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THE RESONANCE (*B-A*) BAND SYSTEM OF THE HYDROGEN MOLECULE

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Abstract

Part I. Experimental procedure. A three meter focal length vacuum spectrograph, designed by Professor J. J. Hopfield, has been constructed at the University of California and used to photograph the extreme ultraviolet hydrogen band spectra. A description of the type of mounting and method used to focus the instrument is given. The greater dispersion and resolving power has made possible the measuring of additional lines. New tables of frequencies are given.

Part II. Lines in sixty-eight bands have been given quantum assignments. On the basis of the old quantum theory the moment of inertia of the hydrogen in the normal (*A* level) state is found to be 0.4673×10^{-40} g cm^2 and the nuclear separation to be 0.7500×10^{-8} cm. In the first electronic excited state (*B* level) the moment of inertia is 1.4225×10^{-40} g cm^2 and the nuclear separation 1.308×10^{-8} cm. Comparison of the present results with those obtained by Richardson and Davidson in their study of bands found in the visible leaves no doubt but that the ultraviolet *B* state also is the lower state of the bands studied by them. This, then, verifies the assumption made by Birge and leads to the conclusion that the ionization potential of H_2 must be 15.34 volts to within a few hundredths of a volt.

Bands connected with vibrational levels $A_0\,A_1$ and A_2 are not observed. In order to obtain the best possible value of I_0, data from all available sources were correlated and averaged. Birge and Jeppesen calculated accurate values of B_0 and B_1, for the normal level, from Rasetti's data on the Raman effect of gaseous hydrogen. Values for B_1 by the two methods agree to one part in seven thousand but their value for B_0 is 0.27 percent higher than the value given by the present method. This discrepancy points to an irregularity in the moment of inertia of hydrogen in the $v=0$ state of the normal electronic level, as has been pointed out by Birge and Jeppesen.

Introduction

INVESTIGATIONS of the fine structure of bands found in the extreme ultraviolet have been handicapped greatly by the low dispersion and resolving power of the instruments used in the photographic work. Professor J. J. Hopfield of the University of California has designed a vacuum spectrograph using a three inch grating, 15000 lines per inch, with a three meter focal length. It has been found that the instrument has a resolving power of 0.1A and a dispersion of 2.76A per millimeter in the second order. The spectrograph has been built in the shop of the Physics Laboratory of the University of California by Mr. W. R. Stamper and his assistants, following the plans furnished by Professor Hopfield.

The hydrogen bands of the extreme ultraviolet were photographed by the writer, this being the first vacuum work completed on the instrument.

Previous to the present work Dieke and Hopfield,[1,2] by obtaining ab-

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[1] Dieke and Hopfield, Zeits. f. Physik **40**, 229 (1926).

[2] Dieke and Hopfield, Phys. Rev. **30**, 400 (1927).

sorption and emission spectrograms, were able to give a complete analysis of the vibrational levels of the three known lower electronic states of the hydrogen molecule. These three states are known as the A, B, and C levels, the A level being the normal state of the molecule.

Schumann,[3] Lyman,[4] Witmer,[5,6] Werner,[7] Hori,[8] and others had photographed and measured H_2 bands in the extreme ultraviolet. The bands photographed and measured by Werner constitute the C-A system, as given by Dieke and Hopfield. The Lyman-Witmer bands now are known to form the B_3-A_v transitions of the B-A system. These B_3-A_v bands are obtained when the discharge tube is filled with a mixture of argon and hydrogen. These same bands appear when only hydrogen is used in the tube, but generally are weaker, some of them being almost completely blended by more intense bands of the B-A system. Richardson, and his students,[9] in a series of papers, have identified a great number of electronic levels of the hydrogen molecule. Birge[10] assumed that the lower level of the Richardson "A" and "B" band systems[11] was identical with the B state of the bands in the ultraviolet. With a Ritz formula for the Richardson band system, Birge found the ionization potential of H_2 to be 15.34 volts. In the same paper a summary of the quantum levels and constants of the hydrogen molecule is given. Starting with the vibrational analysis as given by Dieke and Hopfield,[1,2] Hori[8] has obtained an analysis of the fine structure of the C-A bands. In the same paper he gave a preliminary analysis of the Lyman-Witmer progression (B_3-A_v), based on the assumed presence of R, Q, and P branches. For the latter work Hori used Witmer's measurements.

PART I. EXPERIMENTAL PROCEDURE

The instrument designed by Professor J. J. Hopfield and used for obtaining the spectrogram shown in Fig. 2 is so made that it is possible to obtain on the photographic plate any region of the spectrum. The plates are of such size that a span of 1200 Angstroms, in the first order can be photographed with one exposure. Arrangements have been made so that thirteen exposures may be taken on one plate. However, it has been found that limiting the number to five is more practical.

Type of mounting.

As the space to be evacuated needed to be kept a minimum, a modified form of the Eagle mounting[12] was used, instead of the Rowland type. The

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[3] W. Schumann, Werner Anzerger **29,** 230 (1892).

[4] T. Lyman, Spectroscopy of Extreme Ultraviolet, (1914).

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

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

[7] Werner, Proc. Roy. Soc. **113A,** 107 (1929).

[8] T. Hori, Zeits. f. Physik **44,** 11, 834 (1927).

[9] Richardson and Davidson, Proc. Roy. Soc. **125A,** 23 (1929), and article referred to in this paper.

[10] R. T. Birge, Proc. Nat. Acad. Sci. **14,** 12 (1928).

[11] Richardson and Davidson, Proc. Roy. Soc. **115A,** 528 (1927).

[12] A. Eagle, Astrophys. J. **31,** 120 (1910).

slit, the photographic plate, and the grating were all placed in a cast iron tube three meters long. Five sylphons served as a means for making the adjustments of the plate-holder and grating. These adjustments could be made after a vacuum had been obtained. A grating to be used in this manner must be capable of motion along the tube, and also of rotation about a vertical axis. Fig. 1*A* shows how this was accomplished. The grating is fastened to the carriage *C* which is mounted on the rails *R*. Rods *D* and *E* served to move the grating.

The position of the grating is shown by two dials placed at *A* and *B*. The plate-holder *F-G* is pivoted such that the line of rotation passes through the line of the slit and the radius of curvature of the holder is one-half the radius of curvature of the grating. The slit is at *S*.

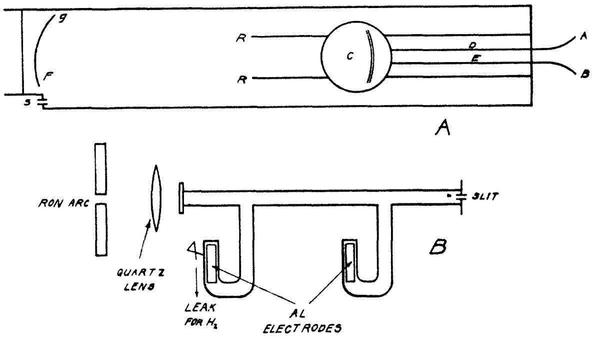

Fig. 1. Diagram of apparatus.

It is well known that in order to obtain the best definition with a concave grating the slit and the grating must be on a circle whose diameter is equal to the radius of curvature of the grating, and, in this case, all the spectral lines are focused on this same circle. The method of mounting fulfills these requirements. It can be seen that the exact position of four variables must be determined to obtain the focus.

Adjustment of the instrument.

The first work to be done was to focus the instrument for all regions of the spectrum. In the case of the Rowland mounting there is a standard method of procedure but in the mounting considered here the method is not so well established.

The first step in the adjustment was the leveling of the grating so that the images would all fall upon the horizontal opening over the plate. Once this position for the grating had been determined, this variable was eliminated.

The second step in the adjustment was to find the approximate settings of the plate, the grating, and the slit with respect to one another, for a definite region of the spectrum.

For convenience, a portion of the visible spectrum of the mercury arc was used. For approximate settings, the eye was used to examine the image which was assumed to be formed on a photographic plate. When the adjustments were found sufficiently close to serve as a starting point, a photograph of the known lines of mercury was taken and examined for the purpose of determining the course of procedure. Upon examining these plates it was found that certain parts of the spectrum were in much better focus than others. This indicated that the angle of the plate-holder was not correct.

The question, then, was one of determining what changes were necessary in order to bring in focus all the spectrum that fell on this plate. This necessitated the determination of the angle of the plate, the angle of the grating and the distance of the grating from the slit.

To obtain these relations, the central part of the grating was covered. By covering the central part, each individual line appears as double, if not in focus.

With the central portion of the grating covered, photographs were taken and the doubling of the lines observed. At least three exposures were taken on one plate with the plate-holder fixed, the grating being moved along the tube.

One of these exposures was taken at what was considered the best focus for some part of the plate, and the other two on opposite sides of this point. On at least two of these exposures doubling occurred. By carefully measuring the distance between these doubled lines and then drawing graphs, the position of the grating for the focus of the line being considered was found. At least two lines on the plate, preferably at extreme ends, were used and from data obtained the position of the grating for the focus of a line that would fall on the slit was calculated. To determine the amount of rotation of the plate it was necessary to know, in addition to the above, the pitch of the screw that moved the grating and also the distance of the lines on the plate from the slit. It must be remembered that the focus moves in and out twice as fast as the grating moves.

If P_0 is the position of the grating for focus on the slit, P_a the position for the focus of the line being considered, k the pitch of the screw moving the grating, and d the distance of the line from the slit, then the grating must be moved approximately

$$\frac{2k(P_a - P_0)}{d} \times 57 \text{ degrees.}$$

By repeated trials the angle of the plate was determined as well as the position of the grating in the tube. Thus the four variables were determined that fixed the focus for the one region. This same process was repeated for each section of the spectrum. Allowance has been made for sufficient overlapping from one region to another.

After obtaining the focus from λ1000 to λ6000, photographs of the iron arc were taken (λ2300 to λ6000) and many of the lines identified and marked on the plates. These plates are on file for use as an easy method of identifying the exact region given by any one position.

Vacuum technique.

Perhaps one of the greatest difficulties to be overcome was the obtaining of a vacuum suitable for photographic work in the ultraviolet. The volume to be evacuated was approximately one hundred eighty liters. The surface of the iron pipe alone was over two and three-quarters square meters. The ends of the spectrograph were sealed with rubber gaskets and held firm by heavy bolts. The opening for inserting plates was sealed in the same manner. Five sylphons, three windows and two outlets also were potential sources of trouble. Several holes were found in the casting.

At first one mercury vapor pump backed by a large General Electric Company vacuum pump was used to evacuate the system. It was found that this was inadequate. A second mercury vapor pump was then inserted in parallel with the first.

The pressure inside the spectrograph under working conditions varied between 0.005 mm and 0.010 mm of mercury, as measured by a McLeod gauge.

Photographic work.

A π-shaped discharge tube, made of Pyrex with aluminum electrodes, was used. As the region photographed reached beyond the limit of transmission of quartz or fluorite, the discharge tube was fastened directly to the spectrograph. Current from a 11,500 volt transformer was used, and a water rheostat in series with the tube was so adjusted as to give a maximum of intensity without melting the tube. Approximately 0.5 of an ampere was run through the tube. Considerable difficulty was found in eliminating the continuous spectrum found when exposing the plate in the second order, but by grinding the inside of the tube until a rough surface was obtained, much of the continuous spectrum was found to disappear.

The hydrogen was generated electrolytically, passed through a drying tube of P_2O_5, then through a capillary leak directly to the discharge tube. As the gas was being removed by a Cenco pump and also through the slit, it was necessary to have a continuous flow of hydrogen.

The evacuating pumps and the flow of hydrogen were started at least two hours before the photographic work, thus insuring a thorough flushing out of the discharge tube. Any trace of air was noticeable at once in the visible spectrum. The best plates obtained show no trace of known impurities. Schumann plates made by Hilger Company were used.

To make sure that no first order hydrogen lines were being photographed the discharge tube was run under the same conditions as were used for the good plates except that a quartz window was placed between the slit and the source of light.

In general, investigators in the extreme ultraviolet have been handicapped not only by low dispersion and low resolving power, but also by lack of suitable standards. As the measurements in this investigation were from plates showing the second order H_2 lines it was found possible to measure them using first order iron arc lines as standards.

TABLE I. *B-A*. *Bands of hydrogen*. (*indicates known blend).

		R-branch			P-branch	
Band	I	$m-\frac{1}{2}$	cm^{-1}	I	$m-\frac{1}{2}$	cm^{-1}
B_0-A_3	2	0	78,462			
	2	1	439	4	1	78,332*
	1B	2	356*	1	2	160
	3	3	203*	5	3	77,937
	0	4	77,996*	4	4	654*
	3	5	733*	4	5	317
				2	6	76,943*
				4	7	496*
				2	8	020*
B_0-A_4	3	0	74,992			
	6	1	973	6R	1	74,856*
	5	2	898	5	2	706
	5	3	767	6	3	501
	1B	4	579*	4B	4	243
	4B	5	343*	8	5	73,937*
	3	6	040*	1	6	562
				2	7	135*
				000	8	72,674*
B_0-A_5	1	0	71,749*			
	4	1	738*	5	1	71,621*
	3	2	674*	4	2	481
	4	3	560*	6	3	293
	1	4	396	3	4	059
	2	5	187	5	5	70,779*
		6		1	6	458*
	00B	7	70,631	2	7	098
B_0-A_6	1	0	68,737			
	5B	1	729	4	1	68 614*
	2	2	678*	1	2	486*
	4	3	581*	4	3	315*
	0	4	441*	5	4	102*
	1	5	258*	3	5	67 851*
				000	6	564*
B_0-B_7	3	0−1	65,953*	1	1	65,836*
	2	2	893*	00	2	721*
	1	3	836*	2	3	567*
	00	4	721	00	4	379*
	2	5	567	1	5	156
	00	6	379	1	6	64,908*
B_0-A_8	3	0−1	63,410*	0	1	63,303*
	0	2	383	1	2	195*
	1	3	314	1B	3	057
		4		1	4	62,862
	4B	5	134*	00	5	717
B_0-B_9	000	1	61,126*	3	1	61,017*
	4	2	112*	2	2	60,919*
				3	3	814*
B_1-A_3	4B	0	79,772*			
	1	1	752*	2	1	79,642
		2		2	2	476
	2	3	503*	4	3	251*
	0B	4	288	2	4	78,965
	3	5	010*	3	5	623
	2	6	78,656*	00	6	228
				1B	7	77,776
B_1-A_4	2	1	76,283	1B	1	76,171
	1	2	204	2	2	020*
	2	3	066	1	3	75,812
				3	4	550
				0	5	237
				2	6	74,873*
B_1-A_5	0	0	73,050			
	00	1	029	2	1	72,928*
	2	2	72,988	0	2	809*
	2	3	849*	1	3	615*
	000	4	674*			
	3	5	458*	2	5	078*
	1	6	186*	1	6	71,749*
B_1-A_6	1	0	70,053			
	4	1	043	3	1	69,933
	2	2	69,984	2	2	802
	3	3	881*	3	3	626*
	2	4	730*	1	4	408
	2	5	540*	4	5	151
	6	6	278	000	7	68,514
B_1-A_7	5B	0−1	67,268*	5	1	67,156*
	2	2	221	4	2	038*
	4	3	133*	5	3	66,880*
	00	4	011*	4	4	686*
	1	5	66,845	4	5	456*
				00	6	196
B_1-A_8	5	0−1	64,729*	3	1	64,619*
	1	2	696	2	2	513
	3	3	619*	1	3	362*
	0	4	526	000	4	204
	1	5	392*	4B	5	003*
B_1-A_9	2	0	62,442			
	1	1	434*	3	1	62,325*
	5	2	421*	000	2	230
	2	3	357*	1	3	115
	3	4	298*	5	4	61,968*
	4B	5	206	1	5	809
	3	6	048*	3	6	612
B_2-A_3	3	1	81,031	1	1	80,934*
	1	2	80,934*	0	2	754
	1	3	768	00B	3	528
		4		1	4	241*
	3B	5	267	3	5	79,982
				3	7	010*
B_2-A_4	4	1	77,562	3	1	77,456
		2		1	2	299
	1	3	329*	5	3	087
				1	4	76,820*
				4	5	496*
B_2-A_5	4B	0	74,343*			
	6	1	327	4	1	74,221*
	1	2	252	4	2	078*
	2	3	125	8	3	73,883
	8	4	73,937*	2	4	637*
	0	5	717*	4	5	344
	0B	6	411*	00	6	008
B_2-A_6	000	0	71,337			
	3	1	319*	2	1	71,212*
	000	2	257	1	2	081
	2	3	146	3	3	70,903*
	0	4	70,994*	1	4	680*
	5	5	779*	1	5	408*
B_2-A_7		1		0	1	68,441*
	1	2	68,492*	4	2	315
	1	3	401*	5	3	168*
	5	5	102*	0	5	67,721*
	1	6	67,906*			
B_2-A_8	5	0–1	66,006*	3B	1	65,901
	1	2	65,967	3	2	793*
	2	3	893*	6	3	650*
	3	4	793*	3	4	475
	6	5	650*	4	5	270
				5	6	040*
B_2-A_9	4B	0–1	63,718*	4	1	63,614*
	1	2	693	2	2	518*
	3	3	638	4	3	396
	000	4	556*	3	4	243*
	1	5	447	4	5	074*
B_2-A_{10}	3	0	61,689*			
	4	1	699	4	1	61,595
	3	2	689*	3	2	513
	3	3	654	3	3	411
	0	4	601		4	
	00	5	527	2	5	154*
				00	6	60,993*
				3	7	814*
B_3-A_3		1		0	1	82,171*
	0	2	82,171*	000	3	81,767
B_2-A_4	00B	0	78,831			
	3	1	808	3	1	78,708*
	3	2	708*	1	2	551*
	3	3	568	4	3	332
	3	4	356*	3	4	062*

TABLE I. *B-A. Bands of hydrogen (Continued).*

	R-branch			*P*-branch		
Band	I	$m-\frac{1}{2}$	cm^{-1}	I	$m-\frac{1}{2}$	cm^{-1}
	1	5	075	3	5	77,733*
				2	7	76,931
B_3A_5	2	0	75,591			
	0	1	569	2	1	75,468
	1	2	492*	1	2	323*
	2	3	358	5	3	125*
				2	4	74,873*
				1B	5	579*
				4	6	221*
				0	7	73,821*
B_3A_6				3	1	72,458*
				2	3	146
				1	5	71,649*
				3	6	319*
B_3A_7	1	0	69,794			
	4	1	784	3	1	69,684*
	2	2	730*	2	2	562*
	2	3	633	4	3	399
	2	4	493	2	4	196*
	00	5	312	3	5	68,955
	00	6	092*	2	6	678*
B_3A_8	0B	0–1	67,248*	4	1	67,133
	000	2	205	4	2	038*
				5	3	66,880*
				4	4	686*
B_3-A_9	3	1	64,961	1B	1	64,859
	2	2	932	2	2	782*
	2	3	871	3	3	638*
	2	4	782*	0	4	486
	2	5	653*	3	5	307
				000	6	106
B_3-A_{10}	1	0	62,934			
	5	1	942	6	1	62,842
	3	2	926	5	2	758
	4	3	887	5	3	653*
	0	4	826	3	4	529
	2	5	745	3	5	387
	5	6	653*	000	6	230
				3	7	048*
B_3-A_{11}	4	1	61,224	000	1	61,126*
		2		1	2	045
	2	3	197	4	3	60,965*
	2	4	154	2	4	871
	4	5	112*	2	5	768
B_4-A_4	0		83,500			
	0	1	477	1	1	83,382*
	1	2	382*	2	2	212
	1	3	200*	2	3	82,976*
	0	4	82,966	000	4	679
				2	5	320*
B_4-A_4	1B	0	80,045			
	2	1	017	3	1	79,921*
	3	2	79,921*	1	2	752*
	4B	3	772*	4	3	544*
	4	4	544	3	4	264*
	3	5	264*	2	5	78,937*
	0B	6	78,887	1	6	551*
				0B	7	127
B_4-A_5	1	0	76,820*			
	2	1	781*			
B_4-A_6	0	0	73,789			
	4	1	770	3	1	73,672
	0	2	699	2	2	538
	2B	3	579	5	3	354
	0	4	411	1	4	124
	3	5	185	2	5	72,849*
B_4-A_7	0	0–1	70,994*	3	1	70,903*
		2		5	2	779*
		3		1	3	608
	1	4	680*	1	4	408
	1	5	458*	000	5	153
				3	6	69,881
				2	7	562*
B_4-A_8	2	0–1	68,458*	1	1	68,360
	1	2	401*	1	2	250*
	4	3	315*	5	3	102*
	5	4	168*	1	4	67,906*
	1	5	004	2	5	704
	2	6	67,737	000	6	409
B_4-A_9	4	0–1	66,171*	4	1	66,073*
	1	2	137	1	2	65,976*
	4	3	073*	2	3	847*
	1	4	65,976*	0	4	691
	2	5	847*	00	5	530
B_4-A_{10}	00	0–1	64,156*	0	1	64,054
	000	3	088	1	3	63,863
	4B	4	003*	00	4	734
	0	5	63,934	1	5	586*
				1	6	436*
				3	7	243*
B_4-A_{11}	5	0	62,421*			
	1	1	434*	3	1	62,325*
	5	2	421*	3	2	258
	3	3	397	4B	3	174*
	2	4	357*	3	4	076
	2	5	298*	5	5	61,968*
				5	6	859
				3B	7	736*
B_4-A_{12}	00	0	60,993*			
	3	1	61,017*	2	1	60,919*
	2B	2	034*	2	2	871*
	2B	3	034	3	3	814*
	2B	4	034	000	4	753*
	00	5	993*	1	5	691*
B_5A_3	1	1	84,655	1	1	84,560*
	1	2	560*	0	2	390
	0	3	368	4	3	153
		4		000	4	83,851
	4	5	83,806	0	5	487*
				4	7	82,551
B_5-A_4				1	2	80,934*
	1	3	80,934*	1	3	719
B_5-A_5	0	0	77,996*			
	2	1	957	1	1	77,863*
	2	2	870*	1	2	712
	1	3	725	5	3	508
				2	4	251
				2	5	76,943*
				00	6	583
B_5-A_6	2	0	74,973*			
	4	1	946	6R	1	74,856*
	2	2	873	0	2	717*
	2	3	746	3	3	531
	1B	4	579	00	4	295
	4B	5	343	3	5	018*
				0	6	73,717*
				3	7	314*
B_5-A_7	0	0	72,186*	2	1	72,078*
				1	3	71,785
	1	5	71,649*	3	5	319*
				0	6	033
B_5-A_8	2	0–1	69,633*	2	1	69,540*
	0	2	584	0	2	428
	0	3	480*	6	3	278
	000	4	367*	00	4	092*
	2	5	196*	2	5	68,871
				4	6	614*
B_5-A_9				5B	1	67,268*
				5	2	156*
	0B	3	67,248	4	3	038*
	4	4	133*	2B–	4	66,865*
				4	5	686*
B_5-A_{10}	3	0–1	65,327*	3	1	65,235
	1	2	304	1	2	149
	2	3	255*	5	3	040*
				1	4	64,908*
				2	5	755*

TABLE I. *B-A. Bands of hydrogen* (*Continued*)

Band	*R*-branch			*P*-branch		
	I	m−½	cm⁻¹	I	m−½	cm⁻¹
B_5-A_{11}	000	0	63,599			
	4	1	614*	2	1	63,518*
	1	2	586*	1	2	436*
	000	3	562*	0	3	350*
	2	4	518*	3	4	247*
	2	5	460	4B	5	134*
				4	6	62,995*
B_5-A_{12}	4B	0	62,174*	6	1	62,100
	3	1	191	3	2	048*
	4B	2–3	206*	5	3	61,989
	3	4	191*	4	4	925
	4	5	149	1	5	821
	1	6	061	3B	6	736*
B_6-A_3	000	0	85,835	00	1	85,706
	000	1	797	2	3	296
	00B	3	501	1	4	84,993
B_6-A_4	1	0	82,375			
	2	1	320*	1	1	82,234
	1	2	234*			
B_6-A_5	3	0	79,148			
	2	1	103*	3	1	79,010
	3	2	010*	3	2	78,864*
	3	3	78,864*	2	3	656*
	2	4	656*	3	4	393
				1	5	082
				3	6	77,733*
B_6-A_7	3	1	73,314*	3	1	73,224
	00	2	248*	00	2	090
	2	3	135*	2	3	72,928*
	1	4	72,988	000	4	714
				3	5	458*
				1	6	186*
B_6-A_8	5	0–1	70,779*	1	1	70,680*
	00B	3	631*	1	3	408*
	1	4	458			
B_6-A_9	1	0–1	68,492*	1	1	68,401
	0	2	441*	1	2	300
	2	3	378*	5	3	168
	1	4	258	1	4	67,986*
	000	5	132	2B	5	812*
B_6-A_{10}		2	66,456*	1B	1	66,377
				4	3	171*
B_6-A_{11}	2	0–1	64,755*	2	1	64,653
	5	2	729*	1	2	583*
	1	3	701	2	3	496
	3	4	638*	1	4	392*
	1	5	583*	3	5	273
B_6-A_{12}	000	0	63,339	6	1	63,261
	0	1–2–3	350*	4	2	217
				4B	3	134*
B_7-A_3	1	1	86,991	1	3	86,410
B_7-A_4	0	0	83,487*			
	000	1	455	0	1	83,363
	0	2	338	1	2	200*
		3		1	3	82,976*
	1	4	82,951	000	4	697
				0	5	346
B_7-A_5	1	0	80,241*			
	2	1	214	1B	1	80,131
		2		0B	2	79,972
	3	3	79,943	2	3	772
		4	752	2	4	503*
		5	476	0	5	189
B_7-A_6	0	1	77,199	00	1	77,113
				2	3	76,784*
				0B	5	257
B_7-A_7	000	0	74,446			
	2	1	426	4B		74,343*
	4	3	221*	3	3	040*
	4	4	078*	0	4	73,821*
	0	5	73,850	1	5	562*
B_7-A_9	3	0	69,626*			
	0	1	603	1	1	69,516
	2	2	562*	0	2	428*
	0	3	480*			
	000	4	367*	000	4	111
B_7-A_{10}	1	1	67,584	3	1	67,496*
	000	2	564*	000	2	409*
	2	3	496*	2	3	296*
	000	4	490*	5	4	156*
	2	5	296*	00	5	011*
B_7-A_{12}	1B	1–2–3	64,449*	1	1	64,362*
	5	5	373	3	2	307*
				3	3	245
				000	5	106
B_8-A_4	1	0	84,560*			
	0	1	526	000	1	84,446
	000	2	432	0	2	280
	1	3	240	2	3	046
	2	4	026	000	4	83,775
	1	5	83,713	1	5	410
				00B	6	004
B_8-A_6	2	0	78,310			
	1	1	286	3	1	78,203*
	3	2	203*	3	2	062*
	3	3	062*	1	3	77,863*
	2	4	77,870	0	4	622
	4	5	654*	1	5	329*
				1	7	76,634
B_8-A_7	1	1	75,492*			
	1	3	323*	5	3	75,125*
B_8-A_8	1	0–1	72,988*	0	1	72,886
	0	3	809*	1	3	615
B_8--A_{10}	1	0–1	68,666*	4	1	68,581*
	000	3	572	1	2	492*
	1	4	486*	2	3	378*
	2	5	378*	1	4	250*
B_8-A_{11}	2	0–1	66,942*	2B	1	66,865
	000	2	906	4	3	686*
	0	3	892	000	4	561
B_8-A_{12}	000	1	65,541	000	1	65,392
	00	2–3	530*	3	2	327*
	2	4	507	2	3	255
B_9-A_6	00	0	79,343			
	1B	1	338	4	1	79,251*
	000	2	235	2	2	103*
	2	3	103*	0	3	78,920
				2	4	656*
B_9-A_8	3	0	74,040*			
	3	1	018*	8	1	73,937*
	8	2	73,937*	0	2	821*
	0	3	850	2	3	637*
				00	5	248*
B_9-A_9	1	0	71,749*			
	4	1	738*	1	1	71,649*
	3	2	674*	4	2	560*
	5	3	621*	1	3	410
				2	4	212*
				1	5	070
B_9-A_{10}	2	0	69,730	1	1	69,649
	3	1	684*	2	2	540*
				0	3	428*
				6	4	278*
				000	5	111
B_9-A_{11}	1	0–1	67,986*	1B	1	67,920*
	1B	3	920*	2B	2	812*
	1	4	906*	0	3	721*
	3	5	851*	2	5	496*
				000	6	409*
				2	7	296*

An iron arc (see Fig. 1*B*) was used as the source of light for the comparison spectrum. The lens and the window shown were of quartz. The iron arc was run for five minutes before starting the hydrogen source and also for five minutes after stopping the discharge, thus enabling one to detect any shift in the lines while making the exposures.

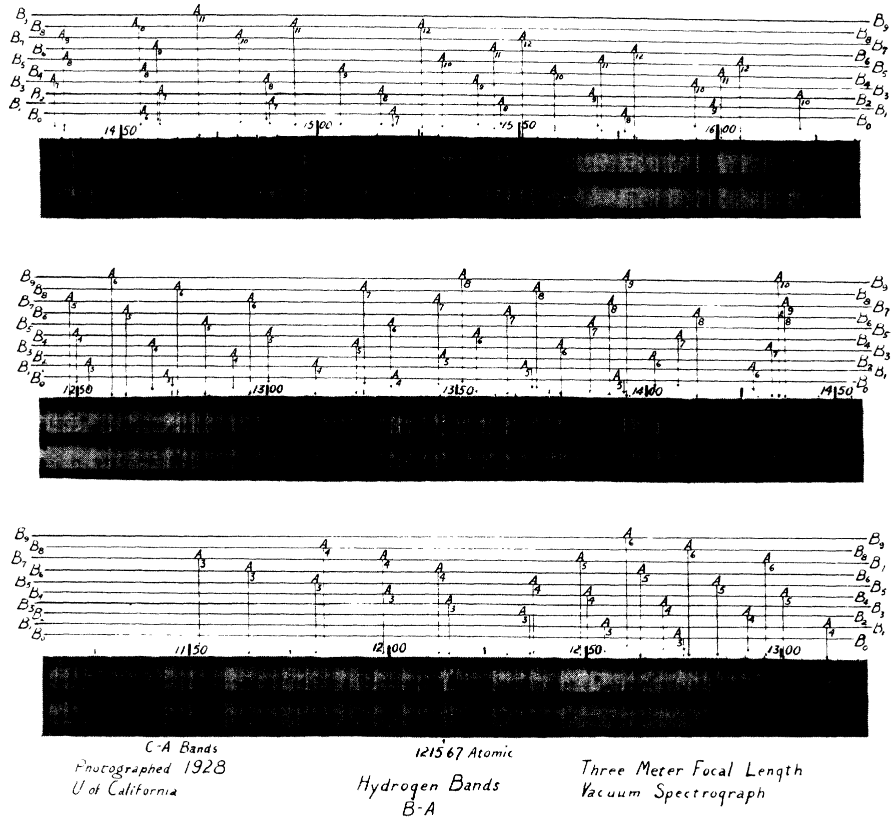

Fig. 2.

The shutter over the plate was so arranged that by turning a screw the iron lines did not cover all the plate that had been exposed to the hydrogen light. The iron lines may be seen in Fig. 2 and are easily distinguished from the hydrogen lines. On the same plate is found also an exposure showing only hydrogen lines.

Only plates that showed no displacement of the iron lines were used for measurement. It was found that the instrument was very sensitive to temperature changes. No special provisions had been made for maintaining a constant temperature, but care was taken in keeping the room as nearly as possible at one temperature while making the exposures.

Many iron lines suitable for standards were found between 2600A and

3300A.[13] For the H_2 lines below 1300A, hydrogen lines were measured in the third order against iron lines as standards and these hydrogen lines were then used as standards in the second order. The iron lines used as standards were spaced approximately 100A or less apart.

The measurements were made on a 200 millimeter comparator purchased by Professor R. T. Birge through the generosity of the Rumford Grant Committee of the American Academy of Arts and Sciences. It is believed that the measurements are in all cases accurate to approximately 0.05A. In general the lines listed were measured from two different plates.

Tables I and II give frequencies of the lines measured and intensities. Intensities are merely visual estimates. Table I also gives the quantum assignments as discussed in Part II.

TABLE II. *Frequencies of lines between λ1260A and λ1640A measured but not identified in this work.*

I	cm^{-1}	*I*	cm^{-1}	*I*	cm^{-1}
1	79,990	000	72,752	2	65,765
3	78,766	0	629	2	743
1	666	1	431	2	627
1	527	000	419	000	593
1	512	000	396	3	226
3	495	000	272	3V	63,884
0	375	1B	051	000	843
000	260	000	71,635	2	806
1	248	0	534	2B	800
1B	182	00	436	0	795
1—	153	000	378	000	505
1	093	1	110	000	490
0	038	0	70,863	00	62,802
0	77,674	0	68,855	23	670
00	615	000B	68,756	2	408
0	356	000	523	1	313
1	188	00	326	2	270
00	149	00	67,398	1	126
00	73,741	000	185	1	120
1	664	1	66,993	1	61,795
00	418	1	413	2B	034
		1	355		
		1	65,985		

The focusing of the instrument was carried out in cooperation with Dr. C. A. Pulskamp, to whom the writer is indebted for his valuable aid in adjusting the instrument. The writer also wishes to express his thanks to Professor J. J. Hopfield, who suggested the problem and under whose direction the experimental work was started.

PART II. ROTATIONAL DATA

While the work on the fine structure of the hydrogen resonance bands was in progress Kemble and Guillemin[14] published an article in which they concluded, on theoretical grounds, that the *B-A* system must consist of *R* and *P* branches only.

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[13] H. Kayser, and H. Konen, Handbuch der Spectroscopie, Vol. 7, (1924).

[14] Kemble and Guillemin, Proc. Nat. Acad. Sci. **14,** 782 (1928).

Richardson and Davidson[11] have completed the fine structure analysis of certain bands found in the visible. It will be shown that there is a definite connection between this band system and the B-A system.

Schaafsma and Dieke[15] have published rotational energy data, based on H_2 plates obtained by Dieke with Hopfield's 50 cm vacuum spectrograph at the University of California. The quantum assignments in the present paper were made entirely independent of their work. Data from their work have been used, with other data available, in calculating the moment of inertia of the molecule in the normal state.

Two brief accounts of the preliminary work on the B-A bands have been published in short articles to Nature.[16,17]

The vibrational analysis as given by Dieke and Hopfield[1,2] serves as a starting point for this work. All results are given in terms of the old quantum theory unless specified otherwise.

Verification of combination principle.

The lines of the three possible branches, P, Q and R of the usual quantum theory are defined as follows[18]

$$R_J = F'_{J+1} - F_J'' \tag{1}$$

$$Q_J = F_J' - F_J'' \tag{2}$$

$$P_J = F'_{J-1} - F_J''. \tag{3}$$

The Q branch is not observed in the B-A bands. Kemble and Guillemin[13] have given as the theoretical reason for this that the B-A bands represent a transition from the $2^1\Sigma$ level to the $1^1\Sigma$ level.

From Eqs. (1) and (3) it follows[19]

$$R_J - P_J = F'_{J+1} - F'_{J-1} = 2\Delta F_J' \tag{4}$$

$$R_{J-1} - P_{J+1} = F''_{J+1} - F''_{J-1} = 2\Delta F_J''. \tag{5}$$

Eq. (4) shows that the values of $2\Delta F'_j$ may be obtained from any band if the R and P branches are known and the relative rotational quantum numbering of the lines has been found. The values of $2\Delta F_J'$ should be identical, within the limit of experimental error, for all bands of the A or n'' progression; that is, these values should be the same for all bands having the same upper level (B).

In the same manner, the values of $2\Delta F_J''$ should be the same for all bands having the same lower level. These facts are illustrated in Fig. 3.

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[15] Schaafsma and Dieke, Zeits. f. Physik **55**, 164 (1929).

[16] Hyman and Birge, Nature **123**, 277 (1929).

[17] Hyman and Jeppesen, Nature **125**, 462 (1930).

[18] R. T. Birge, Chapter 4, p. 144 of Report of Committee on Radiation in Gases, Molecular Spectra in Gases, Bulletin No. 57 of the National Research Council, (1926). This bulletin is referred to hereafter as the "Report." In general the nomenclature in this paper is that used in the Report.

[19] Report, p. 145.

The combination principle was first verified by choosing three bands such that two have the same B level and two the same A level, and finding differences between R and P lines such that equations (4) and (5) were satisfied.

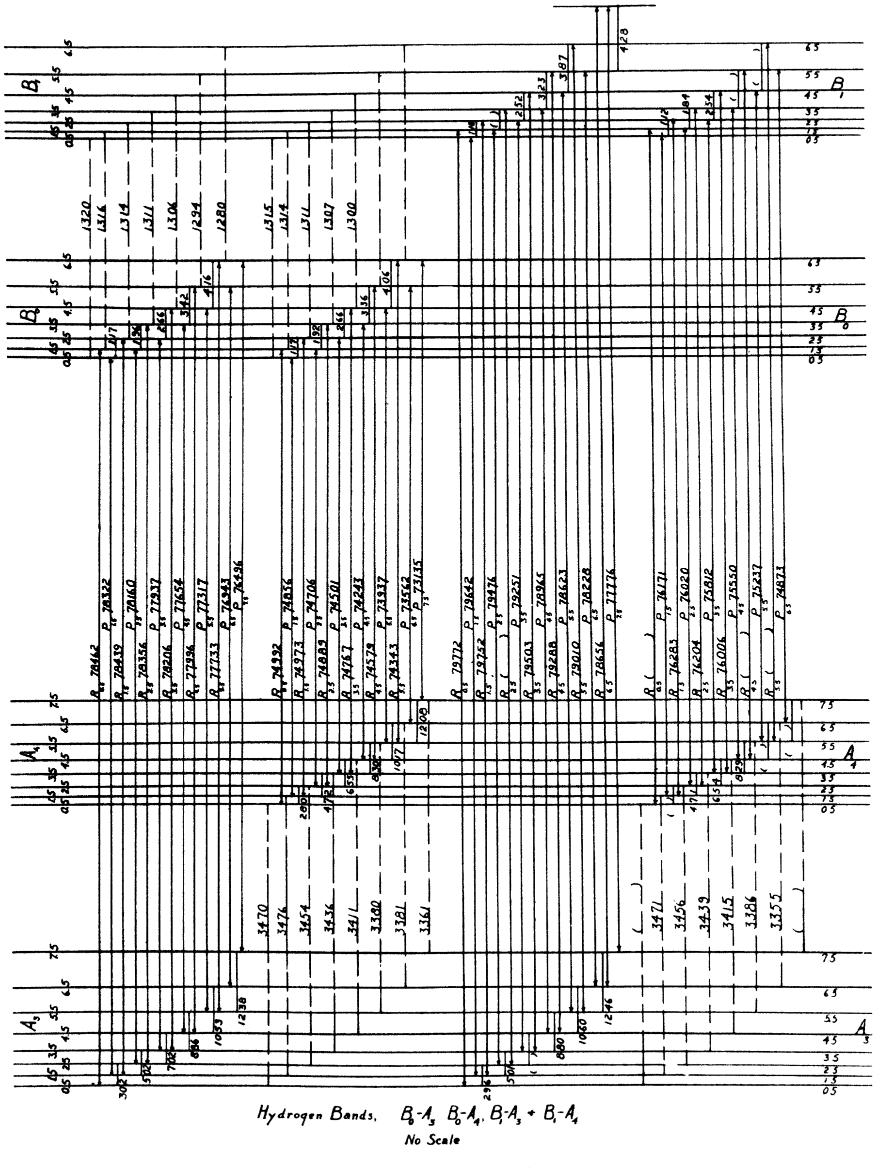

Fig. 3. Energy level diagram.

The vibrational analysis had been found by Dieke and Hopfield.[2] It was not necessary to know the true numbering of the lines in the bands. The method of obtaining this numbering will be explained later. The lines of the individual band were separated into R and P branches by the usual method of second differences.

After verifying the combination principle for these three bands, the work was extended to other bands. The results are collected in Tables I, III, and IV. Lines connected with sixty-eight bands were found. The results show alternating intensity of lines as is to be expected since the H_2 molecule is symmetrical.

TABLE III. *Average values of $2\Delta F'$.*

k	1.5	2.5	3.5	4.5	5.5	6.5
B_0	116.4	192.9	266.3	338	411	475
B_1	111	184	254	324	390	434
B_2	104	176	242	314	375	403
B_3	100	169	234	296	350	419
B_4	97	165	225	279	318	331
B_5	93	155	215	274	324	
B_6	93	146	208	246	315	
B_7	86	138	187	254	287	
B_8	85	146	197	242	312	
B_9	86	115	202	223		

TABLE IV. *Average values of $2\Delta F''$.*

k	1.5	2.5	3.5	4.5	5.5	6.5
A_3	295	502	702	881	1060	1249
A_4	285	475	652	830	1011	1217
A_5	268	445	617	780	923	
A_6	253	416	577	731	869	1033
A_7	230	386	533	679	802	896
A_8	214	364	493	607	755	
A_9	200	324	452	558	681	
A_{10}	175	289	400	500	581	694
A_{11}	169	260	341	426	501	558
A_{12}	148	271	335	414		

TABLE IVa. *Values of $2\Delta F''$ from Witmer and Hori.*

k	1.5	2.5	3.5	4.5	5.5
A_2(H)		529			
A_2 (W)	321	531			
A_1 (H)		557	764	991	1231
A_1 (W)	345	562			
A_0 (W)	356	588			

To find m, the effective rotational quantum number, the $2\Delta F'$ values are plotted and extrapolated to $\Delta F = 0$. m is now to be chosen so that ΔF equals zero when m equals zero and it is found that this condition is satisfied, at least to a close approximation, by assuming half integer values for m. Richardson and Davidson[11] referring to the lower level of bands analyzed by them, state "$m_0 = 0.50013$ and remains very close to $1/2$ throughout the vibrational levels." This level is now known to be identical with the B state as described in this paper.

Continuing the study of the B state later, it will be shown, by using the analytic method,[20] that the value of m is found to be a half-integer to

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[20] Report, p. 173.

within 0.005, that is,[21] α is zero or practically zero. At present we assume[22] $m=k=J-0.5$.

A second check on the assignment of the lines to the R and P branches was found by comparing the values[23] of $\omega_v(m)$ for the B level as obtained by using the different A vibrational states as the base level. In a similar manner, but using different B vibrational states as base levels the values of $\omega_v(m)$ for the A level were found. Tables V and VI give the average values found. In making these averages the numbers obtained from the differences of two frequencies neither of which was from blended lines were given weighted values. Fig. 3 also shows the values of $\omega_v(m)$. The numbers on this diagram are obtained by using P lines. Table V also gives (in parenthesis) the values as obtained by Richardson and Davidson[11] from their analysis of

TABLE V. *B-state. Average values of $\omega_v(m)$ (From both R and P lines). Values in parentheses are those obtained by Richardson and Davidson from bands in the visible.*

m	0.5	1.5	2.5	3.5	4.5	5.5	6.5
B_1-B_0	1318.5 (1318.345)	1315.8 (1316.41)	1312.4 (1312.55)	1307.0 (1306.94)	1300.6 (1299.68)	1289.8 (1290.99)	1279.9 (1280.94)
B_2-B_1	1282.0 (1281.475)	1280.0 (1279.84)	1276.7 (1276.6)	1272.1 (1271.815)	1265.7 (1265.59)	1260.0 (1258.04)	1245 (1249.32)
B_3-B_2	1244 (1246.71)	1244 (1245.25)	1240 (1242.38)	1238 (1238.12)	1234 (1232.61)	1223 (1225.89)	1217 (1218.02)
B_4-B_3	1214 (1213.015)	1212 (1211.76)	1211 (1209.06)	1207 (1205.17)	1200 (1200.10)	1196 (1193.86)	1190 (1186.75)
B_5-B_4	1179 (1179.95)	1180 (1178.77)	1176 (1176.33)	1174 (1172.74)	1167 (1168.03)	1164 (1162.25)	1160 (1155.5)
B_6-B_5	1147 (1147.50)	1152 (1146.32)	1145 (1144.00)	1140 (1140.64)	1139 (1136.15)	(1130.77)	(1124.8)
B_7-B_6	1115 (1115.5)	1112 (1114.32)	1112 (1112.04)	1105 (1108.7)	1102 (1104.3)		
B_8-B_7	1086	1080	1079 (1081.29)	1078–	1068	1071	
B_9-B_8	1052	1047	1038	1030	1028		

TABLE VI. *A-state. Averae values of $\omega_v(m)$.*

m	0.5	1.5	2.5	3.5	4.5	5.5
A_4-A_3	3470.0	3467.2	3454.7	3435.1	3413.5	3392
A_5-A_4	3241.5	3236.0	3223.5	3207.3	3184.5	3153
A_6-A_5	3012	3008.5	2995.8	2979.9	2956	2928
A_7-A_6	2785.3	2774.9	2753.7	2746.1	2720	2692
A_8-A_7	2543.7	2536.8	2524.5	2513	2513	2450
A_9-A_8	2288	2288	2265	2241	2202	
$A_{10}-A_9$	2029	2018	2006	1984	1956	1918
$A_{11}-A_{10}$	1726	1720	1715	1689	1659	1627
$A_{12}-A_{11}$	1423	1414	1380	1358	1324	1303

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[21] Report, p. 137 gives $m=J-\overset{*}{\epsilon}=J-0.5-\alpha=k-\alpha$, where J is an integer and k a half-integer. This is in terms of the old quantum theory as used in this paper. In the new mechanics J is one unit less.

[22] It is to be remembered that the value of $m-1/2$ is the value of J for the new mechanics.

[23] Report, p. 113.

bands in the visible. The Richardson and Davidson measurements are from plates taken using a larger grating and the bands measured are in the visible. Their values of $\omega_v(m)$ are presumably the more trustworthy. It is to be remembered that an error of one-tenth Angstrom in the ultraviolet region considered here represents an error of between six and nine frequency units.

The values of $\Delta F'$ as obtained from the rotational energy function[24] also agree almost identically with those obtained by Richardson and Davidson from their data. They give a value of D_0 (their C) smaller than the theoretical value. The D_0 used in the present report is found theoretically and represents the best known method for obtaining this constant, while Richardson and Davidson have obtained the value empirically. More will be said about these constants later.

Birge[10] in his summary of the quantum levels and resulting constants of the hydrogen molecule has taken the B state of the ultraviolet bands to be also the lower state of the Richardson "A" and "B" bands. This seemed justifiable at that time as the result of the close agreement of the vibrational data of Dieke and Hopfield[2] and of Richardson.[11]

The far more accurate data of the present work confirms the assumption beyond all doubt, since the agreement of the spacings of all levels, both vibrational and rotational, is within the very small limits of experimental error. This verification of the assumption by Birge leads to the conclusion that the ionization potential of H_2 must be 15.34 volts to within a few hundredths of a volt, as given by Birge at that time.

Mention has been made of the rotational energy function

$$F = B_0 m^2 + D_0 m^4 + F_0 m^6 + \cdots . \tag{6}$$

It is from this equation that the actual spacings of the rotational energy levels are found. The value of B_0 is inversely proportional to the moment of inertia for no vibration and infinitely slow rotation.

Birge, in the Report,[25], gives three methods of handling the data obtained. Method one is purely empirical and is not to be considered here.

Method two is a rapid semigraphical method for evaluating B_0.

From the rotational energy function, by assuming $m = k - \alpha$, one obtains, to a very close approximation when α is small.

$$\frac{\Delta F}{k} = 2B_0 - \frac{2B_0\alpha}{k} + 4D_0k^2 + 6F_0k^4. \tag{7}$$

In the present work α is zero, or at least very small. If we assume the value of F_0 to be small[26] we have

$$\frac{2\Delta F}{k} = 4B_0 + 8D_0k^2. \tag{8}$$

This equation represents a parabola with the vertex at $k = 0$.

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[24] Report, p. 141.

[25] Report, pp. 169–173.

[26] Richardson and Davidson gave α equal to 0.0013, $F_0 = 1.3 \times 10^{-5}$.

The values of $2\Delta F/k$ for the B_0 state are

k	1.5	2.5	3.5	4.5
$\frac{2\Delta F}{k}$	77.60	77.16	76.09	75.11

These latter values were plotted against k and from this a fairly accurate value of $4B_0$ found directly.

D_0 is theoretically related to B_0 by the relation

$$D_0 = \frac{-\,4B_0{}^3}{\omega_0{}^2}\cdot \tag{9}$$

ω_0 is found by double extrapolation of the values of $\omega_v(m)$ to find the value of $\omega_0(0)$.

The final result of this extrapolation is that $\omega_0(0) = 1337.82$ cm^{-1}.

Method three is strictly analytic and is the most accurate method of handling the data.

From the rotational energy function the following result is obtained, where $m = k - \alpha$

$$2\Delta \overset{*}{F} = 2\Delta F - 8D_0k^3 - 12F_0k^5 - 16H_0k^7 = (4B_0 + 8D_0)(k - \alpha) \tag{10}$$

if the values of F_0 and H_0 are zero.

The value of $2\Delta \overset{*}{F}$ may be called the reduced value of $2\Delta F$. The values of $2\Delta F$ are found directly. Values of F_0 and H_0 are assumed to be equal to zero. The value, $D_0 = -0.01647$, is found by using the approximate value of B_0(19.46 cm^{-1}) found by method two in the theoretical Eq. (9).

In the equation $2\Delta \overset{*}{F} = 2\Delta F - 8D_0k^3$ the following values are found:

$2\Delta F$	k	$8 - D_0k^3$	$2\Delta \overset{*}{F}$
116.4	1.5	0.4447	116.845
192.9	2.5	2.059	194.959
266.3	3.5	5.649	271.949
338.0	4.5	12.007	350.009

The plot of $2\Delta \overset{*}{F}$ against k is a straight line, as predicted by the above theory.

The least squares solution of the equation

$$2\Delta \overset{*}{F} = (4B_0 + 8D_0)(k - \alpha) \tag{11}$$

accordingly gives the most probable values of B_0 and of α.

The solution gives

$$B_0 = 19.445 \text{ cm}^{-1};\quad \alpha = -\,0.005 \text{ cm}^{-1}.$$

It is believed B_0 has a true probable error not exceeding one part in one thousand. The probable error in α is such that the true value may be zero.

Richardson and Davidson have found $B_0 = 19.455_5$.

The moment of inertia is found from the relation

$$I_0 = \frac{h}{8\pi^2 B_0 c} = \frac{27.66 \times 10^{-40}}{B_0} \text{g cm}^2 \qquad (12)$$

$$= (1.4225 \pm 0.003) \times 10^{-40} \text{g cm}^2.$$

The error in B_0 is also to be found in the value of the moment of inertia. In addition there is a small probable error in the constant[27] 27.66×10^{-40}.

The nuclear separation r_0, in centimeters, is given by the relation

$$r_0 = (I_0/\mu)^{1/2} \qquad \text{where}$$

$$\mu = 1.6490 \times 10^{-24} \frac{m_1 m_2}{m_1 + m_2} \qquad \text{and}$$

m_1 and m_2 are the atomic weights of the two atoms.[28]

The resulting value for the nuclear separation is

$$1.3084 \times 10^{-8} \text{ cm}.$$

The rotational energy function becomes

$$F = 19.445 m^2 - 0.01647 m^4 \qquad (14)$$

$$m = \tfrac{1}{2},\ 1\tfrac{1}{2},\ 2\tfrac{1}{2} \text{ etc.}$$

The following is a comparison of the values of F obtained with those given by Richardson and Davidson:

Richardson and Davidson from bands in visible	$B-A$ bands found in ultraviolet
(cm^{-1})	(cm^{-1})
38.85	38.81
77.30	77.22
115.06	114.85
151.685	151.06
186.955	186.13

In the solution, Richardson and Davidson have used $D = -0.0152$ cm^{-1} instead of -0.01647.

Constants for the normal level.

The evaluation of the moment of inertia of H_2, for the normal electronic level, has been carried out with the cooperation of Mr. C. Rulon Jeppesen, and the results have been reported briefly.[17] In this case the values of $2\Delta F''$, as given in Table IV, begin at the vibrational level $v = 3$. For $v = 0$, 1, and 2, the less accurate and extensive data of Hori,[8] and Witmer,[6] were used. These

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[27] Birge, Phys. Rev. Supplement **1**, 63 (1929) gives

$$h/8\pi^2 c = (27.65_{83} \pm 0.04) \times 10^{-40} \text{g cm}. \qquad (13)$$

[28] Constants used are those given by Birge, reference 27.

data are listed in Table IVa. In order to obtain the best possible value of I_0, data from all available sources were correlated and averaged. These sources include Schaafsma and Dieke,[15] in addition to those already quoted.

The various values of $2\Delta F/k$, resulting from the observations of the different observers, were plotted against k, on a large scale. In this case Eq. (7) becomes

$$\frac{2\Delta F_v}{k} = 4B_v + 8D_v k^2 + 12F_v k^4 \tag{15}$$

and the resulting curve, for each value of v, should be approximately a parabola with its vertex at $k=0$. Smooth curves were drawn through the plotted points, so as to satisfy, roughly, the form of Eq. (15). From these curves we obtain first approximate values of $4B_v$. These values were then plotted against v, and found to form a reasonably smooth curve. What appeared to be the best smooth curve was then drawn, and from— this, smoothed values of $4B_v$ were obtained. These smoothed values were now used to calculate theoretical values of D_v, using the theoretical relation[29]

$$D_v = D_e - \beta(v + \tfrac{1}{2}) \tag{16}$$

where[30]

$$\frac{\beta}{D_e} = -\frac{\omega_e}{24B_e}\left(\frac{\alpha}{B_e}\right)^2 - 5\left(\frac{\alpha}{B_e}\right) + 8x_e. \tag{17}$$

The value of $\omega_e(4368.6\ \mathrm{cm}^{-1})$ was obtained from a smooth curve, using data by Witmer.[6] Still later work[31] has led to 4371 cm^{-1} as the best value of ω_e, but the change is immaterial in connection with β. For B_e we used 60.16 cm^{-1}, as obtained by extrapolating our smooth $B_v{:}v$ curve to $v = -\frac{1}{2}$. The slope of this curve, at $v = -\frac{1}{2}$, gives the value of α (2.68 cm^{-1}).

We could now calculate theoretical values of $8D_v k^2$, in Eq. (15). In order to calculate the final term in Eq. (15), we assumed[32] that

$$F_v = F_e = \frac{D_e^2}{B_e}\left(2 - \frac{\alpha\omega_e}{6B_e^2}\right) \tag{18}$$

The true theoretical expression for F_v, as a function of v, has not yet been derived, but the last term in Eq. (15) is so small that any change of F_v with v is immaterial, for not too large values of k.

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[29] In this case, the new mechanics relations have been used. In equations like (9), one *should* use D_e, B_e, and ω_e (values for $v = -1/2$) in place of D_0, B_0, and ω_0, but numerically the change is insignificant.

[30] This theoretical expression for β/D_e is equivalent to that given by Pomeroy (Phys. Rev. **29**, 59 (1927)), but is much simpler in actual use. It was suggested to us by Professor R. T. Birge.

[31] R. T. Birge and C. R. Jeppesen, Nature **125**, 463 (1930).

[32] Compare "Report," p. 237, Eq. (198).

With these calculated values of D_v and F_v, we now obtained a value of $4B_v$ from selected points on the $2\Delta F_v/k$:k curve, using Eq. (15). A weighted average of the resulting values of $4B_v$, for each value of v, was thus obtained. This process is equivalent to drawing a smooth curve through the plotted $2\Delta F_v/k$ points, having the theoretical *shape*, leaving only the constant term to be evaluated. Such curves, as actually drawn, were found to be quite as satisfactory as the original empirical curves. This is a most gratifying verification of theory, since the "distortion" of the H_2 molecule, with both rotation and vibration, is relatively large.

The new values of B_v were again plotted against v, and found to lie much more closely on a smooth curve than the original approximate values. The changes were, however, so small that it was deemed unnecessary to calculate *new* theoretical values of D_v (method of successive approximations). Since we had used the *finite* differences $2\Delta F_v$, the value of the constant term in Eq. (15) is, strictly, not $4B_v$, but[33] $4B_v+8D_v$. The final smoothed values of B_v, obtained after this correction, are given in Table VII. They were then fitted, by least squares, to a third degree rational integral function, the result being

$$\begin{aligned} B_v = {} & 60.587 - 2.7938(v+\tfrac{1}{2}) + 1.0500 \times 10^{-2}(v+\tfrac{1}{2})^2 \\ & - 24.058 \times 10^{-4}(v+\tfrac{1}{2})^3. \end{aligned} \tag{19}$$

TABLE VII.

v''	B_v'' smoothed observed values	B_v'' calc. values
0	59.19	59.192
1	56.415	56.411
2	53.63	53.630
3	50.835	50.834
4	48.01	48.008
5	45.14	45.138
6	42.20	42.210
7	39.20	39.209
8	36.145	36.120
9	32.92	32.930
10	29.52	29.624
11	25.39	26.187
12	20.565	22.606

The calculated values, according to Eq. (19), are also given in Table VII. In this equation, the absolute term gives the value B_e for the hypothetical state of zero vibration ($v=-1/2$), according to the new mechanics. It corresponds to $I_e=0.4565\times10^{-40}$ g cm^2 and $r_e=0.7412\times10^{-8}$ cm. This is quite different[34] from Hori's value of $I_e=0.467\times10^{-40}$. The value of B_0.

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[33] See Eq. (145), p. 174 of "Report."

[34] See reference 17 for a discussion of this point.

corresponding to $v=0$, is 59.192 cm^{-1}, giving $I_0=0.4675\times10^{-40}$, $r_0=0.7500\times10^{-8}$. These latter are the constants for the actual normal level of hydrogen.

As already noted, accurate data for $2\Delta F''$ values extend only from $v=3$ to 12, inclusive (Table IV). As can be seen from Table VII, Eq. (19) fits the data in a satisfactory manner only up to $v=9$. In fact, the B_v values for $v=10$, 11, 12, were not used in obtaining this equation, since they deviate sharply from any smooth curve. These higher values of v are close to dissociation, and the fact that the corresponding moments of inertia are appreciably larger than those given by the equation is not surprising.

The values of B_0, B_1, and B_2 are not so trustworthy, but they do, perhaps accidentally, fit in very well with the values B_3 to B_9. It would therefore appear that our final value of B_0 is reliable to about 0.2 percent. After this work was completed, Birge and Jeppesen[31] calculated accurate values of B_0 and B_1, from Rasetti's data[35] on the Raman effect in gaseous hydrogen. Their value of B_1 (56.4035 cm^{-1}) is in remarkable agreement with our value of 56.411 cm^{-1}, as given by Eq. (19), but their value of B_0 (59.354 cm^{-1}) is 0.27 percent greater than our value of 59.192 cm^{-1}. This discrepancy points to a real irregularity in the moment of inertia of hydrogen in the $v=0$ state, as discussed by Birge and Jeppesen. They discuss also an apparent irregularity in the frequency of vibration for this same level.

The final conclusion is then that Eq. (19), or Table VII, last column, gives reliable values of B_v'' from $v=1$ to 9 inclusive, but that the true value of B_0 is that given by Birge and Jeppesen, namely $B_0=59.354$ cm^{-1}, corresponding to $I_0=0.4660\times10^{-40}$ g cm,^{2} and $r_0=0.7489\times10^{-8}$ cm^{-1}. Because of the irregularity in the value of B_0, it is impossible to give a reliable value of B_e, but it seems best, in calculating theoretical values of D_e and other derived constants, to use the value given by Eq. (19).

The experimental work and part of the theoretical work, of this investigation, were carried out at the University of California and the writer wishes to express his sincere thanks to Professor R. T. Birge of the University of California not only for the very obliging and valuable assistance that was given while the writer was at the University of California but also for the interest and advice he has given during the past year. He is also indebted to Mr. C. R. Jeppesen for his help in deriving the constants for the normal level.

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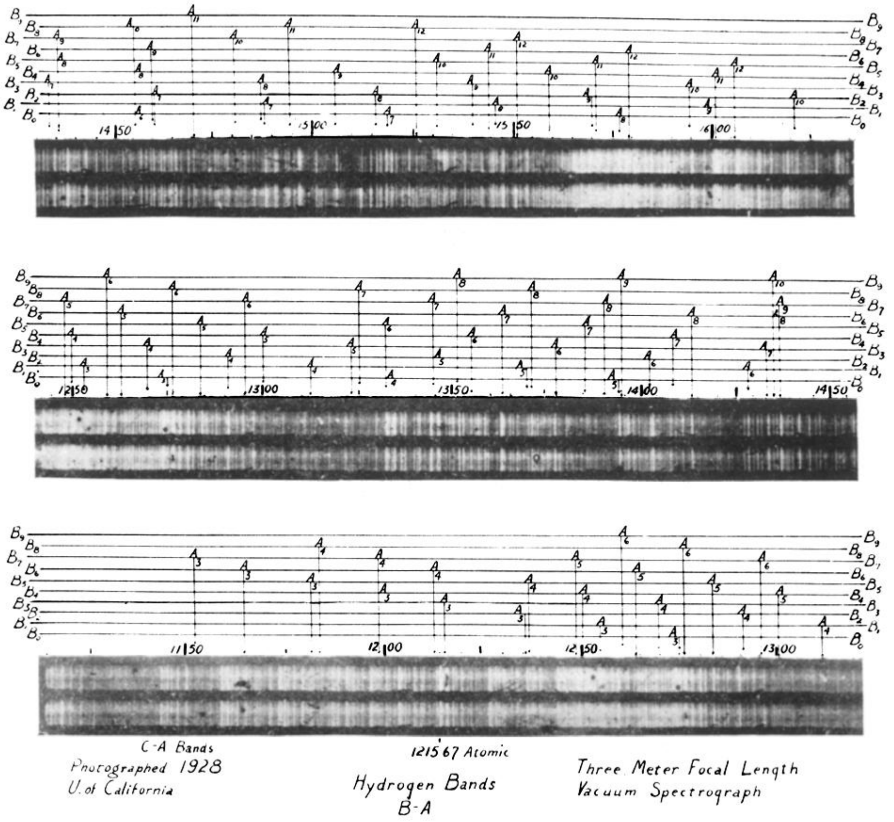
[35] F. Rasetti, Phys. Rev. **34**, 367 (1929).

14|50
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13|00
C-A Bands
Photographed 1928
U. of California
1215.67 Atomic
Hydrogen Bands
B-A
Three Meter Focal Length
Vacuum Spectrograph

Fig. 2.