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The Fulcher Bands of HD and D_2[1]

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First an account is given of the production and photography under high dispersion of the molecular spectra of H_2, HD and D_2 from the ultraviolet to the infrared. Besides the HD and D_2 lines many new H_2 lines were found. The Fulcher bands ($1s\sigma\cdot 3p\pi\ {}^3\Pi\rightarrow 1s\sigma\cdot 2s\sigma\ {}^3\Sigma$ transitions) are given and the constants of these bands compared for the three isotopic molecules. One component of the higher vibrational levels of the initial state is predissociated. From this it follows that the heat of dissociation of the normal molecule must lie between 4.43 and 4.52 volts.

THE discovery of the heavy hydrogen isotope deuterium has provided new possibilities for the study of the molecular spectrum of hydrogen. The available experimental material has tripled, for while we had hitherto only the spectrum of H_2 we now have also the spectra of HD and D_2. The spectra of these three molecules must be very similar in structure but with certain characteristic differences which result mainly from the different masses of the molecules. The study of these differences will furnish a more accurate and detailed test of the theory of band spectra and will permit a more precise evaluation of the molecular constants. Besides, and this is much more important, we can expect that the new spectra of HD and D_2 will be of great help for those parts of the H_2 spectrum which have so far defied analysis or for which the interpretation was uncertain. We have begun the study of the HD and D_2 spectra chiefly with the latter point in view, although the present paper is concerned chiefly with the former.

EXPERIMENTAL PROCEDURE

§1. The preparation of the hydrogen

For the greater part of the work the hydrogen gas was prepared by having small amounts of heavy water react in an evacuated glass tube with metallic sodium which had been distilled into it. The gas passed through an electrically heated palladium tube into the discharge tube. One drop of water was sufficient to run the discharge tube for many hundreds of hours. In the later stages of the experiments when we were anxious to work with D_2 which was as free as possible from HD and H_2, we used pure D_2 which had been obtained by electrolysis in the Princeton Chemical Laboratory.

The quartz discharge tube with tantalum electrodes has been described elsewhere.[3] It was usually operated with about 5000 volts and 0.8 ampere. The electrodes had a considerable

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[1] The results of this paper were presented at the St. Petersburg meeting of the American Chemical Society in March, 1934, and a brief account of them appeared in Nature **133**, 611 (1934).

[2] National Research Fellow.

[3] G. H. Dieke and R. W. Blue, Phys. Rev. **45**, 395 (1934).

amount of H_2 adsorbed. We replaced this gradually by deuterium by admitting D to the tube and operating the tube for a considerable time with the electrodes being allowed to become as hot as possible. The gas then was pumped off, fresh deuterium gas admitted, and the process repeated until the mixture in the tube showed the desired deuterium concentration. This way of replacing the adsorbed H by D would be very inefficient if a very high D-concentration were required in the beginning. Baking out the electrodes in an induction furnace would then lead much quicker to the desired result. We needed, however, the spectrum at several intermediate concentrations and for this our method was most convenient. The D concentration was determined by measuring with the help of a step reducer the ratio of the intensities of $D\alpha$ and $H\alpha$.

§2. Photography of the spectrum

The spectrum was photographed in the first order of a 21 ft. grating with 30,000 lines per inch and a dispersion of about 1.3A per mm. The exposure times necessary to obtain an intense spectrum ranged from less than two hours in the violet to 24 hours or more in the red or infrared. For the region from $H\alpha$ toward the infrared the astigmatism of the grating reduced the intensity so much that good exposures could no more be obtained with reasonable exposure times. By the use of a suitable cylindrical lens between slit and grating the image was made stigmatic and the intensity increased so much that strong exposures could be obtained for wavelengths up to about 8500A. For longer wavelengths use was made of a 15 ft. grating with 15,000 lines per inch and a dispersion of about 3.8A per mm. Eastman spectroscopic plates hypersensitized with ammonia were used which gave the best results in each different region.

In the violet and blue the continuous hydrogen spectrum is superimposed on the molecular line spectrum. Very weak lines can therefore not be obtained because they merge with the continuous background, and increasing the exposure time beyond a certain limit would be of no use because it would not bring out new lines but only strengthen the continuous background. We have reached the limit beyond which an increase of the exposure time will not produce any more new lines also for the rest of the spectrum

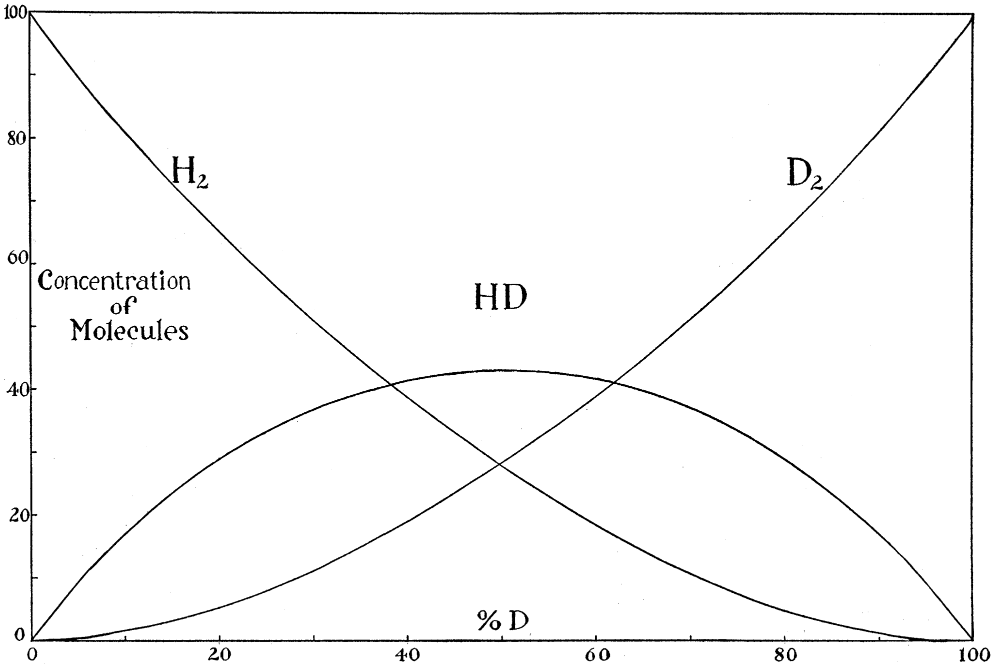

FIG. 1. Concentration of the three types of molecules as function of the deuterium concentration.

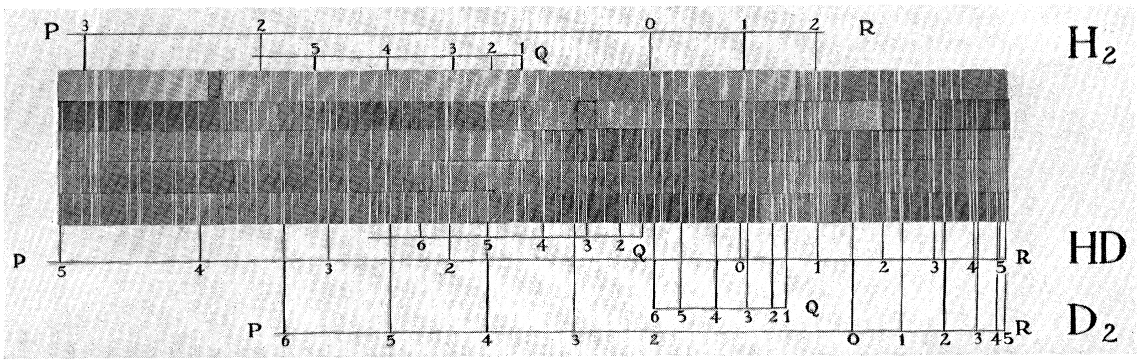

FIG. 2. The 2→2 bands of H_2, HD and D_2. Most of the other lines shown in the figure belong also to the Fulcher bands but are not marked in order to avoid confusion.

except for the longest wavelengths. On the strongest plates the number of lines is so great that neighboring lines begin to flow into each other almost everywhere in the spectrum. As the strong lines are much overexposed on these plates at least one other set is needed with a weaker exposure in order to be able to measure the strong lines. This is necessary for several deuterium concentrations. As the total length of the spectrum is more than 12 feet with our dispersion, we have in this way accumulated several hundred plates which contain many thousand new lines of the hydrogen spectrum.

§3. Measurements

We intend to publish ultimately a complete table of the wavelengths and frequencies of all the lines with their classification, if that is known. Because of the large number of lines to be measured, and because every line should be measured on several plates it will take some time before the complete list is finished. The wavelengths of the present paper are preliminary values, mostly derived from measurements on one plate only, and are possibly subject to slight corrections.

The first task is to ascertain whether a given line is due to H_2, HD or D_2. Theoretically three sets of exposures are sufficient to determine this, one of pure H_2, one of pure D_2 and one of a mixture of approximately equal parts of H and D. This last exposure will show the lines of H_2, HD and D_2 with an intensity ratio of about 1 : 2 : 1. In practice, however, it is advisable to have also exposures at several intermediate concentrations. Fig. 1 shows how the concentrations of the three kinds of molecules depend on the deuterium concentration. If we take photographs of the spectra of mixtures with increasing D concentrations, we find that among the H_2 lines first only HD lines should appear as the D_2 concentration grows only very slowly in the beginning. At higher D concentrations also the D_2 lines appear while the HD lines still increase in strength and the H_2 lines recede. If we get to higher D concentrations than 50 percent the H_2 lines quickly disappear, the HD lines decrease more slowly in strength, whereas the intensity of the D_2 lines still keeps increasing.

It is convenient to mount enlargements of these sets of exposures one below the other (see Fig. 2). A H_2 line will then be strong at the top, diminish in intensity toward the middle and be entirely absent at the bottom. For the D_2 lines just the reverse is true, while the HD lines start fairly well near the top, reach a maximum in the middle and fade out again near the bottom.

In this way it can be easily and surely ascertained to which molecule each line belongs. One advantage of this scheme is that it is easy to recognize blends, which would otherwise not be so easy, unless quantitative intensity measurements were made: e.g., if a line starts at the top but falls off much more slowly than the H_2 lines toward the bottom, it must obviously be a H_2 plus HD blend, whereas if a line starting at the top diminishes in intensity toward the middle but increases again toward the bottom, it must be a H_2 plus D_2 blend. Also, having more than just

TABLE I. *The Fulcher bands of HD.*

J''	P-BRANCH ν	P-BRANCH I	Q-BRANCH ν	Q-BRANCH I	R-BRANCH ν	R-BRANCH I
			1→0			
0	—	—	—	—	18 641.60	8
1	—	—	18 590.89	8	677.11	7
2	18 491.29	2	575.63	8	704.79	5
3	427.48	4	552.87	5	724.44	3
4	357.50	3	522.73	4	735.78	1d
5	281.41	4	485.32	0d		
			2→1			
0	—	—	—	—	18 299.86	9
1	—	—	18 251.46	10	333.35	9
2	18 155.85[1]	8	236.66	10	359.09	7
3	094.38	6	214.54	10	376.66	5
4	026.56	5	185.24	4	385.44	1
5	17 952.50	3	148.96	3		
6	872.03	1	106.02[2]	2d		
			3→2			
0	—	—	—	—	17 969.46	8
1	—	—	17 922.73	10	18 001.97	6
2	17 831.68	5	908.36	10	027.16	7
3	773.31	6	886.90	9	044.57	5
4	708.95	6	858.54[2]	7	053.90[1]	9
5	638.75	1d	823.25	2		
6	562.75	3	781.46	0		
			4→3			
0			—	—		
1			17 604.29	8		
2			590.34	8		
3			569.52	4		
4			541.90	4		
5			507.74	1		
			5→4			
1			17 295.99	1		
2			282.50	1		
			0→0			
0	—	—	—	—	(a)	
1	—	—	16 634.94	7		
2	(a)		623.60	7		
3			606.68	6		
4			584.21	5		
5			556.54	2		
6			523.59	3		
7			485.63	1		
			1→1			
0	—	—	—	—	16 438.78	6
1	—	—	16 390.27	8	476.43	4
2	16 294.91	5d	379.29	8	508.39	6
3	237.52	3	362.88	7	534.36	5
4	175.87	7	341.10	6	554.15	4
5	110.21	6	314.06[2]	5v	567.50	2
6	040.72	3	282.18	3		
7	15 967.71	3	246.35	2		
8	891.40	1				
			2→2			
0	—	—	—	—	16 199.82	7
1	—	—	16 153.53	7	235.40	5
2	16 062.08	5	142.83	7	265.30	3c
3	006.74	6	126.92	7	289.01	4
4	15 947.09	5	105.81	6	305.98	3
5	883.16	4	079.70	5	314.06[3]	(5v)
6	814.80	4	048.62	2		
7	740.73	2				
			3→3			
0	—	—	—	—	15 969.43	6
1	—	—	15 924.78	6	16 003.98	5
2	15 837.73	3	914.43	6	033.22	5
3	785.41	5	898.98	5	056.78	4r
4	729.08	8	878.55	4	073.99	3
5	668.78	5	853.27	3	084.59	1
6	604.56	3	823.23	1		
			4→4			
0			—	—		
1			15 704.24	6		
2			694.22	6		
3			679.29	4		
4			659.54	2		
5			635.14	0		
			5→5			
0			—	—		
1			15 492.22	3		
2			482.57	3		
3			468.18	3		
4			449.14	1		
5			425.58	0		
			0→1			
0			—	—	(a)	
1			14 434.29	3		
2	(a)		427.23	4		
3			416.54[2]	(7)		
4			402.62	3		
5			385.32	1		
6			364.79	0		
7			341.26	0		
			1→2			
0	—	—	—	—	14 338.60[4]	10
1	—	—	14 292.31	5	378.47	4
2	14 201.02	2	285.43	9	414.57	5
3	149.83	3	275.19	6	446.73	5
4	096.36	3	261.66	4	474.69	0
5	040.90	3d	244.84	3		
6	13 983.50	1	224.97	2		
7			201.84	0		
			2→3			
0	—	—	—	—	14 199.64	7
1	—	—	14 155.56	8	237.50	10
2	14 068.14[5]	3	148.93	10	271.39	5
3	018.82	3	139.01	5c	301.11	5
4			125.88	5	326.06	3
5	913.16	2	109.72	4	344.42	1
6	856.61	2	090.45	2d		
7			068.14[6]	3c		
8			043.14	0		
			3→4			
0	—	—	—	—	14 067.34	4
1	—	—	14 024.67	9	103.89	5
2	13 941.58	3	018.25	9	137.08	5
3	895.15	3	008.78	10	166.47	7
4	846.65	2	13 996.17	5	191.60	3
5	796.11	2	980.60	3	211.93	2
6	743.32	0	962.05	3		
			4→5			
1			13 900.36	4		
2			894.22	4		
3			885.16	4		
4			873.15	3		
5			858.31	2		
6			840.75	1		

(a) The *P* and *R*-branches of the 0→0 and 0→1 bands show strong perturbations and the classification of several lines is still uncertain. We therefore omit these branches at present.

[1] $+H_2$; [2] $+D_2$; [3] 1→1, Q_5+D_2; [4] 0→1, P_2; [5] Q_7; [6] P_2.

TABLE II. *The Fulcher bands of D_2*

J''	*P*-BRANCH		*Q*-BRANCH		*R*-BRANCH	
	ν	I	ν	I	ν	I
1→0						
0	—	—	—	—	18 308.38	—
1	—	—	18 274.68	0	332.26	1b
2	18 207.66	0	264.94	3	350.93	1
3	164.68	0	250.36	1	364.09	—
4	117.31	2	231.03	2	369.46	00
5	065.34	0c	207.02	0		
2→1						
0	—	—	—	—	18 042.39	5
1	—	—	18 009.73	3	065.63	2
2	17 945.11	3	000.24	5	085.05	4
3	903.98	1	17 986.03	3	097.64	1d
4	858.54[1]	(7)	967.12	3	106.02[1]	2d
5	809.32	0	943.71	1		
6	756.01	2	915.75	2		
3→2						
0	—	—	—	—	17 783.05	4
1	—	—	17 751.60	4	805.27	3
2	17 689.22	3	742.35	5	822.65	4
3	649.26	2	728.46	3	835.07	1
4	605.11	3	710.03	4	842.10	2
5	556.33	2	687.21	2		
6	504.64	3	659.90	2		
4→3						
0	—	—	—	—	17 530.70	3
1	—	—	17 500.24	2	552.20	3
2	17 440.17	2	491.17	5	569.14	4
3	401.88	4	477.65	3	581.31	1
4	359.36	3	459.67	4c	588.62	4
5	313.02	1	437.34	1	590.72	0
6	262.91	2	410.68	1	586.69	1
5→4						
1			17 255.45	2		
2			246.62	4		
3			233.41	2		
4			215.88	3		
5			194.05	0		
6			168.14	1		
6→5						
1			17 017.27	1		
2			008.63	2		
3			16 995.75	1		
4			978.66	1		
5			957.41	0		
6			932.12	0		
0→0						
0	—	—	—	—	16 695.86	4
1	—	—	16 662.11	3	721.97	2
2	16 595.10	2	654.53	4	744.14	3
3	554.54	2	643.16	5	762.32	2
4	510.57	4	628.09	3		
5	463.55	2	609.37	1		
6			587.09[1]	(5)		
1→1						
0	—	—	—	—	16 493.42	4
1	—	—	16 460.89	4	18.48	2
2	16 396.22	3	453.49	7	39.51	5
3	356.84	2	442.40	4	56.13	2
4	314.06[1]	5v	427.71	5	66.18	3
5	267.77	4	409.47	2		
6	216.02	4	387.73	2		
7			362.88[1]	(7)		
2→2						
0	—	—	—	—	16 296.58	4
1	—	—	16 265.06	2	320.97	3
2	16 202.64	2	257.80	6	341.73	3
3	164.94	3	246.98	3	358.65	1
4	124.18	3	232.64	3	371.71	2
5	080.43	2	214.80	2	382.10	1d
6	033.88	2	193.59	2	384.58	1
7	15 984.70	0				
8	932.99	1				
3→3						
0	—	—	—	—	16 104.82	3
1	—	—	16 074.45	3	128.09	3
2	16 014.27	2	067.41	5	147.67	3
3	15 977.63	3	056.78[1]	4r	163.42	2
4	937.93	3	042.87	3	174.90	2
5	895.17	1	025.36[2]	(7)	180.90	1
6	849.23	2	004.79	1		
4→4						
0	—	—	—	—	15 918.63	5
1	—	—	15 889.26	3	941.22	4
2	15 831.37	4	882.38	7	960.29	5
3	796.22	4	872.00	4	975.78	3
4	758.19	5	858.49	6	987.43	4
5	717.24	3	841.57	3	994.94	2
6	673.56	4	821.42	4	997.32	2b
7	626.98	2	798.13	1		
8			771.79	2		
9			742.48	0		
10			710.33	0		
5→5						
0			—	—		
1			15 709.49	2		
2			702.89	4		
3			692.88	3		
4			679.63	3		
5			663.18	2		
6			643.58	2		
7			620.92	0		
8			595.32	0		
6→6						
1			15 535.59	1		
2			529.09	3		
3			519.39	1		
4			506.52	2		
5			490.54	0		
6			471.53	0		
0→1						
0	—	—	—	—	14 881.02	5
1	—	—	14 848.32	1	908.13	2v
2	14 783.67	2	843.06	3	932.51	2
3	746.54	1	835.20	2		
4	707.03	0d	824.79	3		
5			811.81	2		
6			796.41	3		
7			778.59	0		
8			758.44	1		

[1] +HD; [2] $+H_2$; [3] 3→4, R_2; [4] 1→2, P_5; [5] 4→5, R_4; [6] 3→4, Q_3.

Table II.—*Continued.*

J''	*P*-BRANCH ν	*P*-BRANCH I	*Q*-BRANCH ν	*Q*-BRANCH I	*R*-BRANCH ν	*R*-BRANCH I
1→2						
0	—	—	—	—	14 747.63	5
1	—	—	14 716.22	3	773.79	3
2	14 653.77	3	711.09	6	797.10	6
3	617.81	2	703.39	5	817.09	3
4	579.58	4	693.21	5	831.64	2
5	538.88[3]	5	680.58	4		
6	493.88	5	665.55	4		
7			648.15	2		
8			628.50	2		
9			606.70	0		
2→3						
0	—	—	—	—	14 618.29	6
1	—	—	14 587.86	4c	643.79	4
2	14 527.75	3	582.84	6c	666.75	5
3	493.34	3	575.38	5	686.99	4
4	456.97	4	565.45	6	704.47	5
5	418.74	3	553.11	4		
6	378.78	4	538.48	4		
7			521.54	2		
8			502.41	2		
9			481.22	1		
10			457.93	1		
3→4						
0	—	—	—	—	14 492.69	6
1	—	—	14 463.46	4	517.08	4
2	14 405.47	3	458.60	7	538.88[4]	5
3	372.10	2	451.24[5]	8d	557.89	4
4	336.73	4	441.66	6	573.74	4
5	299.40	3	429.69	3		
6	259.94	4	415.50	5d		
4→5						
0	—	—	—	—	14 372.66	4
1	—	—	14 343.31	4	395.27	3
2	14 289.31	4	338.60[1]	(10)	416.54[1]	(8)
3	255.72	3	331.55	5	435.21	3
4	221.91	5	322.21	7	451.24[6]	8d
5	186.32	2	310.61	3	464.00	1
6	148.93[1]	(10)	296.84	4	472.78	0
7	109.72[1]	(4)	280.95	1		
8			262.98	1		
5→6						
0			—	—		
1			14 227.88	4		
2			223.33	7		
3			216.52	4		
4			207.49	6		
5			196.30	2		
6			182.98	3		
7			167.62	0		
8			150.29	0		
6→7						
0			—	—		
1			14 117.56	3		
2			113.19	4		
3			106.64	3		
4			097.98	4		
5			087.24	2		
6			074.47	2		

the necessary three spectra to compare practically eliminates a difficulty, which otherwise would be met, due to the fact that the relative intensities of many lines are very sensitive to changes in the conditions of the discharge tube, as pressure, current and temperature. Only the classification of some very weak lines may remain doubtful.

Good wavelength measurements by Gale, Monk and Lee[4] exist for the H_2 spectrum, and Finkelnburg[5] supplemented their measurements for shorter wavelengths than Hβ. For the long wavelength region our plates show many new H_2 lines, especially in the infrared.

The plates taken with moderate deuterium concentrations show the H_2 lines with sufficient intensity so that they can be used as standards for the measurement of the HD and D_2 lines. For those plates which do not show sufficiently strong H_2 lines and in the extreme red and infrared where, due to the lack of interferometrically determined values, Gale, Monk and Lee's measurements are less accurate, iron and neon lines were used as standards. In the infrared the second order of the iron arc had to be used against the first order of the hydrogen lines. In a few limited regions the lack of good standards was provisionally overcome by employing HD and D_2 lines, the wavelength of which could be determined with the help of the combination principle from other known lines. This also served when necessary as a means to identify and eliminate possible small shifts between the hydrogen and the comparison spectrum which are at times difficult to avoid.

§4. The Fulcher bands

As mentioned before, the greatest usefulness for the HD and D_2 spectra will be for the analysis of bands not hitherto found and the interpretation of band systems which presented difficulties until now. It is, however, desirable first to investigate fully a band system which is simple

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[4] H. G. Gale, G. S. Monk and K. O. Lee, Astrophys. J. **67**, 89 (1928).

[5] W. Finkelnburg, Zeits. f. Physik **52**, 27 (1929).

Table III. *HD*.

	$R(J-1)-P(J+1)$								
J	1→0	2→1	1→1	3→2	2→2	1→2	3→3	2→3	3→4
1	150.29	144.01*	143.87	137.78	137.74	137.58*	131.70	131.50*	125.76
2	249.63	238.97	238.91	228.66	228.66	228.64	218.57	218.68	208.74
3	347.29	332.53	332.52	318.21	318.21	318.21	304.24		290.43
4	443.03	424.16	425.15	405.82	405.85	405.83	388.00	307.95	370.36
5		513.41	513.43	491.15*	491.18	491.19	469.43	469.45	448.28

	$Q(J)-P(J)$								
J	1→0	1→1	1→2	2→1	2→2	2→3	3→2	3→3	3→4
2	84.34	84.38	84.41	80.81	80.75	80.79*	76.68	76.70	76.67
3	125.39	125.36	125.36	120.16	120.18	120.19	113.59	113.57	113.63
4	165.23	165.23	165.30	158.68	158.72		149.59*	149.47	149.52
5	203.91	203.85	203.94	196.46	196.54	196.56	184.50	184.49	184.49
6		241.46	241.47	234.02*	233.82	233.84	218.71	218.67	218.73

	$R(J)-Q(J)$								
1	86.22	86.16	86.16	81.89	81.87	81.94	79.24	79.20	79.22
2	129.16	129.10	129.14	122.43	122.47	122.46	118.80	118.79	118.83
3	171.57	171.48	171.54	162.12	162.09	162.10	157.67	157.80	157.69
4	213.05	213.05	213.03	200.20	200.17	200.18	195.36*	195.44	195.45
5		253.44*			234.36*	234.70		231.32	231.34

Table IV. D_2.

	$R(J-1)-P(J+1)$													
J	1→0	0→0	2→1	1→1	0→1	3→2	2→2	1→2	4→3	3→3	2→3	4→4	3→4	4→5
1	100.72	100.76	97.28	97.20	97.35	93.87	93.94	93.86	90.53	90.55	90.54	87.26	87.22	83.35
2	167.58	167.43	161.65	161.64	101.59	156.01	156.03	155.98	150.32	150.46	150.45	145.00	144.98	139.55
3	233.62	233.57	225.51*	225.45*	225.48	217.55	217.55	217.52	209.78	209.74	209.78	202.10	202.13*	194.63*
4	(298.75)	298.77	288.32	288.36		278.24	278.22	278.21*	268.29	268.25	268.25	258.54	258.49	248.89
6			350.01*	350.16		337.46	337.83	337.76	325.71	325.67	325.69	313.87	313.80	302.31*
							397.40					267.96		354.28
							451.59							

	$Q(J)-P(J)$													
J	0→0	0→1	1→0	1→1	1→2	2→1	2→2	2→3	3→2	3→3	3→4	4→3	4→4	4→5
2	59.43	59.39	57.28	57.27	57.32	55.13	55.16	55.09	53.13	53.16	53.13	51.00	51.01	50.98
3	88.62	88.66	85.68	85.56	85.58	82.05	82.04	82.04	79.20	79.15*	79.14	75.77	75.78	75.83
4	117.52	117.76	113.72	113.65*	113.63	108.58*	108.46	108.48	104.92	104.94	104.93*	100.31	100.30	100.30
5	145.82		141.68	141.70	141.70*	134.39	134.37	134.37	130.38	130.19*	130.29	124.32	124.31	124.29
6				171.71	171.67	159.74	159.71	159.70	155.38*	155.56	155.56	147.77	147.84	147.91*
													171.13	171.23*

	$R(J)-Q(J)$													
1	59.88	59.81	57.58	57.59	57.57	55.90	55.91	55.93	53.67	53.64	53.62	51.96	51.96	51.96
2	89.61	89.45	85.99	86.02	86.01	83.81	83.93	83.91	80.30	80.26	80.28*	77.97	77.91	77.94*
3	119.16			113.73	113.70	111.61	111.67	111.61	106.61	106.64	106.65*	103.66	103.78	103.66
4			138.43	138.47	138.43	138.90*	139.07	139.02	132.07	132.03	132.08	128.95	128.94	129.03*
5							167.30					153.38	153.37	153.39
6							190.99					176.01	175.90	175.94

in structure, and the interpretation of which presents no difficulties. The obvious choice for such a system is the Fulcher bands, as they are free from the complicated effects of the *L*-decoupling which makes an accurate determination of the band constants practically impossible. Besides, some of the strongest bands of the spectrum belong to this system. The rest of this paper is therefore concerned with a comparison of the Fulcher bands of H_2, HD and D_2.

The data for H_2 are given by Richardson and Das.[6] The Fulcher bands of HD and D_2 are

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[6] O. W. Richardson and Das, Proc. Roy. Soc. **A122**, 688 (1929). All the material of these and the other hydrogen

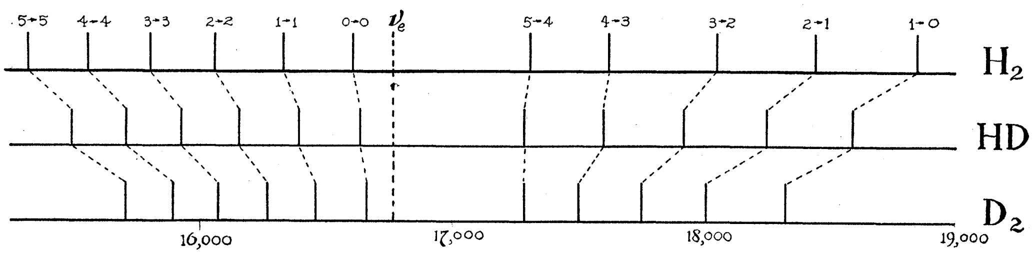

FIG. 3. The Fulcher bands between Hβ and Hα.

presented in the Tables I and II. The intensities are rough estimates only, and the comparison of the intensities of widely separated bands has no meaning as the relative photographic intensities of such bands are chiefly determined by the sensitization of the plate. Recognized blends are designated in the footnotes.

The Tables III and IV give the combination relations for the rotational differences, and can be considered as proof for the correctness of the classification of the lines.

An idea of the appearance of the bands can be obtained from Fig. 2 in which a typical part of the spectrum is reproduced. The top photograph is H_2. The deuterium concentration increases toward the bottom and is about 95 percent in the lowest picture.

Fig. 3 gives a diagram of the position of the bands in the spectrum, whereas Fig. 4 represents the change in the appearance of an individual band. As for H_2, also for HD and D_2 the Fulcher bands form the most conspicuous feature in the green and orange and red, and most of the strong lines in those parts of the spectrum belong to them. Their structure is the same in all three cases with the changes illustrated in Figs. 3 and 4, which originate in the different masses of the molecules. There are other less obvious changes which will be discussed briefly in the last section of this paper.

A very conspicuous feature of the three spectra is the behavior of the intensity alternations. Due to a spin of 1/2, successive rotational lines of the H_2 bands are alternately strong and weak, and the intensity ratio of the strong and weak lines is 3 : 1. Such intensity alternations occur only if the two nuclei of the molecule are identical, and as that is not the case for HD no such alternations must be expected and none are found. In D_2, however, the two nuclei are again identical and accordingly intensity alternations are found. This can be seen easily on Fig. 2, and this figure shows also that the lines with an even number are the strong ones for D_2, whereas for H_2 they were the weak ones. This was found first by Lewis and Ashley,[7] and Murphy and Johnston[8] made quantitative intensity measurements and found that the spin of the D nucleus must have the magnitude 1.

The bands in question are $^3\Pi\rightarrow{}^3\Sigma$ (or more fully $1s\sigma\cdot 3p\pi\ {}^3\Pi\rightarrow 1s\sigma\cdot 2s\sigma\ {}^3\Sigma$) transitions. The triplet separation is, however, negligible, so that the structure of the bands has the appearance of that of $^1\Pi\rightarrow{}^1\Sigma$ bands. This is equally true for all three molecules.

§5. Calculation of the constants

The customary expression

$$F(J)=E_{r/h}=B_v[J(J+1)-\Lambda^2]-D_vJ^2(J+1)^2+\cdots \qquad (1)$$

for the rotational energy forms the basis for the calculation of the rotational constants. The formula represents the first terms of a development with respect to powers of $BJ(J+1)/\omega$. For the hydrogen molecule, because of the exceptionally large value of B this quantity is so large that (1) converges very poorly except for the smallest values of J, and for an accurate representation of the rotational energy more terms should be taken into account. This would unduly complicate the evaluation of the con-

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bands is given also in O. W. Richardson's book, *Molecular Hydrogen and its Spectrum*, Yale University Press, 1934.

[7] G. N. Lewis and M. F. Ashley, Phys. Rev. **43**, 837 (1933).

[8] G. M. Murphy and H. Johnston, Phys. Rev. **46**, 95 (1934).

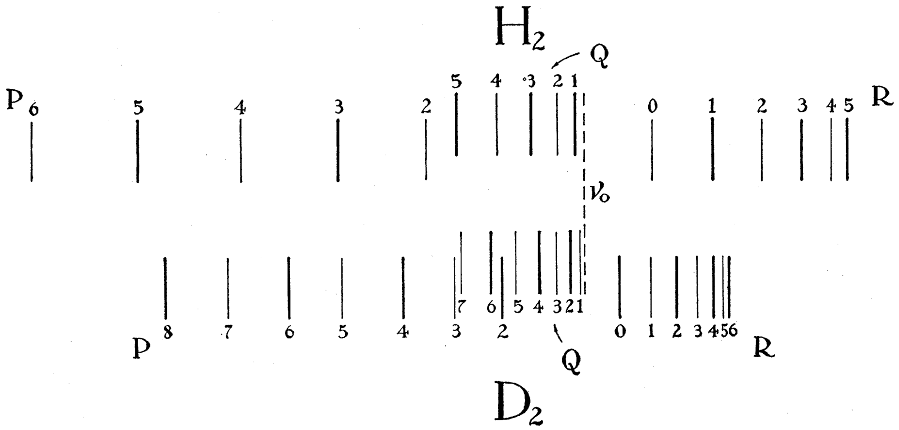

FIG. 4. The change in rotational structure of a typical band.

stants, for it increases the number of constants to be determined empirically. It is true that some of the constants can be expressed in terms of the others and the constants of the vibrational energy. But if one wants to make use of these interrelations in the correct form, the process of evaluating the constants becomes exceedingly tedious. Besides it is hardly certain that at the present stage such a procedure would be of any benefit, for the slight corrections in the wavelengths of some of the lines which the final measurements probably will show will produce changes in the constants of the same order of magnitude as the changes which would result if instead of (1) the more elaborate formula with all refinements were used.

We intend to recalculate the constants making use of all refinements in the final stage of the work, but are confident that this will entail only very minor corrections to the values given in the present paper.

For HD and D_2 the following procedure was adopted. The differences

$$F''(J+1)-F''(J-1)=2(2J+1)B_v'' -D_v''[(2J+1)^3+3(2J+1)]+\cdots \quad (2)$$

of Tables III and IV are most conveniently taken to calculate B_v'' and D_v'' of the final $^3\Sigma$ level.[9] With the help of the relation

$$B_v=B_e-\alpha v+\beta v^2-\cdots \quad (v=0.5,\ 1.5,\ \cdots) \quad (3)$$

the values of B_e and α are found. The most obvious way to calculate the constants of the initial level would be to use the expression analogous to (2). This cannot be done, however, as the $^3\Pi_d$ state which gives rise to the P and R-branches shows many irregularities. The $^3\Pi_c$ state, however, which is the upper level of the Q-branches is regular throughout. The Q-branches are given by

$$Q(J)=A_{v',v''}-B_{v'}'-(B_{v''}''-B_{v'}')J(J+1) +(D''-D')J^2(J+1)^2 \quad (4)$$

and from the frequencies of the Q-lines the constants $A_{v',v''}-B_{v'}$, $B_{v''}''-B_{v'}'$ and $D''-D'$ can be found. As $B_{v''}''$ and D'' are known, the values for $A_{v',\,v''}$ the origin of the band, $B_{v'}'$ and D' can be now determined.

When all the band origins $A_{v',v''}$ are known, the constants in the expression for the vibrational energy

$$E_{v/h}=\omega v-xv^2+yv^3-zv^4+\cdots \quad (v=0.5,\ 1.5,\ \cdots) \quad (5)$$

can be calculated. For simplicity as many bands (nine in our case) were used as were necessary for a direct computation of the constants.

The rotational constants for the $2s\sigma\,^3\Sigma$ state of H_2 were calculated by Richardson and Das, and we used their values. These authors failed,

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[9] In most cases a least square method was used and the term in $J^3(J+1)^3$ was taken into consideration. The constants given here are the same as those reported in *Nature.* Not all the bands of the Tables I and II were used for their compilation, as some were not yet available at that time.

TABLE V. *The constants of the Fulcher bands.*

	1 H_2	2 HD	3 D_2	2 : 1	3 : 1	3 : 2	ρ_{12}^n	ρ_{13}^n	ρ_{23}^n	n
ω'	2371.58	2054.59	1678.22	0.86634	0.70764	0.81682	0.86616	0.70744	0.81675	1
ω''	2664.83	2308.44	1885.84	.86626	.70768	.81693				
x'	66.27	49.74	32.94	.7506	.4970	.6622	.7502	.5005	.6671	2
x''	71.65	53.77	35.96	.7505	.5018	.6687				
B'	30.364	22.810	15.200	.7512	.5006	.6664				
B''	34.216	25.685	17.109	.7507	.5000	.6661				
α'	1.545	1.020	0.5520	.660	.357	.541	.650	.354	.544	3
α''	1.671	1.099	0.606	.658	.363	.551				
D'	0.0191	0.0116	0.0049	.61	.26	.42	.563	.250	.445	4
D''	0.0216	0.0128	0.0055	.59	.25	.43				
y'	0.88	0.58	0.24	.66	.27	.41				
y''	0.92	0.60	0.34	.65	.36	.57				
ν_0	16793.87	16788.86	16783.92							

however, to give the rotational constants of the $3p\pi\ {}^3\Pi_c$ level and the band origins. These constants and the vibrational constants were therefore determined by us in essentially the same way as those for HD and D_2, except that only the three first lines of the Q-branches were used. For these lines the higher terms in (1) are of little importance, and therefore the disadvantage of accidental errors making themselves felt more strongly is compensated by the advantage that systematic errors are less likely to have an influence.

The constants of the three molecules found in the manner indicated above are given in Table V.[10]

COMPARISON OF THE THREE MOLECULES

If we call μ_1, μ_2 and μ_3, respectively, the reduced masses of H_2, HD and D_2, and put $\rho_{ij}=\mu_j/\mu_i$, then every constant occurring in the expressions (1), (3) and (5) for the rotational and vibrational energy, e.g., of HD can be obtained by multiplying the corresponding constant of H_2 by a certain power of ρ_{12}. For this it is essential that it be assumed that the internuclear distance and the forces which hold the molecule together are identical for the two isotopic molecules.

The exponent of ρ_{ij} is: one for ω, two for B_e and x, three for α and y, four for D_e.

Table V shows how accurately these relations are fulfilled by the actual empirical constants of the three molecules. The columns 1 : 2, 1 : 3 and 2 : 3 give the ratios of the respective empirical constants, whereas the columns ρ_{ij}^n give the corresponding theoretical values to which they should be equal.

The theoretical values of ρ_{ij} given in the table were calculated with Bainbridge's values 1.007775 for the mass of the proton and 2.01363 for the mass of the deuton. The contribution of the two electrons to the moment of inertia is *not* taken into account.

An inspection of the table reveals at first sight that all the constants vary with the proper power of ρ_{ij}, but that there are deviations of the observed ratios from their theoretical values which seem to be outside the range of the errors of measurements.

There are three independent causes which may be responsible for these discrepancies. In discussing them let us take the vibrational frequency ω as an example as it is the constant which can be determined with the greatest numerical accuracy.

(A) If we compare the electronic motion of the three isotopic molecules, we would find it exactly the same if the nuclei were kept at rest, as the electronic motion, and therefore also the equilibrium distance and the form of the potential curve would be determined then completely by the charges of the nuclei which are the same in all cases. Of course an actual molecule with the nuclei at rest does not exist. We have to extrapolate to the vibrationless and rotationless molecule. This we do with the help of the formulae (1) to (5). But this is not actually the same as if we took a molecule with fixed nuclei, which becomes apparent from Kronig's treatment of the problem.[11]

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[10] This table is calculated from the same material as the table given in *Nature* (reference 1). The changes are due to a numerical error (omission of the term with Λ^2) in the previous calculations.

[11] R. de L. Kronig, Physica 1, 617 (1934).

Both the internuclear distance and the form of the potential curve which determines the value of ω may be slightly different for the different isotopes, but the exact magnitude of this deviation can only be found, if the wave functions of the electronic state are known.

(B) Even if the potential curve were completely known, there would be still an uncertainty in the relations between the constants of the three isotopic molecules. The electrons contribute to the moment of inertia and the magnitude of this contribution is not known, as long as the electronic wave functions are not sufficiently known. The values of ρ_{ij} given in the table, calculated without taking the mass of the electrons into account, are certainly not the correct ones for our case as it is certain especially as the levels are excited ones that $\psi\bar{\psi}$ is different from zero for a considerable distance from the axis of rotation. Perhaps a better approximation is to take the electrons as coinciding with the nuclei. In that case we obtain

$$\rho_{12}=0.86620 \qquad \rho_{13}=0.70754 \qquad \rho_{23}=0.81683.$$

These values are a little closer to the observed ones, but this can hardly be taken as justification for this assumption, as long as we are not certain of the contribution of the other causes.

(C) The third possible cause for the discrepancies is of a different nature from the two previous ones. In calculating ω use is made of (5) which is only an approximation. Neglecting the higher terms causes systematic errors in the values of the constants which though slight are of sufficient magnitude to account for the discrepancies. That a considerable part of the discrepancies is probably due to this cause is made probable by the fact that if the fourth power term in (5) is neglected, the discrepancies become much larger and of the opposite sign. The same causes can also be held responsible for the deviations of the other constants, but as their accuracy (except for ν_0) is less, practically only the third cause will be of any importance.

There may be a considerable error in the value of B_e if there is any L decoupling. This produces an additional term in $J(J+1)$ which unless it can be determined separately, gives a wrong value for the equilibrium distance and also wrong values for the ratios. For the two levels under consideration this effect is, however, absent as the lower level is a $s\sigma\Sigma$-term[12] which has no L decoupling and the upper level is a $p\pi\Pi$ term. One of the components of such a level does not show any effects of L decoupling and it is very probable that our $p\pi\Pi_c$ level for which the constants were calculated is this level.

Finally we come to the origins of the systems, which should correspond to the pure electronic transition. We find that the origin of the HD system lies almost exactly halfway between that of H_2 and D_2. The separation of 5 cm^{-1} between H_2 and HD and HD and D_2 is unquestionably real and cannot be produced wholly by experimental errors. It must be attributed to the kind of interactions mentioned under (A). It may be noted that the separation is of the opposite sign as the separation between $H\alpha$ and

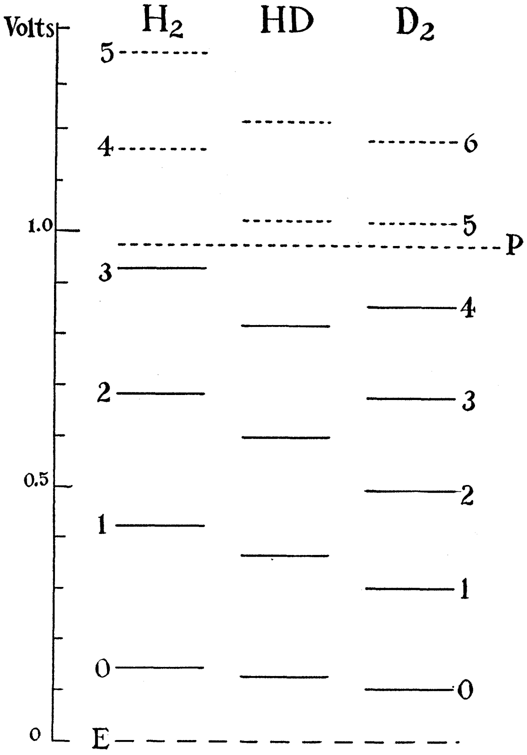

FIG. 5. The vibrational levels of the $3p\pi\ {}^3\Pi$ state. Those above P have their Π_d component predissociated.

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[12] The designation $s\sigma$ etc. refers to the second electron. The first electron is in all levels under consideration $1s\sigma$ and can be omitted for convenience from the term symbols without giving rise to ambiguities.

Dα. It is clear that the cause of this latter separation, namely that the nucleus moves about the common center of gravity of nucleus and electron plays a very much smaller part if two electrons are present, which are on opposite sides of the nucleus.

The isotopic separation of the origins of the Fulcher bands is of the same order of magnitude as the separation of the origins of the far ultraviolet bands.[13]

PERTURBATIONS

There are irregularities in the rotational levels of the $3p\ {}^3\Pi_d$ state in all three molecules which result in irregularities in the P and R-branches. We shall postpone a discussion of the details of these perturbations until a later paper as for their complete understanding a knowledge of the perturbing level is necessary. It is practically certain that this perturbing level is the level called by Richardson $3p\sigma\ {}^3\Sigma$ but the analysis of the bands originating from it is not yet complete.[14]

Richardson noticed that the R and P-branches are absent for all of the H_2 Fulcher bands for which $V' \geq 4$. The same is true for HD, but for D_2 the $4\rightarrow3$, $4\rightarrow4$ and $4\rightarrow5$ bands show well developed P and R-branches while they are absent for $V' \geq 5$. The explanation for this behavior must be that those vibrational states of the $3p\pi\ {}^3\Pi_d$ level which are not observed interact with a dissociated level which cannot interact with the Π_c level. (A $p\sigma\ {}^3\Sigma$ level would be such a level.) If this is the case we have a method to determine the heat of dissociation of hydrogen independent of any of the other methods used for H_2 before.

Fig. 5 shows the vibrational levels of the $3p\pi\ {}^3\Pi$ states. Those for which ${}^3\Pi_d$ is predissociated are represented by broken lines. The limit of dissociation which is with sufficient approximation the same for the three molecules must lie between the highest complete level which is $V=3$ of H_2 and the lowest predissociated one which is $V=5$ of D_2.

These two levels lie 0.78 and 0.87 volt above the lowest vibrational level of the $3p\pi\ {}^3\Pi$ state of H_2. This level, according to Richardson is 13.80 volts above the ground level of the molecule. Therefore the two limiting levels have a total energy of 14.58 and 14.67 volts, respectively. The products of dissociation are evidently a normal atom and an excited one with 10.15 volts of energy. The heat of dissociation of the normal molecule must lie therefore between 4.43 and 4.52 volts. This agrees excellently with the value 4.465 volts determined by other means.

It is a pleasure to thank Professor H. S. Taylor of Princeton for the heavy hydrogen which made this investigation possible, and we are indebted to Dr. C. R. Jeppesen who carried out some of the measurements.

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[13] C. R. Jeppesen, Phys. Rev. **45**, 480 (1934). The separation is given in the paper as 135 cm^{-1}. This large value, Dr. Jeppesen informs us is due to a numerical error. The correct value is 9 ± 5 cm^{-1} which is in agreement with the value obtained by K. Mie (Zeits. f. Physik **91**, 475 (1934)).

[14] *Note added with proof.* The analysis of the perturbing bands has been completed in the meantime and will appear in the *Physical Review*. It confirms all the statements made here concerning the nature of the perturbations and the predissociation.

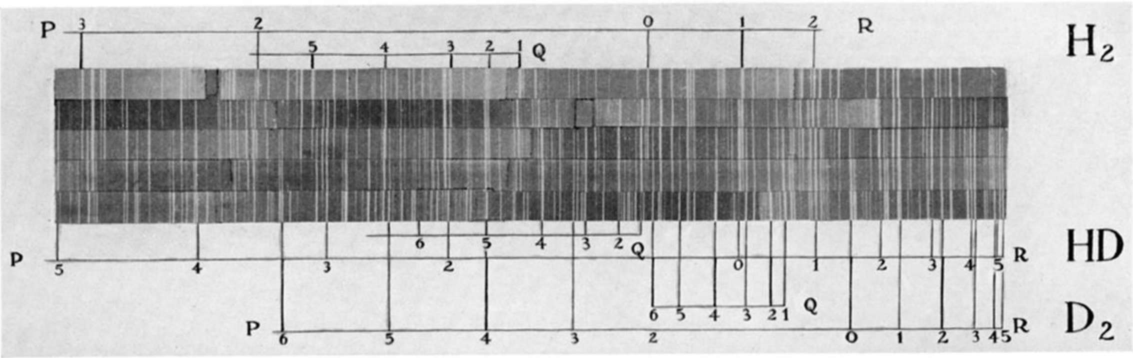

FIG. 2. The 2→2 bands of H_2, HD and D_2. Most of the other lines shown in the figure belong also to the Fulcher bands but are not marked in order to avoid confusion.