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THE STRUCTURE OF THE ULTRA-VIOLET SPECTRUM OF THE HYDROGEN MOLECULE[1]

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Abstract

The absorption spectrum of the hydrogen molecule has been photographed and also the emission spectrum under various discharge conditions. In the region between 1000A and 1650A the bands belong chiefly to two systems with a common final electronic state, which is the lowest state of the molecule. The correctness of the classification is proved by combination relations and the variation of the rotational energy with the vibrational quantum number. The *Lyman bands* are emitted when, by collisions of the second kind with excited metastable argon atoms, the hydrogen molecule is brought into the first excited electronic state with three vibrational quanta. From the energy diagram which is obtained from the analysis of the spectrum it follows that the *resonance potential of the hydrogen molecule* is 11.1 volts. The *heat of dissociation of the hydrogen molecule* is found by two independent methods to be 4.34 and 4.38 volts, respectively.

1. Introduction

THE existence of a spectrum very rich in lines below 1675A which must be attributed to hydrogen was first discovered by Schumann.[2] This spectrum was extended beyond the absorption limit of fluorite by Lyman[3] who investigated it more in detail and gave wave-length measurements of its lines. There could not be any doubt that the spectrum in question, as well as the many lined spectrum in the visible and near ultra-violet, is emitted by the hydrogen molecule. As all the lines belonging to the normal state of the hydrogen molecule must be expected in this region, one can hope to get some information about the structure of the molecule by the study of the spectrum. This seems especially important, because the hydrogen molecule must be the simplest of all molecules. Moreover, all the information which one can get from other sources is so meager and uncertain that results obtained from the spectrum are needed to check it. In the visible spectrum some regularities are known, but until very recently they have been practically useless for getting information about the structure of the molecule, because little connection between the different bands had been found. A knowledge of the ultra-violet bands is certain to aid in interpreting also the structure of the visible spectrum.

In the present paper an account is given first of experimental work in obtaining the emission and absorption spectrum and then of the interpretation of the experimental results.

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[1] The main results of this article have been published in Zeits. f. Physik **40**, 299 (1926).

[2] V. Schumann, Wiener Anzeiger **29**, 230 (1892); Smith. Contrib. No. 1413 (1903).

[3] Th. Lyman, The spectroscopy of the extreme ultra-violet, (1914).

2. Experimental Arrangement

The photographs which form the basis of the present investigation were taken with the vacuum spectrograph described by one of us elsewhere.[4] The discharge tube with which most of the emission pictures were taken was essentially of the same type as that used by Wood[5] in his work on the hydrogen spectrum and the same phenomena could be observed. The electrodes were of aluminum. Wood observed that in the visible[6] the molecular spectrum is most strongly developed in the "white" stage of the discharge which occurs after the tube has run for several hours with pure, dry hydrogen. The same was found for the molecular spectrum in the extreme ultra-violet, and in the "white" stage the atomic lines had practically disappeared from the spectrum. Some of the emission pictures were taken with a tube of the same type as used in obtaining the absorption pictures.

The hydrogen was generated electrolytically, dried over phosphorous pentoxide, and admitted to the discharge tube by a capillary valve[7] which allowed one to regulate the flow of gas and to maintain any desired pressure by simply turning a pinch cock. The discharge tube and spectrograph were pumped out separately by two independent sets of oil and mercury diffusion pumps. The pressure in the spectrograph could be measured by a McLeod gauge and was usually less than 10^{-3} mm. In the discharge tube the pressure was estimated from the character of the discharge and was varied between wide limits. The current for the discharge tube was obtained from a 10 kilowatt transformer with a potential difference of 11500 volts. The spectrum was not appreciably changed when the current was rectified by a kenotron.

Commercial argon was used in the experiments with argon and no attempt was made to purify it. It was generally admitted directly from the reservoir, where it was stored over water, by a capillary and a capillary valve, as it was found that the small traces of water vapor did not appreciably change the spectrum. The argon contained air as impurity. If the pressure in the discharge tube was very low, the impurities practically did not show at all, neither in the pocket spectroscope nor in the ultra-violet spectrum. With increasing pressure (without changing the percentage of impurities) the nitrogen bands appeared very strongly in the visible, and no trace of the argon spectrum could be detected at pressures of a few millimeters. In the ultraviolet the nitrogen bands were also very strong as well as the line spectrum of nitrogen, although the argon resonance lines at 1048 and 1067Å always remained intense.

Two gratings were used in this work, both with a radius of curvature of 50 cm. The one which was in use during the earlier part of the work has 15000 lines per inch. It had been used before with chlorine, selenium, and other corroding substances and had lost much of its reflecting power,

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[4] J. J. Hopfield, Phys. Rev. **20,** 573 (1922).

[5] R. W. Wood, Proc. Roy. Soc. **A97,** 445 (1920); Phil. Mag. **42,** 729 (1921).

[6] Under the visible spectrum is understood in this paper always the secondary spectrum in the visible and near ultra-violet.

[7] J. J. Hopfield, Jour. Opt. Soc. **12,** 391 (1926).

especially in the higher orders. The other grating, ruled by Professor R. W. Wood, has 30000 lines per inch, thus giving twice the dispersion of the old one. The measurements have nearly all been made on photographs taken with this grating.

The special films were prepared by the method communicated previously by one of us.[4]

3. The Absorption Spectrum[8]

As hydrogen absorbs in a region, where even fluorite is no longer transparent, no windows of any kind could be used between the light source and the absorption chamber. Therefore the whole spectrograph was filled with hydrogen at pressures up to 70 mm, and was separated from the discharge tube, as usual, by the narrow slit. This arrangement allows one to maintain a fairly large difference of pressure between the spectrograph and the discharge tube. As the light path in the spectrograph is one meter, a relatively low density of the hydrogen was sufficient to produce strong absorption.

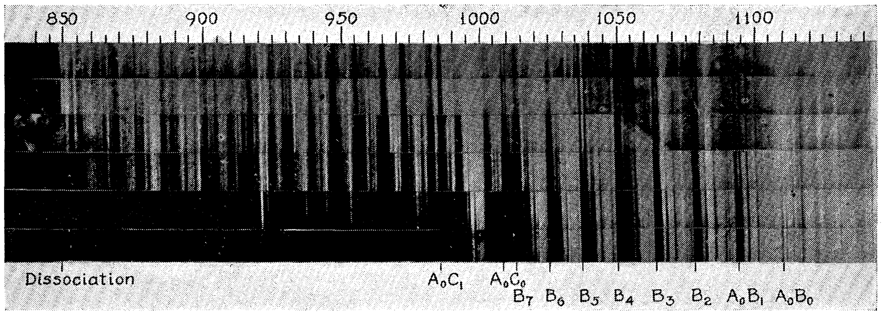

Fig. 1. Absorption spectrum of hydrogen at pressures of 2, 4, 8, 15, 36 and 50 mm, respectively.

Lyman[9] discovered that if a strong condensed discharge is passed through a narrow glass capillary, a continuous spectrum is emitted between 900 and 1900A which is practically independent of the nature of the gas in the tube. We used this spectrum as a continuous background for the absorption. Our tube, which was of Pyrex glass, was of the same type as that described by Lyman. The spectrum consisted of a continuous background with superimposed bright lines and extended towards the region of short wave-lengths to about 850A where it was cut off by the strong continuous absorption of hydrogen.

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[8] J. J. Hopfield and G. H. Dieke; Nature, **118,** 592 (1926). Note. In this first communication of the absorption spectrum of H_2 it was stated, "This adds a new electronic level to the three already obtained." As a result of our more careful study of the absorption spectrum and its correlation with the emission spectrum it was found that an earlier note concerning the emission spectrum. (G. H. Dieke and J. J. Hopfield, Phys. Rev. **28,** 849, 1926) contained an error, so that there are but three electronic levels of H_2, A, B, C, known from the ultra-violet spectrum instead of the four implied in the "Nature" letter. Also the absorption bands of H_2 start at 1116A rather than at 1245A as mentioned there.

[9] Th. Lyman, Astrophys J. **60,** 1 (1924). Compare also Nature **118,** 156 (1926).

Fig. 1 shows the absorption spectrum of hydrogen obtained in this way with hydrogen pressures of about 2, 4, 8, 15, 36, and 50 mm of hydrogen in the spectrograph. The hydrogen molecule begins to absorb at about 1115A. There are on our plates a few absorption bands on the side of longer wave-lengths, but they must apparently be attributed to traces of impurities, as control experiments with other gases show. In particular, a strong band at 1245A, which appears very easily, seems to belong to oxygen or an oxygen compound. The line 1215A of the hydrogen atom appears as a sharp absorption line and forms a good standard for the measurement of the absorption plates.

TABLE I

Absorption lines of hydrogen in the extreme ultra-violet.

λ	Int.	ν	Designation	λ	Int.	ν	Designation
849.43		117726*		1036.56	4	96473	a, B_5-A_0
986.14	3*b*	101405	C_1-A_0	36.98	4	434	
87.73	1	242		38.13	4	327	*b*
89.45	0	066		38.52	4	291	
91.25	3	100883	a, B_9-A_0	40.21	0	134	*c*
91.86	3	821		41.04	0	058	
92.60	3	746	*b*	43.44	0	95837	*d*
92.47	3	758		49.45	2	288	a, B_4-A_0
95.84		418		49.90	2	248	
1001.65	2	99835	a, B_8-A_0	51.22	4	128	*b*
02.29	2	772		53.18	00	94950	*c*
03.21	2	680	*b*	53.95	0	881	
03.90	2	611		56.33	00	668	*d*
05.20	1	483	*c*	63.29	5*d*	048	a, B_3-A_0
06.29	1	375		64.74	5	93919	*b*
08.42	3	165	a, C_0-A_0	66.95	0	752	*c*
09.71	3	039	*b*	67.49	0	678	
10.78	1	98933	*c*	70.14	0	446	*d*
12.77	3	739	a, B_7-A_0	77.16	4	92837	a, B_2-A_0
13.40	3	677		77.80	4	782	
14.21	3	599	*b*	79.07	4	672	*b*
14.80	3	541		92.23	3	91556	a, B_1-A_0
16.32	1	395	*c*	92.70	3	517	
17.28	1	301		94.16	3	395	*b*
19.34	0	103	*d*	96.57	2	194	*c*
20.54	0	97987		99.84	2	90922	*d*
24.43	1	615	a, B_6-A_0	1108.17	0	239	a, B_0-A_0
24.91	2	570		08.68	2	197	
25.67	2	497	*b*	10.09	2	083	*b*
26.36	1	431		12.57	2	89882	*c*
27.89	1	287	*c*	14.00	0	767	
28.87	1	194		14.68	0	712	
				15.72	2 *br*	628	*d*

*Limit of continuous absorption.

The absorption spectrum of the hydrogen molecule shows a number of regularly grouped bands of the same structure as the bands of the emission spectrum. The first bands are clearly resolved and can be measured satisfactorily. Toward the short wave-lengths the bands overlap and at about 850A a strong continuous absorption begins. The measured absorption lines are tabulated in Table I.

4. MEASUREMENTS

One great difficulty in obtaining accurate wave-lengths is that there are, in the region under investigation, no satisfactory standards which could be used. On the best hydrogen pictures no traces of lines belonging to impurities could be detected. The atomic lines, the wave-lengths of which are accurately known, are very weak on the photographs which show the secondary spectrum in its best development. Only the two first members of the Lyman series can be found on such plates. In addition λ1215 is usually very broad and very probably blended with secondary lines, and λ1025 is an unresolved doublet, the one component of which is a molecular line (b of C_2-A_3). Both lines are therefore, as a rule, useless as standards. On one photograph, which was taken after the tube had been operated with oxygen for some time, the secondary spectrum is strongly developed and at the same time at least five members of the Lyman series show up. The lines 972.54, 949.74, and 937.80 could here be used as standards for the part of the spectrum below 1000A, although also here the possibility remains that they are blended with molecular lines. On the films taken with the older grating some of the secondary lines could be measured in the third and fourth order between the Balmer lines $H\gamma$, $H\delta$, and $H\epsilon$ as standards. ($H\beta$ is superimposed on the fourth order of λ1215.67 which is very broad on these pictures and therefore unsuitable as a standard.) Other secondary lines were measured on plates which show lines of impurities, such as oxygen, nitrogen, and mercury lines which were used as standards. The values of the wave-lengths of molecular lines determined on these films were then used as standards on the other films.

Owing to this procedure the values of the wave-lengths may be in error by more than 0.1 of an Angstrom unit. The relative accuracy of clearly defined lines is however much greater, and the error does not exceed a few hundredths of an Angstrom unit, as can be seen from the coincidence of the wave-lengths of the same line obtained on different films and from the accuracy with which the combination relations hold. For very weak and diffuse lines and blends and lines which lie very close together and the absorption lines, the error may be considerably greater.

Because it is intended to re-photograph the spectrum with a larger grating, no attempt has been made to obtain the best possible values for the wave-lengths from our plates. Therefore corrections for the nonnormality of the spectrum, etc., were not applied as the relative wave-lengths are sufficient to establish the regularities. Wave-lengths of lines obtained from different plates between different standards have, however, been reduced when necessary, in such a way that they are consistent with each other.

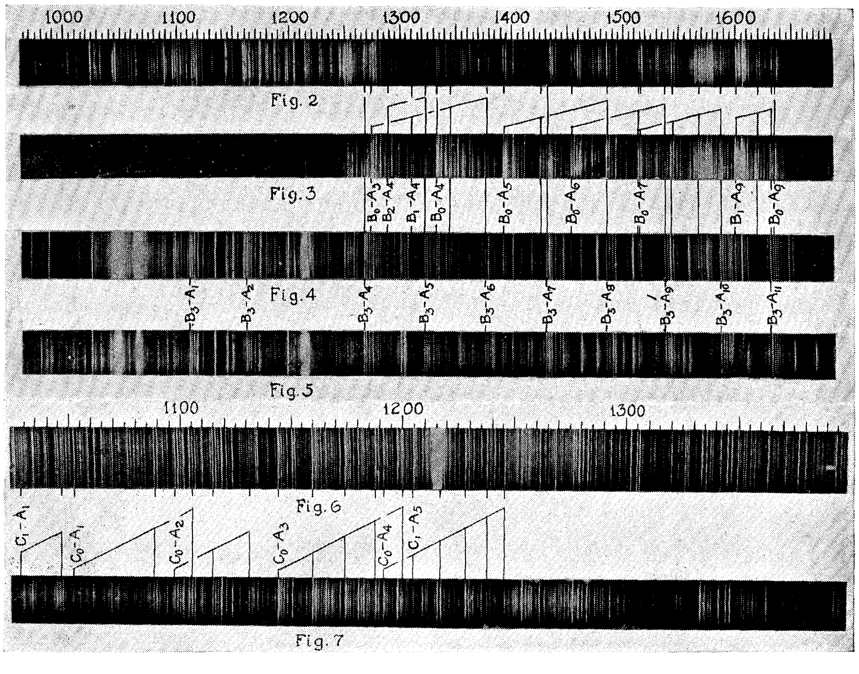
The lines below 1330A could be measured in the second order of the new grating the dispersion of which is 8.3A per millimeter. The remaining lines had to be measured in the first order of the new grating (dispersion 16.6A per mm) or in the third order of the old grating (dispersion 11.1A per mm).

5. NOMENCLATURE

An electronic state is designated by a capital letter, and an added number shows the vibrational state of the molecule (e.g. A_5). A band is then, for instance, characterized by C_3-A_5, or some times by the wave-length of its first line. In this paper only the electronic and vibrational states will be dealt with and the rotational structure will be regarded only as far as can be used for proving the correctness of the vibrational scheme and as far as it is independent of any special assumption. In order not to anticipate anything about the rotational structure, a discussion of which is reserved for another paper, the successive lines in one band are designated by the letters $a, b, c, \cdots$.

6. CLASSIFICATION OF THE LINES

Figures 2 to 7 give the appearance of the spectrum under ordinary conditions (uncondensed discharge and low pressures in the discharge tube). As with the visible, the ultra-violet spectrum is very rich in sharp lines. The most striking feature of the spectrum is the presence of several groups of lines of apparently the same structure between 1100 and 1200A. In the other parts of the spectrum the regularities are not so obvious. We have, however a much simpler form of the spectrum in either the absorption spectrum or in the emission spectrum, when it is produced in a discharge tube filled with a



Figs. 2–7. Emission spectrum of hydrogen under various conditions of discharge.

mixture of argon and hydrogen, as first observed by Lyman.[10] These simplified spectra can be used as a first method of attack in the analysis.

In order to obtain the simplified emission spectrum, pictures with argon containing traces of hydrogen were taken. Usually it was not necessary to introduce hydrogen in the discharge tube, as the aluminum electrodes gave off enough hydrogen to bring out the hydrogen bands quite strongly. By varying the conditions in the discharge tube it was possible to obtain the hydrogen spectrum in all stages of transition from the most simplified form to its full development with no argon present. Fig. 5 shows the spectrum in the stage at which only the bands found by Lyman (the "Lyman bands") are present and Fig. 4 gives an intermediate stage. The bright background on Fig. 5 is due to the impurities in the argon and is not present on Lyman's plates.

While the present work was in progress, a paper by Witmer[11] appeared in which he analyzed the simplified spectrum, using recent photographs of Lyman. He derived critical potentials and the heat of dissociation from this spectrum. We shall discuss his results presently.

TABLE II

Wave-lengths and frequencies of the Lyman bands.

	λ	Int.	ν		λ	Int.	ν		λ	Int.	ν
	λ1112, B_3-A_1.				λ1323, B_3-A_5.				λ1539, B_3-A_9.		
a_1	1112.01	3	89 928	*a*	1323.31		75 568	*a*	1539.50	3	64 956
a_2	12.57	3	882	*b*	25.09		467	*b*	41.94	5	854
b	13.81	3	782	*c*	27.63		322	*c*	44.24	*2	757
c	16.18	4	591	*d*	31.14		123	*d*	47.16	*3	635
d	19.52	4	324	*e*	35.61		74 872	*e*	50.66	4	489
e	23.77	1	88 986					*f*	55.13	2	303
	λ1162, B_3-A_2.				λ1378, B_3-A_6.				λ1589, B_3-A_{10}.		
a_1	1162.79	2	86 000	*a*	1378.03	1	72 568	*a*	1589.10	10d	62 929
a_2	63.32	2	85 961	*b*	80.07	4	460	*b*	91.48	*6	836
b	64.75	3	856	*c*	82.63	2	326	*c*	93.57	*4	752
c	67.16	3	678	*d*	86.13	3	144	*d*	96.20	8	649
d	70.56	3	429	*e*	90.50	1	917	*e*	99.41	5	523
e	74.90	0	114					*f*	1503.02	3	382
	λ1268, B_3-A_4.				λ1432, B_3-A_7.				λ1633, B_3-A_{11}.		
a_1	1268.64	*6	78 825	*a*	1432.90	10d	69 789	*a*	1633.76	*6	61 208
a_2	68.91	*2	808	*b*	35.14	5	685	*b*	36.44	5	108
b	70.53	4	707	*c*	37.59	*4	561	*c*	38.30	5	039
c	73.11	3	548	*d*	40.95	*6	399	*d*	40.40	5	60 961
d	76.64	*3	331								
e	81.06	1v	060		λ1486, B_3-A_8.§						
				a	1486.73	*6dr	67 262				
				b	89.21	*5	150				
				c	91.83	5	032				
				d	95.32	*4	875				

§ This band practically coincides with the strong band B_1-A_7, and only very poor measurements were possible.
* These lines are probably blended with others.

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[10] Th. Lyman, Astrophys J. **33**, 98 (1911). Spectroscopy of the extreme ultra-violet p. 79.

[11] E. E. Witmer, Proc. Nat. Acad. Sci. **12**, 238 (1926).

The wave-lengths and frequencies of the Lyman bands are given in Table II. The intensities in the tables are rough estimates on plates under fairly normal conditions. The relative intensities change considerably with changed conditions in the discharge tube. The successive bands can be represented by a Deslandres formula, and the sign of the quadratic term shows that they have a common initial level and are due to transitions from this level to a set of levels with the same electronic and successive vibrational quantum numbers. It is easy to obtain the absolute values for the vibrational quantum numbers, if we regard also the absorption spectrum the other simplified

TABLE III

Other hydrogen bands in the region from 1275A to 1632A.

	λ	Int.	ν		λ	Int.	ν		λ	Int.	ν
	λ1275, B_0-A_3				λ1310, B_1-A_4				λ1289, B_2-A_4		
a_1	1274.92	3	78 436	a	1310.87	3	76 285	a	1289.29	2	77 562
a_2	75.65	2	391	b	12.79	4	174	b	91.04	1	457
b	76.81	*3	320	c	15.42	2	022	c	93.62	1	302
c	79.48	2	157	d	19.04	4	813	d	97.19	3	090
d	83.10	5	77 937	e	23.63	0	550				
e	87.73	2	656								
	λ1333, B_0-A_4.				λ1427, B_1-A_6.				λ1345, B_2-A_5.		
a	1333.85	6	74 971	a	1427.74	8	70 041	a	1345.46	4	74 324
b	35.93	6	854	b	30.01	7	69 930	b	47.37	6r	219
c	38.62	3	704	c	32.90	10d	787[2]	c	50.68	3	075
d	42.31	6	498	d	36.23	*8r	627	d	53.54	5	73 880
e	46.91	8d	244	e	40.95	*6	399	e	58.04	3	636
	λ1394, B_0-A_5.				λ1486, B_1-A_7.				λ1515, B_2-A_8.		
a	1394.94	10	71 739	a	1486.73	*6dr	67 262[3]	a	1515.19	5	65 998
b	96.24	6	621	b	89.21	*5	150[4]	b	17.61	4	893
c	99.00	6	480	c	91.83	5	032[5]	c	20.08	3	786
d	1402.69	*8	292	d	95.37	*10r	66 873[6]	d	23.40	6	643
e	07.34	*4	056	e	99.71	5	680	e	27.44	2	469
f	12.89	8	70 777	f	1504.93	5	448				
	λ1455, B_0-A_6.				λ1545, B_1-A_8.				λ1569, B_2-A_9.		
a	1455.05	*6	68 726	a	1544.90	*5v	64 729	a	1569.59	4	63 711
b	57.56	5	608	b	47.56	*3	618	b	72.16	4	607
c	60.20	*4	484	c	50.23	2	506	c	74.51	4	512
d	63.94	7d	309	d	53.62	*5	366	d	77.46	10bd	393
e	68.53	4	096	e	57.65	1	199				
f	73.96	3	67 845								
	λ1516, B_0-A_7.				λ1602, B_1-A_9.				λ1621, B_2-A_{10}.		
a	1516.33	5	65 949	a	1601.67	*2	62 435	a	1621.03	6d	61 689
b	18.88	5	838	b	04.63	4	319	b	23.62	4	591
c	21.77	2	713	c	unmeasurable			c	25.79	3	509
d	25.34	4	559	d	09.92	2	115	d	28.48	5	407
e	29.53	2u	379					e	31.70	3	286
	λ1636, B_0-A_9.				λ1655, B_1-A_{10}.						
a	1636.44	5v	61 108[1]	a	1655.16	*1	60 417				
b	38.99	3	013	b	58.16	1	308				
c	41.58	4	60 917	c	60.36	0	228				
d	44.48	4	810	d	63.10	2	129				
e	48.63	0	656	e	66.32	0	013				

* These lines are probably blended with others.

[1] Coincides with *b*, B_3-A_{11}.

[2] Coincides with *a*, B_3-A_7.

[3] Coincides with *a*, B_3-A_8.

[4] Coincides with *b*, B_3-A_8.

[5] Coincides with *c*, B_3-A_8.

[6] Superimposed by heavy line.

form of the spectrum. The first Lyman band (in emission) which can be recognized on our plates lies at 1112A. It cannot be due to transitions to the normal state of the molecule, because it is not found in absorption. The next band on the short wave-length side would be obscured on the argon plates by one of the heavy argon resonance lines. But in the place where it is to be expected is the fourth absorption band λ1063, which must be due to transitions from the first excited state with three vibrational quanta (B_3)

TABLE IV

Hydrogen bands which dominate the spectrum below 1250A.

	λ	Int.	ν
	λ1052, C_0-A_1		
a	1052.58	2b	95 005
b	54.00	2	94 877
c	55.12	0	776
d	56.82	0	624
(*e*	58.81	2	445)
	λ1097, C_0-A_2.		
a	1097.90		91 083
b	99.41		90 986
c	1100.46		871
d	02.10		736
e	04.29		556
	λ1144, C_0-A_3.		
a	1144.20	5	87 397
b	45.85	8	272
c	46.87	5	194
d	48.44	7	074
e	50.78	6	86 898
f	53.03	1	728
	λ1191, C_0-A_4.		
a	1191.49	3d	83 928
b	93.20	5	809
c	94.17	8	740
d	95.62	5	639
e	97.87	2	482
	λ1027, C_1-A_1.		
a	1027.75	0	97 300
b	28.77	1	204
c	30.16	1d?	073
d	31.80	0	96 917
	λ1114, C_1-A_3.		
a	1114.92	5	89 693
b	16.34	*8	578
c	17.43	4	491
d	18.99	6	367
e	21.15	5	194

	λ	Int.	ν
	λ1159, C_1-A_4.		
a	1159.68	5	86 231
b	61.25	8	114
c	62.25	5r	040
d	63.75	6	85 929
e	66.04		761
	λ1204, C_1-A_5.		
a	1204.89		82 995
b	06.60		877
c	07.51		815
d	08.91		719
	λ1046, C_2-A_2.		
a	1046.56	5	95 551
b	47.79	5	438
c	48.94	2	333
d	50.64	3	180
e	not resolved from *a*, C_0-A_1.		
	λ1088, C_2-A_3.		
a	1088.64	7d?	91 858
b	89.95	5	748
c	91.02	1	657
d	92.68	2	520
	λ1131, C_2-A_4.		
a	1131.34	2	88 391
b	32.68	3	286
c	33.69	0	208
d	35.27	4	085
e	37.00	2	
	λ1174, C_2-A_5.		
a	1174.28	3	85 159
b	75.79	6	049
c	76.74	2	84 980
d	78.21	7	875
e	80.42	5u	716
	λ1217, C_2-A_6.		
a_1	1217.28	3	82 151
a_2	17.64	3	
b	18.92	6	040
c	19.77	3	81 983
d	21.05	3	896

	λ	Int.	ν
	λ1024, C_3-A_2.		
a	1024.74	2	97 586
b	not resolved from 2nd member of Lyman series		
c	26.98	0	374
d	28.77	1	204
	not separated from *b*, C_1-A_1		
	λ1105, C_3-A_4.		
a_1	1105.71	1	90 439
a_2	06.03	1	414
b	07.08	5	328
c	08.17	1	239
d	09.79	2	107
	λ1187, C_3-A_6.		
a	1187.77	7	84 192
b	89.33	5	081
c	90.22	3	018
d	91.49	3d	83 928
	not separated from *a*, C_0-A_4		
e	93.20	5	809
	coincides with *b*, C_0-A_4		
	λ1228, C_3-A_7.		
a	1228.18	4	81 421
b	29.95	8bd?	304
c	30.72	4	254
d	31.90	3	176
	λ1199, C_1-A_7.		
a	1199.89	*4bd	83 338
b	1201.78	4d	210
c	02.57	3	156
d	03.86	2	066
	λ1237, C_4-A_8.		
a	1237.89	*4	80 782
b	39.48	5	679
c	40.16	3	635
d	41.24	2	565
	λ1245, C_5-A_9.		
a	1245.79	5	80 270
b	47.27	5	175
c	48.79	3	134
d	49.26	3	078

to the normal state A_0 of the molecule, and can be written in our notation B_3-A_0. The Lyman bands are then due to transitions from the same initial state B_3 to the successive vibrational levels of the lowest electronic state, and they must therefore be designated by B_3-A_n.

On photographs of the emission spectrum in pure hydrogen the Lyman bands can all be easily identified, though they are not as prominent as in the pictures with argon. There are a number of bands, some of them very strong, which are due to transitions from other B states to the same set of final A levels. They are given in Table III and their arrangement into the system can be seen from the upper part of Table V in which the bands are given by the wave-length of the head and the frequency of the b-line. The a-line is in many cases an unresolved doublet and is therefore not suitable for representing the regularities.

The bands which dominate the spectrum below 1250A if pure hydrogen is used, belong to another system which has the same final electronic state A but a different initial electronic state C. They are listed in Table IV, and the vibrational scheme is given in the lower part of Table V. These bands have a structure analogous to that of the $B-A$ bands, and also in this system the absolute values of the vibrational quantum numbers can be determined from the absorption spectrum. The first two members of the absorption series C_n-A_0 can be measured and are found in the places where they must be expected. The presence of further members of the series can be recognized on the plates. They are, however too much confused with the $B-A$ bands to allow measurements.

TABLE V

	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	A_{11}
B_0	1108 90 083			1275 78 320	1333 74 854	1394 71 621	1455 68 608	1516 65 838		1636 61 013		
B_1	1092 91 396				1310 76 174		1427 69 930	1486 67 150	1545 64 618	1602 62 319	1655 60 310	
B_2	1077 92 672				1289 77 457	1345 74 219			1515 65 893	1569 63 607	1621 61 591	
B_3	1063 93 919	1112 89 782	1162 85 856		1268 78 707	1323 75 467	1378 72 460	1432 69 685	1486 67 141	1539 64 848	1589 62 836	1633 61 108
B_4	1049 95 128						1355 73 661			1511 66 063		
C_0	1008 99 039	1052 94 887	1097 90 986	1144 87 272	1191 83 809							
C_1	985	1027 97 204		1114 89 578	1159 86 114	1204 82 877						
C_2			1046 95 438	1088 91 748	1131 88 286	1174 85 049	1217 82 040					
C_3			1024 (97 492)		1105 90 328		1187 84 081	1228 81 304				
C_4								1200 83 210	1237 80 679			
C_5										1245 80 175		

The structure of most of the bands can immediately be recognized on the plates, and these bands are, of course, the most important ones for establishing the regularities. In some parts of the spectrum the regularities are obscured, because several of the bands overlap, and the resolution of the grating is there insufficient. The wave-length measurements in such parts have therefore considerably less accuracy and such lines cannot be used to prove anything. Many gaps in Table V have their explanation in the fact that the corresponding bands must lie in places where other bands are strongly developed. Their existence is therefore still doubtful, and they have been omitted from the tables for that reason. That is, for instance, the case for the bands of the $B-A$ system which correspond to transitions between small numbers of the vibrational quantum numbers and which lie in the region where the most intense bands of the $C-A$ system occur.

7. COMBINATIONS

The correctness of the above classification can be tested by an application of the combination principle. A band line can always be written in the form:

$$\nu = B(n', m') - A(n'', m'')$$

in which A and B are two arbitrary electronic states, n the vibrational, and m the rotational quantum number. If we take two bands with the same initial state (vibrational and electronic) i.e. two bands of the same horizontal row of Table V, and form the difference of corresponding lines, the result

$$\Delta\nu = A(n_1, m) - A(n_2, m) \qquad (2)$$

is entirely independent of the initial state. We can therefore form the corresponding differences for each row of Table V, and they must all have the same value. These differences are given in Table VI, as a rule for the

TABLE VI

Wave-number differences between the various A terms as calculated from the wave-number differences of various band lines.

		a	b	c	d	e
A_2-A_1	B_3	3921	3926	3913	3895	3872
	C_0	3922	3919	3905	3891	
A_3-A_1	C_0	7607	7605	7582	7549	
A_3-A_2	C_0	3686	3686	3677	3661	3658
	C_2	3693	3691	3676	3660	
A_4-A_2	B_3	7153	7148	7130	7089	7054
	C_0	7157	7149	7131	7097	
	C_2	7146		7133		
A_4-A_3	B_3	3465	3466	3453	3438	3411
	C_0	3471	3463	3454	3436	3416
	C_1	3462	3464	3451	3437	
	C_2	3467	3462	3449	3435	
A_5-A_4	B_0	3232	3233	3224	3206	3188
	B_2	3238	3238	3227	3209	3187
	B_3	3240	3241	3226	3208	3188
	C_1	3236	3237	3225	3210	
	C_2	3232	3237	3227	3210	3186
A_6-A_5	B_0	3013	3013	2996	2983	2961
	B_3	3001	3007	2996	2980	2956
	C_2	3008	3009	2997	2978	2365
A_6-A_4	B_0	6245	6246	6220	6189	6150
	B_1	6244	6244	6233	6186	6151
	B_3	6240	6247	6222	6187	6144
	C_3	6247	6247	6221	6179	
A_7-A_6	B_0	2777	2770	2771	2750	2716
	B_1	2780	2780	2756	2753	2719
	B_3	2779	2775	2765	2745	
	C_3	2771	2777	2765	2753	
A_8-A_7	B_1	2533	2532	2525	2508	
	B_3	2527	2535	2529	2524	2481
	C_4	2555	2531	2521	2501	
A_9-A_8	B_1	2295	2299		2251	
	B_2	2287	2286	2274	2249	
	B_3	2305	2296	2275	2241	
A_9-A_7	B_0	4840	4825	4796	4750	4723
	B_1	4827	4831		4760	
	B_3	4832	4831	4804	4764	
$A_{10}-A_9$	B_1	1996	2011		1986	
	B_2	2022	2016	2003	1986	
	B_3	2027	2028	2004	1985	

successive bands of the rows. The second column gives the common initial state. It is seen from the table that the relations derived from the combination principle hold well within the limits of the experimental errors. The agreement is very satisfactory, if one considers that an error of 0.1A in the wave-lengths would give an error of 7 wave numbers at 1200A. As mentioned before, the wave-lengths could generally be measured with a much greater precision, but the errors in the four wave-lengths concerned may work together in some cases. Also if the lines whose differences have been calculated lie in parts of the spectrum which have been measured between different standards, the error may be greater. In judging the coincidence for the line *a* it must not be forgotten that this line is often an unresolved doublet with varying separation of the components. Relations corresponding to those expressed by Eq. (2) hold, of course, for bands with the same final state.

8. Variation of the Rotational Energy with the Vibrational Quantum Number

Though the rotational structure of the bands is not discussed in this paper, we can use some general features of it which are entirely independent of any special assumption to obtain additional evidence for the correctness of the vibrational scheme as given in Table V. The rotational energy can always be written in the form Bhm^2, in which $B=h/8\pi^2 I$ (I is the "effective" moment of inertia) and m the rotational quantum number (not necessarily an integer or a half-integer). As a first approximation B depends linearly on the vibrational quantum number[12]

$$B=B_0-\alpha n. \tag{3}$$

A line of a band can then be written

$$\nu=\nu_0+B'm'^2-B''m''^2$$

and if we form in all bands of a horizontal row of Table V the differences of two corresponding lines

$$\Delta\nu=B'(m_1'^2-m_2'^2)-B''(m_1''^2-m_2''^2),$$

in this difference only B'' changes from band to band. Therefore, on account of (3), we must obtain approximately a straight line, if we represent $\Delta\nu$ as a function of n'', and all lines which belong to different initial states must be parallel to each other. Figs. 8 and 9 show the differences $b-c$ and $c-d$, and it is seen that within the limits of experimental errors the lines have exactly the properties which we must expect. The lines for the B_1-A_n and B_2-A_n bands for which fewer and less accurate data are available have been omitted in order not to crowd the figures.

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[12] A. Kratzer, Zeits. f. Physik. **3**, 269, (1920); Ann. d. Physik. **67**, 127 (1922).

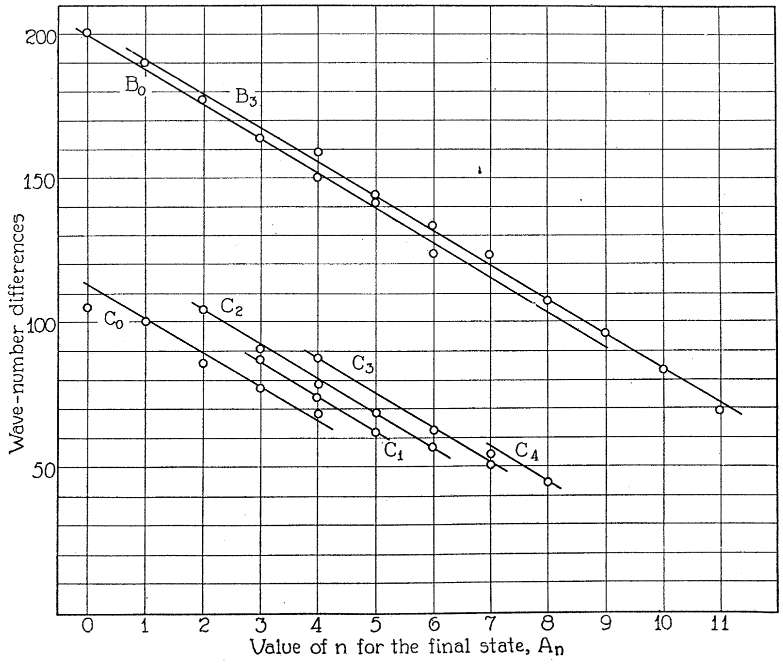

Fig. 8. Wave-number differences between the *b* and *c* members of the bands as functions of the vibrational quantum number of the final state.

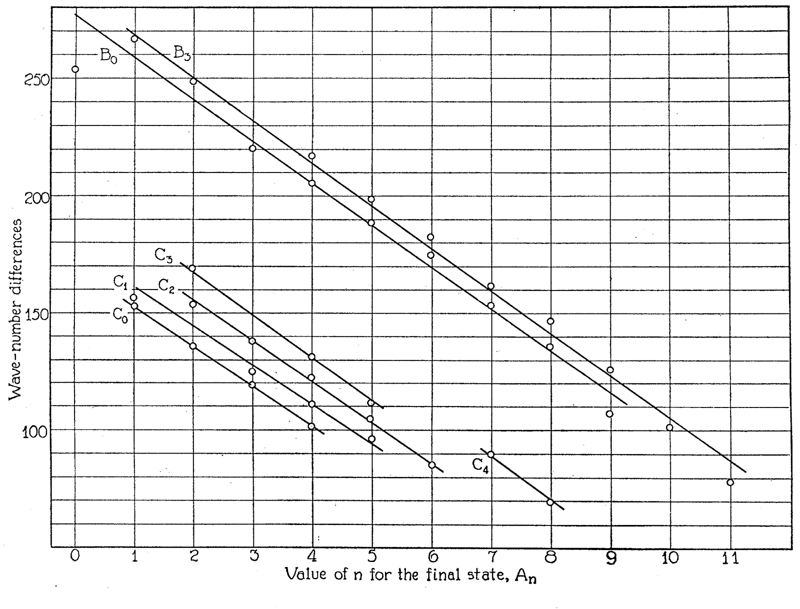

Fig. 9. Wave-number differences between the *c* and *d* members of the bands as functions of the vibrational quantum number of the final state.

9. Energy Levels

Fig. 10 gives a representation of the relative position of the levels as they have been determined from the preceding data. The absorption measurements show that A is the lowest electronic state so that A_0 can be called the normal state of the molecule. The two observed systems can be represented approximately by the usual formula.

$$\nu=\nu_e+(\omega_0'n'-x'n'^2+\cdots)-(\omega_0''n''-x''n''^2+\cdots). \qquad (4)$$

In this formula ν_e is the share of the electronic energy, ω_0 the vibrational frequency for infinitesimal amplitudes, and x a constant which is determined by the non-harmonic character of the law of force between the two nuclei.[12] According to the more recent investigations n has half-integer values.[13] The constants for the hydrogen molecules are given in Table VII. In order to enable a direct comparison with older data on other molecules the values for the constants, if integer vibrational quantum numbers are used in (4), are given in parentheses. The numbers which have been used to characterize the different vibrational states are always half a unit lower than the true vibrational quantum numbers.

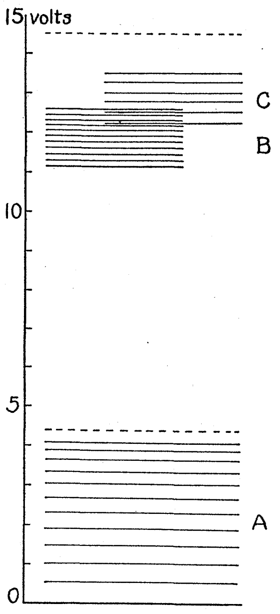

Fig. 10. Energy level diagram for the hydrogen molecule.

TABLE VII

Constants of the hydrogen molecule.

		$B-A$		$C-A$	
ν_e		91 562		99 986	
		(90 083)		(99 039)	
	A		B		C
ω_0	4362		1355		2444
	(4247)		(1337)		(2377)
$2x$	229		36		134

Strictly speaking the constants have only the above meaning if formula (4) represents the zero lines of the bands. The deviations, if a real line is taken (in our case the b-line), are however only small. It is very remarkable how much ω_1 changes in a transition from the B to the A-state.

[13] R. S. Mulliken, Phys. Rev. **25,** 259 (1925); W. Heisenberg, Zeits. f. Physik **33,** 879 (1926).

10. Critical Potentials

It follows from the preceding scheme that the resonance potential of the hydrogen molecule is 11.1 volts, and electrons with 11.3, 11.4, 11.6 volts energy must be able to bring the molecule into the B_1,B_2,B_3, state respectively, while the C_0 state is excited at 12.2 volts. The agreement of these values with those determined by direct experiments is not very satsifactory. The discrepancy can however be understood, if we realize that a critical potential in a molecule is something different from a sharply defined critical potential of an atom. As the molecules are distributed over the different rotational states each of which has its own values for the critical potentials, the breaks in the curves cannot be expected to be sharp. As the bands are degraded towards the red, the lines corresponding to a high rotational quantum number require a lower excitation potential than those corresponding to the lower states. In hydrogen the excitation potential for the *a*-line is more than 0.1 volt higher than that of the *e*-line. Therefore it is difficult to decide, what we ought to call the critical potential for a band, and its value cannot be given with great accuracy and will be slightly variable with temperature. What is measured is always a value which is obtained by extrapolation of the curve representing the electronic current before and after the critical potential. It is apparent that this procedure will give only an average value. Furthermore the breaks corresponding to the successive critical potentials must be expected in a distance of about 0.15 volt and probably cannot be resolved by the experiments. The observations give therefore an average value which is dependent on the relative probabilities of the transitions. In our case the first members of the absorption series are very weak, which means also that the probability that an electron excites one of the first states must be expected to be small, and that would shift the observable average critical potential considerably to higher values.

The Lyman bands are due to transitions from the B_3 state to the different A states. This shows that in an argon-hydrogen mixture they must be excited almost exclusively by collisions of the second kind with excited argon atoms. For, if direct electron impacts would also play any considerable role, the B-levels with vibrational quantum numbers smaller than three would necessarily have to be excited as well. Bands which belong to transitions from these states are practically absent on the argon-hydrogen plates, though they are very strong in pure hydrogen. It is remarkable how strong in this case is the selection of the levels which are excited by the collisions of the second kind. In other cases it has been observed that those states are most strongly excited by collisions of the second kind, for which the least amount of energy is converted into translational energy, and we seem here to have a particularly good example of such a resonance effect. The matter is complicated somewhat by the fact that four excited argon levels $1s_5$ with 11.50, $1s_4$ with 11.57, $1s_3$ with 11.67, and $1s_2$ with 11.77 volts energy[14] must be taken into account.

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[14] Compare K. W. Meissner, Zeits. f. Physik **37,** 238 (1926).

[15] K. W. Meissner, Ann. d. Physik **76,** 124 (1925); H. B. Dorgelo, Zeits. f. Physik **34,** 766 (1925).

For the corresponding states of neon it has been shown by absorption experiments in the excited gas[15] that most atoms are in the metastable states s_3 and s_5, and these will therefore probably be the most important ones for the excitation of the hydrogen molecules. From a purely energetic point of view, however, it remains unexplained, why the B_2 and B_4 states are not also excited to an appreciable extent.

From an analysis of the Lyman bands only, Witmer[10] concluded that in an argon hydrogen mixture the hydrogen molecule is brought by both electronic collisions and collisions of the second kind into the first excited electronic state with no vibrational energy. The critical potentials which result from this conception of the bands are considerably higher, but they cannot be brought into accordance with the absorption spectrum and the full analysis of the emission spectrum.

11. DISSOCIATION

The maximum of vibrational energy which a molecule can have determines the heat of dissociation of the molecule and this has recently been determined spectroscopically with more or less precision for a number of molecules.[16] For hydrogen the heat of dissociation can be determined from the ultraviolet band spectrum according to two independent methods.

In the first method the mechanical vibrational frequency $\omega_n = (1/h)\partial E/\partial n$ is represented as a function of the vibrational quantum number n, and the curve obtained in this way is extrapolated to $\omega_n = 0$. The heat of dissociation is then $h\int\omega_n dn$ and can be found by graphical integration of the $\omega_n = F(n)$ curve. The accuracy of this method is the greater the longer the portion of the curve which has been determined by the observations. Witmer applied this method to the final state of the Lyman bands, which is, as we have seen, the lowest state of the molecule and found 4.34 volts for the heat of dissociation. We can take over his results. Though a large part of the ω_n-curve is empirically known, the uncertainty of the extrapolation must be estimated to be about 0.1 volt.

The second method for determining the heat of dissociation which can be applied in the case of hydrogen uses the limit of the continuous absorption. By the absorption of light of the right frequency the hydrogen molecule can be brought from the normal state A_0 to a series of excited states with increasing amounts of vibrational energy. For high values of the vibrational quantum number the corresponding bands lie closer and closer together until, in our case, they are no longer resolved. If the vibrational energy exceeds a certain limit which is the heat of dissociation the nuclei do not stay together any longer, i.e. dissociation takes place and a continuous spectrum is absorbed, because the two atoms can separate with any arbitrary amount of translational energy. The limit of this continuous absorption is particularly sharp for hydrogen. It lies at λ849.4 or 14.53 volts. The hydrogen molecule

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[16] J. Franck, Trans. Faraday Soc. **21**, part 3 (1925). E. G. Dymond, Zeits. f. Physik **34**, 553 (1925); R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

must fall apart into one normal and one excited atom in the two quantum state which has 10.15 volts energy. We have therefore the energy equation

$$D+10.15=14.53 \text{ volts},$$

from which we obtain the value 4.38 volts for the heat of dissociation D which agrees better than could be expected with the value found by the first method. On the energy diagram (Fig. 10) the dissociation is marked by the dotted lines.

It seems probable that both the B-A and the C-A absorption series converge to the limit 14.53 volts. A rough extrapolation which cannot claim any accuracy gives 14.2 and 14.8 respectively for the two limits. Now the experimental facts have shown that, in dissociating, a molecule can fall apart only into atoms which are in definite quantum states. To dissociate a hydrogen molecule into one normal and one excited atom in the three quantum state 16.4 volts are required. The values found by extrapolation lie sufficiently close to 14.5 volts to justify the conclusion that this is the common limit of the B-A and C-A series. This means that if the nuclear distance of a hydrogen molecule in a B or C state is increased adiabatically the molecule, falls apart into one normal and one excited molecule with the electron in a two quantum orbit. The different character of the B and C state makes it probable that in the one case the electron moves in a 2_1 and in the other in a 2_2 orbit.

We must in some cases expect an emission analogue to the continuous absorption spectrum. For if a molecule makes a transition from an excited to a lower level, it is possible that it gains so much vibrational energy that it dissociates into two atoms. A continuous spectrum is then emitted extending towards the longer wave-lengths from a limit which is given by

$$h\nu=E'-D,$$

where E' is the energy before the transition and D the heat of dissociation. This continuous spectrum starting at the end of a series like the Lyman bands must be expected to be very intense, if the bands, which correspond to high values of the final vibrational quantum number are strong. That is the case in hydrogen for the B-A system, and it is very probable that the continuous spectrum which extends from the ultra-violet band spectrum towards the visible must be regarded as a dissociation spectrum in the above sense. The end-product is here two *normal* atoms and not one normal and one excited atom as in the case of the continuous absorption spectrum. This conception of the continuous hydrogen spectrum is identical with the modified Franck-Blackett interpretation.[17] All our observations in the ultra-violet can be brought into accord with it. It extends with great intensity to about 1650, the long wave-length limit of the Lyman bands. Farther to the ultra-violet its presence is obscured by the great number of ultra-violet lines. Of course, in our case, we must not expect the continuous spectrum to extend only to

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[17] P. M. S. Blackett and J. Franck, Zeits. f. Physik **34,** 389 (1925); J. Franck and P. Jordan, Anregung von Quatensprüngen durch Stösse, p. 266 (1926).

the long wave-length limit of the Lyman bands, as other similar progressions may also be followed by a continuous spectrum. The intensity of the continuous spectrum seems quite independent of the intensity of the atomic lines. On some plates even the strong line λ1215 is scarcely visible while the continuous spectrum is very strong. Under the conditions under which our pictures were taken the secondary spectrum was always present with great intensity when the continuous spectrum was strong. This is in accord with what we must expect if we interpret the spectrum as a dissociation spectrum. The behavior of the intensity of the *visible* secondary spectrum with respect to that of the continuous spectrum, must, however, be quite different and it must be possible to get a strong continuous spectrum without any trace of the visible molecular spectrum. An experimental decision between the dissociation explanation and an interpretation of Schüler and Wolf[18] could probably be obtained in this way.

It is of course of great importance to find connections with the visible many lined spectrum of hydrogen. In the visible the Fulcher bands are the only known regularities of a sufficient extent to enable a direct comparison with the ultra-violet bands. It seems certain that the Fulcher bands do not belong to one of the levels A, B, C, of this paper. There are however a number of lines in the blue which belong probably to transitions to the B-levels. The results are however still too uncertain to comunicate them at this time.

The latter part of this work was done when one of the authors, Mr. Dieke, was a National Research Fellow, and we wish to express our thanks to the National Research Council and to the International Education Board.

NOTE. This paper has been in the present form for almost a year. Its publication, however, has unfortunately been delayed by the authors. Since this article was written two papers dealing with the ultra-violet spectrum of hydrogen appeared and it seems desirable to state briefly their relation to our work. The first article is the full paper of Witmer[19] giving a more detailed account of his work on the Lyman bands discussed above. He gives some additional bands which he interprets as belonging to the same system as the Lyman bands. They are, however, identical with the strongest $C-A$ bands according to our interpretation. The article by Werner[20] contains measurements of bands which are also identical with bands of the $C-A$ system.

UNIVERSITY OF CALIFORNIA,
July 1, 1927.

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[18] H. Schüler and K. L. Wolf, Zeits. f. Physik **33,** 42 (1925); **35,** 477 (1926).

[19] E. E. Witmer, Phys. Rev. **28,** 1223 (1926).

[20] Werner, Proc. Roy. Soc. **A113,** 107 (1926).

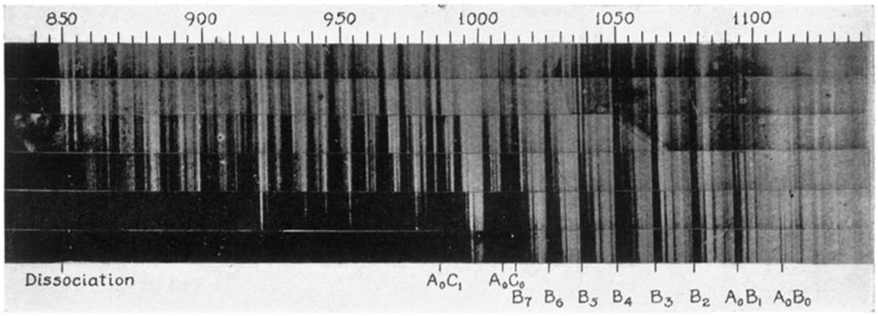
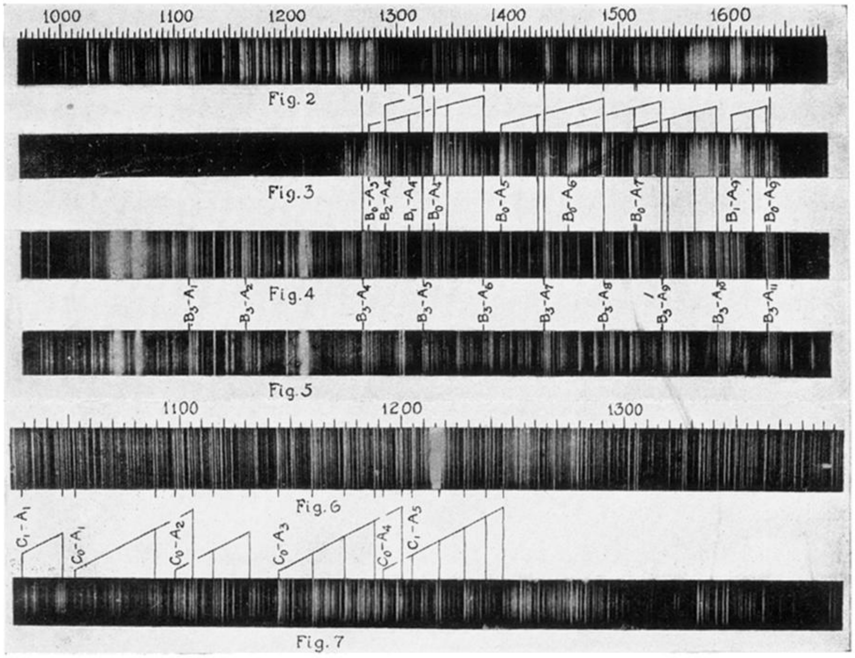


Fig. 1. Absorption spectrum of hydrogen at pressures of 2, 4, 8, 15, 36 and 50 mm, respectively.



Figs. 2–7. Emission spectrum of hydrogen under various conditions of discharge.