PHYSICAL REVIEW VOLUME 76, NUMBER 2 JULY 15, 1949

The Molecular Spectrum of Hydrogen. The Fulcher Bands of TH and T_2

G. H. Dieke and F. S. Tomkins
Argonne National Laboratory, Chicago, Illinois*

(Received April 11, 1949)

The spectra of TH and T_2 were photographed under high dispersion. The analysis of the $3p^3\Pi\rightarrow 2s^3\Sigma$ bands of these molecules is presented and the constants of the two states given.

I. INTRODUCTION

The spectrum of the hydrogen molecule is now fairly well known.[1] Nevertheless, a further study of its spectrum is highly desirable because of the fundamental nature of the hydrogen molecule as the simplest of all molecules.

Among the known regularities in the H_2 spectrum are some the interpretation of which is little or not at all understood. These are chiefly due to levels with both electrons excited or to levels which, because they interact with other levels, have a highly irregular structure. The information concerning those that can be extracted from the H_2 spectrum alone is not sufficient to get a clear picture. It is fortunate that the hydrogen molecule exists in several isotopic species which differ only in the mass of the nuclei. The molecules HD and D_2 that contain deuterium have been studied successfully and the information obtained from them has proved very valuable.[2-4] More recently the radioactive isotope tritium with mass three has become available, which offers the possibility of studying the spectra of TH, TD, and T_2. This doubles the empirical material for the study of the structure of the hydrogen molecule.

It is well known that the results of all theoretical calculations for a system as complex as the hydrogen molecule can be obtained only in approximation formulas, which are usually expressed as series. This is true, for instance, for the vibrational and rotational energies which are given by the well-known formula

$$E(V, K)=\Sigma_{l,n}\, Y_{l,n}(V+\tfrac{1}{2})^l K^n(K+1)^n, \qquad (1)$$

where V and K are the vibrational and rotational quantum numbers respectively, and $Y_{l,n}$ constants which can be expressed in terms of the constants occurring in the potential energy of the molecule.

The usual procedure is to express the energies found empirically from the spectrum by the formula (1) and thus obtain the constants $Y_{l,n}$ which can then be used to obtain certain features concerning the structure of the molecule. This procedure is legitimate only if the expression (1) converges rapidly so that a few terms suffice to represent the energy satisfactorily. For this the situation is particularly bad in H_2 and a reasonable convergence can only be expected for the lowest values of V and K and even then the convergence is not very good, so that a number of terms is required. These can be obtained from the empirical data only by going to fairly high values of V and K where the convergence is so bad that the formula is practically useless. This presents a dilemma which makes it very difficult to obtain reliable constants for H_2 with the help of the spectroscopic data and formula (1).

The use of the isotopic species makes it possible to overcome this difficulty. With certain restrictions the rotation-vibration energies of all isotopic species are given by (1) where the constants $Y_{l,n}$ of the various molecules are related to each other by simple known expressions. The heavier the molecule the better is the convergence. For this reason D_2 is better for the computation of the molecular constants than H_2, and T_2 is even better than D_2. There is one additional fact which makes the calculation of the molecular constants much more reliable if several isotopic species are available. As many independent empirical energy differences are required as the number of desired constants $Y_{l,n}$. For instance, if the six constants $Y_{1,0}$, $Y_{2,0}\cdots Y_{6,0}$ are wanted, six vibrational differences are required, which would involve all vibrational quantum numbers from zero to six. As mentioned before, for H_2 the convergence of the formula would be bad except for $V=0$ or 1 and even in T_2 no satisfactory convergence would exist for $V=6$. If, however, instead of the six differences in *one* molecule, one for each of the six molecules is used, the levels need only involve tkose with $V=0$ and $V=1$, where the convergence is satisfactory. Much more reliable results can thus be expected.

By the reasons just set forth and others, we were convinced that considerable effort was justified to obtain the spectra of the hydrogen molecules containing tritium. The present paper deals with the general procedure by which the spectra were obtained and then deals with the so-called Fulcher bands, one of the most extensive band systems in the molecular spectrum of hydrogen.

II. EXPERIMENTAL PROCEDURE

The preliminary work was done with a sample having about 35 percent T and 65 percent H. Samples of higher tritium content were obtained later.

---

* The work on which this paper is based was begun jointly at the Argonne National Laboratory. It is being continued as a collaborative effort between the Argonne National Laboratory and the Johns Hopkins University under a contract with the AEC.

[1] For a general review of the H_2-spectrum up to 1934, see O. W. Richardson, *Molecular Hydrogen and Its Spectrum* (Yale University Press, New Haven, 1934).

[2] G. H. Dieke and R. W. Blue, Phys. Rev. **47**, 261 (1935).

[3] G. H. Dieke, Phys. Rev. **48**, 606 (1935); **50**, 797 (1936).

[4] G. H. Dieke and M. N. Lewis, Phys. Rev. **52**, 100 (1937).

Table I. The $3p^3\Pi \rightarrow 2s^3\Sigma$-band system of TH.

The *intensities* in column I are photographic densities multiplied by 100, taken from uncalibrated plates. Different regions of the spectrum are not necessarily on the same scale.

Blends are designated in the appropriate column as follows:

x: Line appears abnormally broad or diffuse and is probably not single.
y: Intensity appears too high. Another line must coincide with it.
z: Known blend with another classified line.
A means that the coinciding line is a H_2 line.
D means that it is a TH line.
F means that it is a T_2 line.
c: Because of confusion with other lines no reliable density reading can be obtained.

	P-branch			*Q*-branch			*R*-branch		
K	ν	*I*	Blends	ν	*I*	Blends	ν	*I*	Blends
				0→0 Band					
0	—	—		—	—		16 688.48	180	
1	—	—		16 643.92	200*		723.39	200	
2	16 554.59	133		633.34	200*	*z, AF*	753.03	200*	
3	501.07	200*		618.30	200*		777.21	180	
4	443.34	200*		598.30	200*		795.72	126	
5	381.80	200*		573.54	200*		808.48	70	
6	316.61	151		544.15	200		815.39	22	
7	248.06	111		510.20	130		816.45	8	
8	176.41	66		471.94	57				
9	101.85	26		429.40	85	*z, F*			
				0→1 Band					
0	—	—		—	—		14 605.40	31	
1	—	—		14 562.42	43		642.33	56	
2	14 477.08	6		555.88	64		675.55	68	
3	428.82	6		546.15	67		705.02	67	
4	378.25	4		533.28	*c*		730.63	51	*y*
5	325.52	2		517.27	30		752.18	33	
6	270.74	3		498.33	8		769.65	71	*yy*
7				476.49	3		782.76	8	
				1→0 Band					
0	—	—		—	—		18 538.20	122	*y*
1	—	—		18 493.38	132		570.00	109	
2	18 404.48	16		480.01	145		594.79	114	
3	347.69	28		460.02	160		612.52	109	
4	285.16	22		433.52	103		623.05	90	
5	217.19	15		400.59	68		626.28	47	
6	144.00	9		361.54	19		622.02	27	
7				316.37	20				
				1→1 Band					
0	—	—		—	—		16 455.44	170	
1	—	—		16 412.25	200*		488.88	200*	
2	16 326.95	109		402.40	200*		517.23	200*	
3	275.46			387.65	200*		540.28	200	*z, F*
4	219.99	155		368.34	200*		557.92	165	
5	160.89	150		344.30	200*	*z, F*	569.92	81	
6	098.16	116		315.88	170	*x, z*	576.14	45	
7	032.06	155	*z, F*	282.69	107	*z, F*			
8	15 962.99	62		245.62	18				
9	890.88	13							
				1→2 Band					
0	—	—		—	—		14 464.14	36	
1	—	—		14 422.68	32		499.33	64	
2	14 340.84	5		416.33	48		531.11	80	
3	294.53	8		406.87	43		559.40	78	
4	245.96	32	*y*	394.33	22		583.98	60	
5	195.39	10		378.83	10		604.51	29	
6	142.91	*c*		360.54	22	*z, D*	621.08		
7	088.69	3		339.34	8	*z, D*			
8	032.83	2							
				2→1 Band					
0	—	—		—	—		18 220.62	15	
1	—	—		18 177.62	29		250.38	15	
2	18 092.12	3		164.21	51		273.04	12	
3	037.02	10		145.17	61		287.59	7	
4	17 975.84	8		119.39	30		289.94	4	
5	908.14	10		087.46	13				
6	830.21	5		049.52	25	*y*			
7				005.28	5	*z, F*			
				2→2 Band					
0	—	—		—	—		16 229.38	128	
1	—	—		16 188.12	165		260.81	175	*z, F*
2	16 106.11	62		178.54	200*		287.02	125	
3	056.14	96		164.28	200*	*z, F*	306.75	116	
4	001.84	94		145.48	165		315.88	170	*x, z*
5	15 942.70	86		122.11	125				
6	875.01	47		094.30	70				
7				062.24	29				
				2→3 Band					
0	—	—		—	—		14 360.54	42	*z, D*
1	—	—		14 287.75	47		390.06	23	
2	14 209.15	10		281.58	67		414.89	18	
3	164.28	16		272.42	64		430.98	3	
4	116.75	26*c*		200.27	57				
5	065.94	25		245.28	51*c*				
6	008.24	20		227.46	11				
7				206.98	7*c*				
8				183.90	2				
				3→2 Band					
0	—	—		—	—		17 912.91	12	
1	—	—		17 871.30	39		942.02	15	
2	17 789.59	4		858.66	44		964.68	14	
3	737.27	9		839.76	36		980.62	10	
4	679.55	17		814.67	29		989.62	5	
5	616.60			783.65	11				
6				746.67					
7									
				3→3 Band					
0	—	—		—	—		16 010.99	162	*z, F*
1	—	—		15 970.99	102		041.74	77	
2	15 892.74	65		961.77	130		067.80	85	
3	845.42	57		947.96	115		088.86	86	
4	794.44	80		929.61	87		104.53	37	
5	739.90	57		906.92	59		114.54	34	*y*
6	681.83	32		879.94	30		117.92	12	
7	620.18	155		848.86	9				
8	554.46	85							
				3→4 Band					
0	—	—		—	—		14 196.31	26	
1	—	—		14 158.08	47		228.76	41	
2	14 083.13	8		152.15	59		258.17	60	
3	040.79	25		143.30	58		284.15	39	
4	13 996.38	21		131.58	36		306.42	19	
5	950.02	17		117.08	32*c*		324.61	6	
6	901.71	15		099.91	12		339.34	8	*z, D*
7	851.47	7		080.14	18	*z, F*			
8				057.90	30	*z, F*			
	4→3 Band			4→4 Band			4→5 Band		
1	17 574.15	12		15 761.13	35		14 034.20	46	
2	561.84	19		752.22	53		028.44	110	*z, F*
3	543.47	175	*yz, D*	738.83	44		019.95	56	
4	519.11	190	*y, F*	721.03	29		008.73	37	
5	488.94	18		699.10	15		13 394.82	26	
6				672.99	5		978.48	13	*x*
7				642.89	2		959.35	4	
				5→5 Band			5→6 Band		
1				15 558.86	46		13 916.87	31	
2				550.21	70		911.40	41	
3				537.25	59		903.29	49	
4				520.06	75	*y, A*	892.61	25	
5				498.81	21		879.31	17	
6				474.36	10		863.29	14	*z, F*
7							844.75	5	
8							823.52	6	

* Line overexposed, density unreliable.

The discharge tube was of a type described before.[5] It was made entirely of quartz and immersed in running water. Graded quartz to Pyrex seals connected it with the vacuum system. The horizontal part was silvered and the observations made end on. This kind of tube will easily stand 1.5A discharge current. The electrodes were aluminum in one tube, nickel in another one.

The gas was admitted through a palladium valve to the tube. Palladium transmits *H* more readily than *T* and therefore the initial part of the sample admitted through palladium has a lower tritium concentration than the supply and the later part is considerably higher in tritium content. Our set-up did not lend itself readily to a quantitative determination of the separation factor. The initial tritium concentration obtained from the 35

---

[5] G. H. Dieke and R. W. Blue, Phys. Rev. 47, 261 (1935).

TABLE II. The $3p^3\Pi\rightarrow 2s^3\Sigma$-band system of T_2. (See caption of Table I for interpretation of symbols under blends.)

K	ν	I	Blends	ν	I	Blends	ν	I	Blends
				0→0 Band					
0	—	—		—	—		16 706.43	115	
1	—	—		16 683.72	150		723.77	170c	
2	16 638.73	2		678.59	139		738.66	27	
3	611.38	200*		671.00	200*		750.93	175	
4	581.69	12		660.87	69		760.48	68	
5	549.80	111		648.25	200*		767.26	160	
6	515.74	13		633.34	200*	z, D	771.42	21	
7	479.68	140		615.79	148		772.76	66	
8	441.37	84		595.96	36				
9	401.36	145		573.54	200*	z, D			
10	359.50	29		549.35	62	y			
11				522.92	16				
				0→1 Band					
0	—	—		—	—		15 212.55	6	
1	—	—		15 190.59	42		230.62	57	
2	15 146.98	3		186.84	16		246.84	17	
3	121.48	18		181.10	77		260.99	43	
4	094.37	5		173.54	25		273.08	8	
5	065.63	36		164.10	94		283.07	28	
6	035.36	7		152.79	25		290.95	7	
7	003.63	25		139.98	135	y	296.78	11	
8	14 970.44	29	y	124.82	22		300.51	2	
9	936.05	9					301.90	5	
				1→0 Band					
0	—	—		—	—		18 034.17	4	
1	—	—		18 011.48	10		050.33	10	
2				005.28	5		063.60	3	
3	17 938.05	4		17 995.83	29		073.43	17	
4	906.85	3		983.34	4		080.26	6	
5	872.41	8		967.88	27		083.49	8	
6									
7				933.73	4				
8									
9									
				1→1 Band					
0	—	—		—	—		16 540.32	130	z, D
1	—	—		16 518.35	114		557.24	121	
2	16 474.74	27		513.39	28		571.67	13	
3	448.09	147		505.92	200*		583.48	125	
4	419.27	69		496.00	39		592.73	7	
5	388.15	180		483.63	180		599.25	72	
6	355.07	83		468.91	19		603.14	30	y
7	319.86	150		451.82	97		604.33	20	
8	282.69	107	z, D	432.40	60				
9	243.65	94		410.70	160				
10	202.74	53							
11	159.98	40		360.75	43				
				1→2 Band					
0	—	—		—	—		15 093.07	20	
1	—	—		15 071.75	135		110.69	108	
2	15 029.27	6		068.12	75		126.31	30	
3	004.61	88		062.41	180		139.98	135	z, F
4	14 978.23	29		055.00	64		151.76	26	
5	950.33	102		045.71	160		161.55	105	
6	920.79	68	z, D	034.69	44		169.00	13	
7	890.02	80		021.93	112		174.48	39	
8	857.76	20		007.40	16				
9				14 991.22	66				
10				973.34	9				
11				954.04	15				
				2→1 Band					
0	—	—		—	—		17 825.39	11	
1	—	—		17 803.28	37		841.55	35	
2	17 758.93	6		797.12	8		854.29	9	
3	732.37	18		787.91	88		863.91	34	
4	701.87	5		775.71	10		870.31	12	
5	668.53	24		760.43	67		873.52	21	
6				742.29	6				
7				721.15	30				
8									
9									
				2→2 Band					
0	—	—		—	—		16 378.33	40	
1	—	—		16 356.60	190		394.90	153	
2	16 314.56	21		351.74	114		408.84	162	
3	288.82	128		344.30	200*	z, D	420.43	170	
4	260.81	175	z, D	334.69	111		429.31	85	
5	230.63	150		322.59	200*		435.63	125	
6	198.43	150	z, F	308.17	70		439.36	17	
7	164.28	200*	z, D	291.34	150		440.57	103	y
8	128.09	17		272.35	26				
9	090.12	55		251.12	77				

TABLE II.—*Continued.*

K	ν	I	Blends	ν	I	Blends	ν	I	Blends
				2→3 Band					
0	—	—		—	—		14 976.61	53	
1	—	—		14 955.53	200*		993.79	200	
2	14 914.70	12		951.89	109		15 009.04	180	z, D
3	890.79	108		946.40	200*		022.37	180	
4	865.28	40		939.14	126		033.72	56	
5	838.17	145		930.10	200*		043.09	172	
6	809.58	34		919.28	74		050.45	23	
7	779.58	105		906.73	200		055.76	70	
8	748.26	46		892.52	25		059.05	9	
9	716.13	10		876.67	82		060.29	18	
10				859.22	9		059.46	5	
11				840.20	23		056.56	12	
12				819.62	5		051.70	5	
13				797.32	15		044.76	4	
				3→2 Band					
0	—	—		—	—		17 620.86	4	
1	—	—		17 599.52	63		636.26	37	
2	17 557.58	86	zz, F	593.53	17		648.57	5	
3	530.16	21		584.50	138		657.83	39	
4	500.47	4		572.38	52	y	663.99	5	
5	468.08	14		557.58	86	z, F	666.99	24	
6									
7									
8									
9									
				3→3 Band					
0	—	—		—	—		16 219.16	25	
1	—	—		16 198.43	150	z, F	235.13	100	
2	16 157.27	5		193.62	70		248.67	24	
3	132.17	90		186.48	170		259.81	96	
4	104.92	30		176.92	64		268.44	20	
5	075.59	95		165.04	141		274.48	59	
6	044.17	38		150.88	53				
7	010.99	162	z, F	134.51	99				
8				115.87	10				
9				095.02	29				
				3→4 Band					
0	—	—		—	—		14 862.18	61	
1	—	—		14 842.06	200*	z, F	878.81	200	
2	14 802.17	24		838.50	200*	z, F	893.57	86	
3	778.84	152		833.13	200*		906.49	200*	
4	754.00	52		826.11	160		917.50	68	
5	727.68	158		817.15	200*		926.56	160	
6	699.92	39		806.74	200	xy			
7	670.83	111	z, F	794.31	175				
8				780.53	104	z, F			
9				764.94	82				
10				747.90	13				
				4→3 Band					
0	—	—		—	—				
1	—	—		17 399.96	41		17 435.42	35	
2						c			
3	17 332.41	55	y	385.36	98		452.82	66	
4				373.65	12				
5	268.55	23							
6									
7									
				4→4 Band					
0	—	—		—	—				
1	—	—		16 043.78	67		16 079.13	50	
2				039.13	31		091.67	11	
3	15 979.10	27		032.06	155	z, D	099.52	68	
4	952.04	7		022.71	21				
5	920.72	21		010.99	162				
6				15 997.21	12				
7				981.39	30				
				4→5 Band					
0	—	—		—	—		14 750.96	51	
1	—	—		14 731.50	200*		766.83	200	
2	14 692.64	15		727.98	125		780.53	104	z, F
3	669.87	150		722.74	200*		790.21	129	
4	645.13	89		715.77	148	z, F			
5	618.70	200		707.13	200*				
6				696.82	76				
7				684.84	152				
8				671.27	34				
9				656.13	56				
10				639.48	8				
11				621.32	34				

percent sample was only about 20 percent. (Some of this may have been due to dilution due to hydrogen being released from the electrodes or the walls on the tube.) The final portion had a tritium concentration of about 55 percent. The most useful pictures so far were made with a 77 percent sample which showed the HT and T_2

TABLE II.—*Continued.*

K	ν	I	Blends	ν	I	Blends	ν	I	Blends
				5→5 Band					
0	—	—		—	—		15 912.38	86	
1	—	—		15 892.71	200*	z, D	927.40	150	
2	15 835.96	40		888.17	90		940.08	51	
3	830.21	170		881.35	200*	z, F	950.14	12	
4	804.50	100		872.16	*c*				
5	776.65	140		860.72	175				
6				847.17	53				
7				831.43	148				
8				813.76	63				
				5→6 Band					
0	—	—		—	—		15 642.89	46	
1	—	—		14 623.91	190		658.44	175	
2	14 586.31	9		620.51	90		670.83	111	z, F
3	564.39	110		615.40	200		684.32	170	
4				608.61	150				
5	516.18	120	z, F	600.14	190				
6				590.06	43				
7				578.40	103				
8				565.13	22				
9				550.40	28				
10				534.19	75	y			
	6→6 Band			6→7 Band			7→8 Band		
1	15 745.36	73		14 519.49	102		14 418.56	35	
2	740.86	25		516.07	120	z, F	415.32	12	
3	734.13	112		511.18	154		410.43	94	z, F
4	724.84	42		504.59	44		404.14	13	
5	714.14	103		496.36	130		396.07	58	
6				486.54	14		386.57	6	
7				475.18	40		375.56	21	
8				462.25	7		363.00	2	
9				447.93	6	z, F	349.13	3	
	8→9 Band			9→10 Band			10→11 Band		
1	14 321.42	21		14 228.29	14		14 139.71	7	
2	318.19	3		225.29	2		136.88	2	
3	313.56	37		220.76	22		132.56	14	
4	307.36	6		214.76	3		126.86	2	
5	299.58	40		207.34	19				
6	290.40	3		198.53	2				
7	279.77	11		188.24	6				
8									
9	254.22	1							

* Line overexposed, density unreliable.

bands well developed with the H_2 band very much weakened.**

After an initial run, the first tube with aluminum electrodes showed only the atomic silicon lines as impurity lines. Mercury that was initially present disappeared gradually. If atomic silicon is present, which evidently originates from some disintegration of the quartz by the discharge, it is expected that the SiH bands might appear. Their presence is not obvious. They lie, however, in a region where the hydrogen lines are very crowded. It would be possible to say with certainty whether the SiH bands were present weakly only after this part of the spectrum has been measured and analyzed.

TABLE III. Rotational differences of the $2s^3\Sigma$-state.

				$F(K+1)-F(K-1)$				
K	$V=0$	1	2	3	4	5	6	7
				TH				
1	133.84	128.51	123.29	118.24	113.25	108.69		
2	222.28	213.40	204.73	196.30	188.03	179.79		
3	309.65	297.20	285.15	273.37	261.74	250.36		
4	395.34	379.48	364.01	348.91	334.02	319.57		
5	479.06	459.78	441.01	422.70	404.64	386.92		
6	560.43	537.88	515.81	494.34	473.26	452.37		
7	638.96	613.23	588.17	563.42				
8	714.60	685.75		630.06				
				T_2				
1	67.69	65.59	63.77	61.90	60.05	58.29	56.58	
2	112.40	109.18	106.09	102.98	99.98	96.98	94.05	91.08
3	157.01	152.44	148.11	143.77	139.60	135.32		
4	201.08	195.33	189.76	184.22	178.80	173.51	168.20	
5	244.68	237.70	230.92	224.16	217.58	211.07		
6	287.02	279.46	271.43	263.51	255.74	248.12		
7	329.91	320.50	311.26	302.18		284.17		
8	371.32	360.76	350.37	329.76				
9	411.84		388.56					

The second tube, with nickel electrodes, was first outgassed in vacuum by heating the electrodes to dull red heat in an induction furnace. In the initial stages this tube showed so strong contamination by CO_2, OH, and related molecules that the H_2 spectrum was completely obliterated. The origin of these impurities was not quite certain. Possibly they originated from the action of hydrogen atoms on stopcock grease present on a stopcock in the vacuum line about one foot away from the tube. That this was probably the case was corroborated by the fact that when the tube was filled with helium the helium spectrum was fairly pure, whereas under the same conditions a hydrogen discharge would start out as a typical H_2 discharge but change in a few minutes into a bluish CO discharge.

After elimination of the stopcock and insertion of platinum asbestos in the line as a catalyzer which would prevent hydrogen atoms from traveling any further, the tube could be cleaned up with helium discharges to drive out remnants of gases present. After this the spectrum would show, besides the atomic silicon lines, only the OH bands very faintly as impurity lines.

The small amounts of tritium available made it important that none of the gas was wasted. The tube with the aluminum electrodes showed a considerable cleanup effect. The pressure would fall rapidly from one millimeter, at which most of the pictures were taken, to below the value where a discharge could be sustained, sometimes within an interval of less than one hour. Unfortunately, time did not permit an investigation of the mechanism by which the gas disappeared. After the initial experiments the tube was operated with argon to drive out hydrogen from the electrodes. This was only partly successful, but the treatment profoundly altered the properties of the tube. The voltage necessary to run the tube with H_2 became higher. Apparently a very considerable amount of argon must have been driven into the electrodes. After the argon treatment the tube was again run with hydrogen. The pressure remained constant now, indicating that no hydrogen was disappearing any more. The spectrum after the argon treatment always showed argon lines in the H_2 spectrum. In the beginning the argon lines, particularly in the near infra-red, were much stronger than the H_2 lines. Repeated new fillings with hydrogen and pumping down to a pressure below 10^{-5} mm between the fillings would not bring any change.[6] The intensity of the argon lines was

---

** Later results have shown that with a given sample the apparent tritium concentration, determined spectroscopically, may depend very much on the discharge conditions.

[6] A small McLeod gage was used to measure pressures between about 10^{-3} mm and one mm. An ionization gage served to measure pressures below 10^{-3} mm. The ionization gage became useless, of course, once tritium had been admitted to the system, as the

Table IV. Constants of the $2s\,{}^3\Sigma$-state.

	TH			T_2		
V	B_V	D_V	ω_V	B_V	D_V	ω_V
0	22.363	0.00951		11.2848	0.00271	
1	21.470	0.00924	2082.88	10.9506	0.00231	1493.82
2	20.601	0.00899	1991.28	10.6418	0.00238	1447.23
3	19.756	0.00887	1901.98	10.3290	0.00226	1401.73
4	18.926	0.00880	1814.61	10.0282	0.00224	1256.93
5	18.117	0.00872		9.7230	0.00202	
Y_{10}		2177.01			1541.57	
$-Y_{20}$		47.84			24.47	
Y_{30}		0.502			0.312	
$-Y_{40}$		0.015			0.016	
Y_{01}		22.819			11.4374	
$-Y_{11}$		0.9182			0.3258	
Y_{21}		0.0123			0.00273	
Y_{02}		0.0097			—	
$-Y_{12}$		0.00038			—	

gradually reduced while the tube was operated for many hours with H_2 at high current levels during a period of several weeks, but they never disappeared and were still present with considerable intensity when the tube finally was discarded. During the end of its life this tube again showed a considerable cleanup effect. It would be interesting to investigate whether the reappearance of the cleanup effect was directly connected with the disappearance of the argon from the electrodes.

The tube with nickel electrodes showed only a very moderate amount of cleanup, which was not objectionable.[7]

The technique of obtaining the spectrum of hydrogen containing tritium differs but little from the technique when only H_2 or D_2 are present. While the radioactivity of tritium is considerable, the beta-rays are soft and no activity can penetrate glass. It is, therefore, completely safe to use tritium in a glass container. When pumping was necessary the outlet from the pump was directly led into a ventilating shaft so that not even small amounts of tritium could escape into the room. Neither deuterium nor tritium seems to exchange with the hydrogen contained in stopcock grease. It is, therefore, quite permissible to use stopcocks whenever they can be tolerated for other reasons. Possibly the beta-activity will decompose the stopcock grease, but a possible dilution of the tritium by hydrogen coming out of stopcocks because of this was of no importance for our purposes.

It need hardly be emphasized that any equipment that has contained tritium must be treated with the greatest care, and, if possible, should be discarded afterwards unless all traces of radioactivity can be removed.

III. RESULTS

The molecular spectrum of hydrogen was photographed in the second order of a three-meter grating spectrograph from about 3300A where the discrete spectrum begins to about 8800A. The exposure times ranged from a few seconds to two hours. Under these conditions the spectrum could be obtained with the lines everywhere dense, that is, an increased exposure would not have yielded additional lines. The long wave-length region is an exception and first-order plates were also taken there. In the short wave-length region below about 4800A fourth-order plates were also obtained. The comparison of several sets of plates taken with increasing tritium concentration made it possible to ascertain whether a given line belonged to H_2, HT, or T_2. Eventually, when it will be possible to obtain the spectrum of pure T_2, the identification of the species to which they belong will be considerably simpler. Even in that case the availability of spectra with different concentrations will make it possible to get the necessary information in case of blends which are rather frequent in a spectrum of such complexity. Microphotometer traces of all important plates were taken, with which a good estimate of the intensities could be obtained, even if the plates are not calibrated.

The wave-lengths were measured with a comparator in the usual way.***

It is hoped that, as the wave-length measurements accumulate, a rather complete analysis of the spectra of TH, TD, and T_2 can be given, which will include features which so far have not been elucidated in the H_2 spectrum. Naturally, the completion of this task will take some time, as each of the spectra contains in excess of 10,000 lines. The present paper gives an account of the so-called Fulcher bands of TH and T_2. It is hoped that this will shortly be followed by an analysis of the analogous bands for TD. A detailed comparison of the various molecules will be postponed until the TD data are also available.

Tables I and II present the analysis of TH and T_2, respectively. These bands are due to a $3p\,{}^3\Pi \rightarrow 2s\,{}^3\Sigma$ transition and lie chiefly in the wave-length region from 5400 to 7200A. The wave numbers should be accurate to within a few hundreths wave numbers for good lines.

The intensities listed in the I column are densities taken directly from representative plates. They are not corrected for changes of plate sensitivity with wave-length and can be regarded as preliminary values only until there is an opportunity to make quantitative measurements. They are, however, considerably better than the usual visual estimates.

It may be said that the degree of certainty with which the classification can be relied on is about the same as for the corresponding H_2 bands or better. This means that there practically cannot be any doubt about most of the lines, with the possible exception of some weak lines near the ends of the branches. The probability of

---

ionization produced by the tritium radioactivity would upset the calibration completely.

[7] It was later sealed off with tritium at about 2-mm pressure and operated successfully for many additional hours.

*** The earlier measurements were made with the comparator of the Physics Department of the University of Chicago. We wish to thank Drs. R. S. Mulliken and J. R. Platt for making this instrument available to us.

blends that distort the wave-length measurements is fairly high in a complex spectrum that is the superposition of that of three different gases (H_2, TH, and T_2). This situation will be considerably relieved for T_2 when purer tritium samples will become available.

A more complete analysis of all the bands in this region will make a recognition of these blends easier. Finally, when more measurements will have accumulated, a slight revision in the wave-lengths may be expected. All these things may eventually make a recalculation of the constants advisable. Such a revision, however, will not produce any substantial changes in the principal constants.

The chief intensity of the Fulcher bands lies in the sequences where V changes by ±1 or 0. There are fragments of weaker bands with $\Delta V = \pm 2$ which, however, are not complete enough to deserve recording.

IV. EVALUATION OF CONSTANTS

The $2s^3\Sigma$-State

The rotational energies of a Σ-state can be represented with sufficient approximation by the usual formula

$$F(K) = BK(K+1) - DK^2(K+1)^2. \tag{2}$$

The differences

$$\begin{aligned} F(K+1) - F(K-1) &= R(K+1) - P(K+1) \\ &= 2(K+1)B - [(2K+1)^3 - (2K-3)]D \end{aligned} \tag{3}$$

can be directly obtained from the experimental data. Averages are listed in Table III. For the computation of the averages data from other bands which have the same final state were included.

The constants B and D were calculated by a least square method from the first four differences of TH and from the first six differences for T_2. More differences were used for T_2 than for TH because the expression (2) will be a good approximation for higher values of K for T_2. The values of B_v and D_v thus obtained are given in Table IV.

TABLE V. Constants of the $3p^3\Pi$-state.

	TH			T_2		
V	B_V	D_V	ω_V	B_V	D_V	ω_V
0	19.797	0.00810		9.999	0.00213	
1	19.002	0.00797	1851.36	9.701	0.00207	1328.35
2	18.211	0.00794	1766.89	9.412	0.00200	1285.47
3	17.435	0.00787	1684.80	9.129	0.00198	1243.47
4	16.677	0.00772	1604.59	8.846	0.00187	1202.31
5	15.907		1526.30	8.579		1161.78
Y_{10}		1936.93			1372.11	
$-Y_{20}$		43.439			22.135	
Y_{30}		0.459			0.159	
$-Y_{40}$		0.036			0.002	
Y_{01}		20.219			10.150	
$-Y_{11}$		0.823			0.3050	
Y_{21}		0.0080			0.0038	
Y_{02}		0.00812			0.00217	
$-Y_{12}$		0.00008			0.000065	
ν_0		16767.05			16770.61	

The vibrational energy is given by the usual formula

$$\begin{aligned} E(V) = Y_{10}(V+\tfrac{1}{2}) + Y_{20}(V+\tfrac{1}{2})^2 \\ + Y_{30}(V+\tfrac{1}{2})^3 + Y_{40}(V+\tfrac{1}{2})^4 + \cdots. \end{aligned} \tag{4}$$

The differences between successive vibrational levels for a given K can again be found directly from the observed frequencies. With a knowledge of the rotational constants they can be extrapolated to $K=0$. From these differences

$$\begin{aligned} E(V) - E(V-1) = Y_{10} + 2VY_{20} \\ + (3V^2 + \tfrac{1}{4})Y_{30} + (4V^3 + V)Y_{40} + \cdots, \end{aligned}$$

the constants Y_{10} etc. can be obtained. As the convergence of (4) is generally poor except for low values of V it is advantageous to use only as many differences as constants are required.

Finally from

$$B_v = Y_{01} + Y_{11}(V+\tfrac{1}{2}) + Y_{21}(V+\tfrac{1}{2})^2 + \cdots, \tag{5}$$

and

$$D_v = Y_{02} + Y_{12}(V+\tfrac{1}{2}) + \cdots, \tag{6}$$

we obtain the constants $Y_{01} \cdots Y_{11}$, etc.

The $3p^3\Pi$-State

Every Π-state is double. The separation between the two components, Π^- and Π^+ is the Λ-doubling. It has been shown before[8] that the $3p^3\Pi^+$-state is usually irregular due to perturbations by the higher vibrational states of $3p^3\Sigma$. Rotational constants derived from this state would have no simple meaning. On the other hand the $3p^3\Pi^-$-state cannot be perturbed and, therefore, it should be used for the calculation of the rotational constants of the $2p^3\Pi$-state. It gives rise to Q branches only and, therefore, the differences (3) cannot be obtained directly for this state. The procedure for the calculation of the constants is as follows:

The rotational energies of a $p^3\Pi$-state except for a constant are given by

$$F(K) = B[K(K+1)] - D[K^2(K+1)^2 - 1]^2,$$

which differs from (2) only by the presence of the subtractive *one* in the second term. As the influence of the second term is negligible for small values of K, no appreciable error is made if the one is neglected as compared with $K(K+1)$. If B' and D' are the values of B and D for the $2p^3\Pi$-state and B'' and D'' the same value for the $2s^3\Sigma$-state, the Q branches are given by

$$\begin{aligned} Q(K) = A - (B'' - B')K(K+1) \\ + (D'' - D')K^2(K+1)^2. \end{aligned} \tag{7}$$

The values A (origins of the bands), $B'' - B'$ and $D'' - D'$ were obtained again by a least square method from the first six lines of each band, and it turned out that (7) represents the Q lines within the limits of the errors of measurement.

---

[8] G. H. Dieke, Phys. Rev. 48, 610 (1935).

As B'' and D'' are known from Table IV the rotational constants B' and D' for the $2p^3\Pi$-state can be obtained. The vibrational constants of this state are found in a way analogous to that used for $2s^3\Sigma$-state. The constants thus obtained are listed in Table V, which also contains the electronic frequencies of the bands.

V. NUCLEAR SPIN OF TRITIUM

Successive rotational lines in a band of a homonuclear diatomic molecule should alternate in intensities with a ratio $(I+1)/I$ when I is the nuclear spin. No such alternation should occur for a molecule with two different nuclei. None is observed for TH. For T_2 the ratio appears to be 3:1, the same as for H_2. This shows that the spin of tritium is $\frac{1}{2}h/2\pi$. This is in agreement with the findings of Bloch, Graves, Packard, and Spence,[9] who obtained this value by an entirely different method. Only rough intensity measurements are necessary to establish the value of the spin from the band spectrum as it is only necessary to decide whether the ratio is 3:1 or 1.67:1, etc. However, some quantitative measurements have been made more recently which confirm the value 3:1 with considerable accuracy.

VI. PERTURBATIONS AND PREDISSOCIATIONS

The $3p^3\pi^-$-state cannot be influenced by any close lying state because none with the required symmetry can be present. On the other hand the $3p^3\Sigma$-state partly overlaps the $3p^3\Pi$-state and it has the required symmetry for interaction with the $3p^3\Pi^+$-state. This interaction results in a shift of the $3p^3\Pi^+$-state from its unperturbed position. This shift is called Λ-doubling and can be obtained easily from the experimental data, as the unperturbed levels should coincide with the $3p^3\pi^-$-levels. The experimental values for the Λ-doubling are listed in Table VI. The magnitude of the Λ-doubling is determined chiefly by two states. The level with the same K and V of $2p^3\Sigma$ has a relatively large influence even though it is fairly distant because the matrix element of the interaction is relatively large. On the other hand, levels with the same K but any value of V may have a strong influence if they are very close. The close approach of such levels does not follow any simple law and, therefore, the influence of such close lying levels appears rather haphazard and accounts for the irregular behavior of the Λ-doubling as function of V. If the levels come very close we have a typical perturbation. Such a perturbation exists for $V=2$ of TH and $V=4$ of T_2.

TABLE VI. Λ-doubling of the $3p\Pi$-state.

	TH				T_2					
K	$V=0$	1	2	3	0	1	2	3	4	5
1	0.25	0.28	0.12	0.46	0.10	0.07	0.44	0.12	0.01	0.17
2	0.84	0.85	0.22	1.23	0.13	0.11	0.66	0.26	−0.02	0.28
3	1.54	1.66	0.08	2.27	0.27	0.34	0.96	0.52	−0.33	0.51
4	2.37	2.56	−1.21	3.42	0.44	0.51	1.18	0.72	−2.84	0.71
5	3.26	3.58	−7.55	4.46	0.67	0.78	1.48	1.20		
6	4.13	4.46		5.02	0.96	1.03	1.82	1.61		
7	4.90	5.38			1.09	1.28	2.28			
8	5.80	5.96			1.44	1.57	2.65			
9					2.00					
10					2.01					

Beyond a certain limit the $3p^3\Sigma$-level is dissociated which means that no sharp energy levels exist. The $3p^3\Pi^+$-levels that coincide with such dissociated $3p^3\Sigma$-levels take on the properties of the interacting levels. They appear predissociated which means here that the corresponding molecular states disappear before the molecule has had the time to emit the line. This has as consequence that the P and R branches of all bands disappear when the upper state lies beyond the dissociation limit of $3p^3\Sigma$. The data show that this is true for $V=4$ for TH and for $V=6$ for T_2 (see Table VI). The Q branches are unaffected. This can be used to narrow the limits for the dissociation energy of H_2. It is best, however, to postpone a discussion of the details of this until also use can be made of the TD-data.

---

[9] Bloch, Graves, Packard, and Spence, Phys. Rev. **71**, 551 (1947).