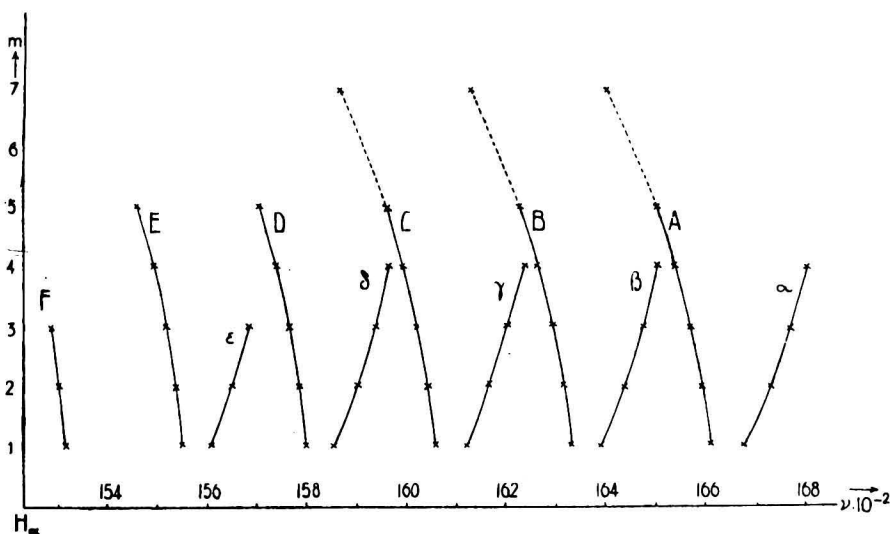

Fig. 1.

The branches marked with Greek characters may be taken for positive branches, and are therefore due to transitions $m + 1 \rightarrow m$. Whether a negative branch is present, could not be established with any certainty (see later on). In the fig. the six bands of the red group have been drawn. Every band, which in this case contains two branches, is characterized by the oscillation quantum numbers n_1 and n_2 of initial and final state of the molecule. In the group $n_1 - n_2$ is constant. The groups in green and blue have an analogous structure, but are less complete.

[1]) T. R. MERTON and S. BARRAT Phil. Trans. A 222 p. 369, 1922.

In the following tables I, II, III the wavelengths and frequencies of the lines are given according to the measurements of MERTON and BARRATT and also the intensity according to MERTON and BARRATT (M), WATSON (W) and PORLEZZA and NORZI (P).

TABLE I. Red group.

m	λ JÅ	ν	Δν	Intensity			F	m	λ JÅ	ν	Intensity			F
				M	W	P					M	W	P	
A (m)								α (m)						
1	60 18.29	166 11.43	0.00	10	9	7	S_3	1	59 94.05	166 78.59	6	4	4	S_4
2	23.74	165 96.41	−0.01	7	4	4	S_2	2	75.43	167 30.58	10	8	8	S_7
3	31.80	74.14	+0.11	10	5d	10	S_1	3	59.70	74.72	8	3	3	
4	42.70	44.32	−0.09	5				4	47.27	168 09.80	6	3	2	
5	56.10	07.73	0.00	5	0	2		5						
6														
7	(93.83	164 05.52)		2		2								
B (m)								β (m)						
1	61 21.76	163 30.66	0.00	10	10	9	S_3	1	60 98.23	163 93.66	6	3	2	S_4
2	27.40	15.64	−0.50	9	6	6	S_2	2	60 80.78	164 40.52	9			S_7
3	35.34	162 94.53	+0.05	8	6	10	S_1	3	66.64	79.03	4	1		
4	46.17	65.80	−0.04	3		2		4	54.74	11.43	0			
5	59.58	30.39	0.00	4	0	3								
6														
7	(97.05	161 32.25)		5	2	4	S_6							
C (m)								γ (m)						
1	62 24.81	160 60.31	−0.02	9	10	9	S_3	1	62 01.15	161 21.59	5	2	3	S_4
2	30.23	46.34	+0.01	7	2	3	S_2	2	61 82.98	68.96	8	4	6	S_7
3	38.39	25.35	+0.02	8	6	7	S_1	3	67.74	162 08.93	3	0	1	
4	49.15	159 97.74	−0.07	3	0	1		4	55.61	40.85	5	0	3	
5	62.49	63.68	+0.05	4										
6														
7	(99.42	158 70.09)		7	5	6	S_6							

TABLE I. (Continued).

m	λ JÅ	ν	Δν	M	W	D	F	m	λ JÅ	ν	M	W	D	F
			D (m)							δ (m)				
1	63 27.07	158 00.73	0.00	8	8	7	S₃	1	63 03.46	158 59.93	3	0	1	S₄
2	32.46	157 87.28	+0.06	5	1	3	S₂	2	62 85.37	159 05.58	?	4	4	S₇
3	40.57	67.10	+0.01	6	2	4	S₁	3	71.31	41.24	3	2	2	
4	51.28	40.51	+0.04	1		1		4	60.31	69.69	[−]			
5	64.64	07.46	−0.09	2	0	2								
			E (m)							ε (m)				
1	64 28.10	155 52.41	+0.03	5	2	4	S₃	1	64 04.01	156 10.91	3		1	
2	33.47	39.43	−0.02	2	0	1	S₂	2	63 87.87	50.36	1		1	
3	41.50	20.05	−0.06	3	0	3	S₁	3	72.19	88.85	3	0	1	
4	52.13	154 94.49	−0.08	0		1								
5	65.22	63.12	+0.14	0										
			F (m)											
1	65 27.35	153 15.93		4	1	2	S₃							
2	32.62	03.57		1		1								
3	40.53	152 85.07		2		1								
4	(*)50.60	152 61.56)				1								

*) Wavelength according to PORLEZZA.

The column Δν gives the differences between the frequencies observed and the frequencies calculated according tho the equation (2). In the last column is given FULCHER's notation for the lines found by this investigator.

Reliability of the data.

The red group is the strongest, and the observations referring to it are by far the completest. Therefore, the constants for it could be determined with a much greater accuracy than for the two other groups. For the same reason, the probability that the lines have

been wrongly arranged is smallest in the red group and generally smaller in the zero than in the positive branches. Only an experimental

TABLE II. Green group.

m	λ JÅ	ν	Δν	Intensity M	W	P		m	λJÅ	ν	Intensity M	W	P
			A (m)							**α (m)**			
1	53 03.15	188 51.49	−0.14	8	2	6 S₃		1	52 84.50	189 17.98	4	0	3
2	09.03	30.62	+0.10	4		2 S₂		2	72.29	61.84	5	2	4
3	17.90	187 99.22	+0.14	4	0	2 S₁		3	63.81	92.38	2		
4	29.74	57.43	−0.10	1		1							
5	44.27	06.45	−0.02	[−]	0	1							
			B (m)							**β (m)**			
1	54 19.90	184 45.52	+0.16	6	4	6 S₃		1	54 01.06	185 09.75	1	1	2
2	25.96	24.83	−0.16	3	1	5 S₂		2	53 91.22	43.52	1		
3	34.83	183 94.72	+0.05	3	1d	5 S₁		3	(78.41	87.71)	3		1
4	46.70	54.66	−0.06	0		2							
5	61.50	04.93	−0.51	1									
			C (m)							**γ (m)**			
1	55 37.45	180 53.86	−0.17	7	3	6 S₃		1	55 18.48	181 15.91	2		3
2	43.41	34.42	+0.18	2	0	3 S₂		2	05.51	58.61	4	2	6
3	52.52	04.85	+0.03	2	0	3 S₁		3	(54 95.98	90.09)	2	0	4
4	64.53	179 66.00	−0.03	2		1?							
5	79.47	17.88	−0.36	0		1							
			D (m)										
1	56 55.75	176 76.22	−0.23	5	1	4 S₃							
2	61.72	57.58	+0.24	3	0	3 S₂							
3	70.89	29.03	+0.12	3	0	2 S₁							
4	83.05	175 91.33	−0.13	2									
5	(99.20	41.46)	−3.88	0									

TABLE III.   Blue group.

m	λ JÅ	ν	Intensity		
			M	W	P
A (m)					
[1]) 1	44 90.45	222 63.24	5	5	4
2	93.67	47.29	2	1	2
3	98.52	23.31	2	4	5
4	45 04.90	221 91.84	[—]		
5	12.81	52.96	1	0	
B (m)					
1	45 54.13	219 51.97	4	3	3
2	57.32	36.61	2	2d	2
3	62.24	12.96	2	2	2
4					
5	76.54	218 44.45	0		
C (m)					
1	46 17.49	216 50.73	3	3	4
2	20.72	35.61	1	0	1
[1]) 3	25.39	13.76	(4)	2	6
4					
5	(40.47	215 43.50)	[—]		
D (m)					
1	46 80.43	213 59.62	2	1	0
2	(83.79	44.26)	5	4	7
3	88.43	23.15	0		0
E (m)					
1	47 43.40	210 76.06	3	1	2
2					
3	51.59	39.75	1	0	1

[1]) These lines show the ZEEMANeffect.

investigation can give certainty on the correctness of the classification. Lines which seem to belong to these bands, but which are still doubtful, have been placed between brackets. A number of lines, which must very probably be attributed to these or analogous bands, is omitted for the reason of being too doubtful. Because of the great number of lines, the existence of relations between wave numbers alone is of little value.

FULCHER and LENZ regarded the lines $A(m)$, $B(m)$, $C(m)$ etc., m being a constant, as belonging to one band. But accepting this explanation, one cannot find a reason for the existence of several bands with small characteristic differences between them.

Therefore the lines, which LENZ and SOMMERFELD regarded as belonging to the same oscillation, but to different rotational quantum numbers, are interpreted in this paper as being due to the same rotational transitions but to different oscillation jumps.

GEHRKE and LAU [1]) also investigated the many-lined spectrum and confirmed FULCHER's results, viz. that the lines in question are much more strongly excited with low velocity cathode rays, than with rays of high velocity. They were the first to observe the blue group, but propounded another conception of the structure of the groups. They, as well as FULCHER, pointed out that the regularity in the arrangement of the lines is specially manifested in the wavelengths and they therefore called these bands $\Delta\lambda$ bands.

It seems to me that most of the regularities found by CROZE must be attributed to chance.

KRATZER [2]) deduced certain relations between the constants of a band system. The fact that these relations are satisfied here may be considered as a proof that the lines are correctly arranged and interpreted.

The fact that the first lines of every band satisfy a quadratic equation, suggests that the electron impulse in the direction of the line connecting the nuclei is zero. If the influence of the rotation on the motion of the electrons is neglected, the rotational term may be written

$$F(m) = B(m-\varrho)^2 - Bu^2(m-\varrho)^4 + \ldots$$

in which $B = \dfrac{h}{8\pi^2 J} - \alpha n$ (J moment of inertia), ϱ the component of the electron impulse vertically on the line connecting the nuclei,

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[1]) E. GEHRKE and E. LAU Berl. Ber. 1922 p. 453; 1923 p. 242.

[2]) A. KRATZER ZS. f. Phys. 3 p. 289, 1920, Ann. d. Phys. 67, p. 127, 1922.

and $u = \dfrac{h}{4\pi^2 J v_0}$ (v_0 frequency of the nuclear oscillations at very small amplitudes); B is thus depending on the oscillation quantum number n. The small value of the moment of inertia J causes u to be larger here than in most other bandspectra, and therefore a deviation from DESLANDRE's law will take place already for rather small values of m. If in a certain electron- and oscillation transition the rotational quantum is unchanged, we get the zero branch

$$Q(m) = A + C m'^2 - D m'^4 \qquad . \quad . \quad . \quad . \quad . \quad (2)$$

in which

$$C = B_1 - B_2 \qquad D = B_1 u_1{}^2 - B_2 u_2{}^2 \quad \text{and} \quad m' = m - \varrho.$$

The observations indicate that m' has the values 1,5, 2,5 .... as is also the case with the infra-red bands of HCl and the ultra-violet cyanogen bands. As the lines belonging to the transitions $0,5 \to 0,5$ do not appear, it would be obvious to give ϱ the value of $-\frac{1}{2}$. There are however other likely possibilities, so that in this respect nothing can be deduced as yet. The interpretation of the structure of the bands given here is not affected by it.

In table IV the values A and C are given, computed from equation (2). The column Δv in the tables I and II indicates that the lines are in agreement with the equation within the limits of experimental errors. The agreement would be still greater, if for every band an individual value D had been taken. As D must be computed from differences of differences a reliable value cannot be calculated from one band. In the red and green group the average of the computed values of the separate bands is taken. Thus we found for the red group $D = 0,00201$ and for the green $D = 0,004$. The latter value however is of no importance as in the green group the constants in every case were computed out of the first four lines.

In the blue group the data are so few that here the simple equation (1) was used.

If the branches indicated by Greek characters belong to the transitions $1,5 \to 0,5$, $2,5 \to 1,5$ etc. the difference between the corresponding lines of the positive branch and the nullbranch must be equal to

$$B_2 - \beta_2 + 2 (B_2 - 2\beta_2) m' - \beta_2 (6 m'^2 + 4 m'^4), \quad . \quad . \quad . \quad (3)$$

in which $\beta = u^2 B$.

The values of B_2 computed from this expression are given in the third column of table IV. They must be taken as provisional values, however.

TABLE IV.

Band	A	B_2	$-C$	$\angle C$
Red group				
A	166 19.90	33.68	3.769	
B	163 38.85	31.75	3.647	0.122
C	160 68.24	30.71	3.519	0.128
D	158 08.35	30.00	3.393	0.126
E	155 59.74		3.259	0.134
F	153 22.94		3.115	0.144
Green group				
A	188 63.56	33.41	5.313	
B	184 56.87	32.28	5.126	0.187
C	180 65.21	31.15	4.979	0.147
D	176 87.26		4.812	0.167
E	173 27.03			
Blue group				
A	222 72.22		3.99	
B	219 60.72		3.87	0.12
C	216 59.27		3.78	0.09
D	213 67.83		3.65	0.13
E	(210 84.23		3.63)	0.02

The values B_2 and C depend according to KRATZER's theory on the oscillation quantum numbers

$$B_2 = B_2^{\,\circ} - a_2 n_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(4)}$$

$$- C = B_2^{\,\circ} - B_1^{\,\circ} - (a_2 - a_1) n_2 + d a_1 \quad . \quad . \quad . \quad \text{(5)}$$

Here a_1 and a_2 are numbers proportional with u, which contain the coefficients of the potentional development of the forces between the nuclei, and $B_1^{\,\circ}, B_2^{\,\circ}$ the values of B_1, B_2 when there are no oscillations of the nuclei; $d = n_1 - n_2$ is constant in one group.

The values of B_2 are not known with sufficient accuracy to test

the linear decrease of B_2 with n_2 with any certainty. The decrease is, however, in the right direction and of the correct order of magnitude. On the contrary, column ΔC in table IV shows that the linear decrease with n_2 of $-C$ really takes place. The small rate of the differences, which seems to be real in the red group, may be due to the fact that the terms of higher order in (4) and (5) are neglected. We can attach most value to the numbers of the red group, because all the constants in the two other groups could not be determined with the same degree of accuracy.

Intensity of the lines.

The sharp decrease of intensity is to be expected on account of the small moment of inertia of hydrogen, and is to a less extent also observed in the band spectrum of helium [1]). The tables show that the different investigators give greatly divergent intensities, and therefore a wholly regular course cannot be expected.

But there is one peculiarity, in which all investigations agree and which ought to be mentioned. The lines with an even value of m in the Q-branches are weaker than might be expected from the intensities of the preceeding and the following line. From this fact one could come to the conclusion that the lines 1, 3, 5 ... of the zero branch might be connected more closely and also the lines 2, 4, 6 ... Something of this kind would occur, if the odd lines belonged to the rotational transitions $m - \frac{1}{4} \rightarrow m - \frac{1}{4}$ and the even lines to the transitions $m + \frac{1}{4} \rightarrow m + \frac{1}{4}$. But we will not insist on this question, the experimental data being not yet sufficient to decide with any certainty in favour of one or the other assumption.

Changes by external influences.

According to the measurements of DUFOUR and CROZE, the band lines have no ZEEMANeffect. A few exceptions from this rule in the blue group will have their origin in the coincidence with other lines.

The first lines of each band in the red group are weakened by a condensed discharge and enhanced by lower pressure in the discharge bulb. The further lines show a more irregular behaviour with changes of the conditions of the discharge. The lines of the

[1]) W. E. CURTIS Proc. Roy. Soc. A 101 p. 38. 1922.

A 103 p. 315. 1923.

[2]) The values $m \pm \frac{1}{4}$ are also found in the spectrum of helium. A. KRATZER Z.S. f. Phys. 16. p. 353, 1923.

green and blue group behave in the same manner, but the observations are less complete.

A much more regular progression of intensities than in a discharge bulb, where the conditions are too complicated, must be expected, if the lines are excited by temperature radiation in an electric furnace. With high temperatures, the higher lines in a band must be enhanced and more lines will probably appear. Also the intensity of bands with high oscillation quantum numbers must increase. It must be expected that these and analogous bands will be prominent in the spectrum if the temperature is not too high, and that the lines enhanced by a condensed discharge will be relatively weak. In this manner, it is possible perhaps to decide, whether the classification of the lines in this paper is correct and to find new bands with some certainty.

The zero lines of the bands in each group follow approximatively DESLANDRE's formula. We shall not insist now on a possible connection between the three groups. Nor the initial nor the final state of the bands can be the normal state of the molecule, and therefore a direct information on this state cannot be got from these bands. The bands originating in the normal state must, as may be seen from the resonance potential, lie in the extreme ultraviolet. Unfortunately the accuracy of the wave lengths measurements [1]) of the so called first spectrum of SCHUMANN is not sufficient to find such bands among the extraordinary great number of lines.

If the branches marked with Greek letters are interpreted as positive branches, as indicated above, the moment of inertia of the hydrogen molecule in the final state is of the order of magnitude $0,82.10^{-40}$, whereas LENZ calculated $0,19.10^{-40}$ from the FULCHER bands.

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[1]) Th. LYMAN, Astroph. J. 23. p. 181, 1906.