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The $2s\ {}^1\Sigma \rightarrow 2p\ {}^1\Sigma$ Bands of the Hydrogen Molecule

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The so-called ${}^1X \rightarrow 2p\ {}^1\Sigma$ bands of H_2 have been considerably extended and the analogous systems of HD and D_2 discovered. The discovery of the new bands shows that the properties of the upper level of these bands are considerably different from those assumed until now, and the new facts allow a quite unambiguous identification of this level as $2s\ {}^1\Sigma$. This state has an equilibrium distance of $1.0087 \cdot 10^{-8}$ cm slightly greater than the corresponding triplet level and is slightly less firmly bound. For the estimate of the significance and accuracy of the various constants the comparison of the three isotopic molecules is of great help. The $2s\ {}^1\Sigma$ state shows marked class *B* perturbations and the perturbing state is very probably $(2p\sigma)^2\ {}^1\Sigma$ which should lie roughly 3500 cm^{-1} above $2s\ {}^1\Sigma$. This would explain also the fact that the $2s\ {}^3\Sigma$ state does not show any perturbations.

§ 1. INTRODUCTION

THERE is a band system in the infrared part of the spectrum of the hydrogen molecule discovered by Richardson and Davidson[1] which is of especial interest from several points of view. The lower state of this system is the well-known level $2p\ {}^1\Sigma$ which is the initial state of one of the systems in the vacuum ultraviolet and the final state of the extensive and strong singlet systems found in the visible part of the spectrum. The initial state called ${}^1X$ by Richardson is much lower than any of the other initial levels of the visible bands. For this reason its interpretation should be comparatively simple. For there is only a small number of levels of such low energy possible and they should have rather simple properties. This is quite different from the situation for the higher states where many levels lying very closely together give rise to complicated interactions. Accordingly the interpretation of such highly excited levels must be expected to present great difficulties, and, as is well known, there are a great number of the levels found empirically by Richardson and his co-workers which have not yet been classified satisfactorily.

The surprising fact about the ${}^1X$ level is that it does not at all behave as one should expect at first hand for such a low lying level. If one restricts oneself to states for which only one of the two electrons is excited, the only possible theoretical level with which ${}^1X$ can be identified is $2s\ {}^1\Sigma$.[2] Weizel[3] emphasized the difficulties connected with this identification and proposed to identify the ${}^1X$ state with $(2p\sigma)^2\ {}^1\Sigma$, a state thus for which both electrons are excited. There were, however, also difficulties to this point of view, and Richardson[4] favored $2s\ {}^1\Sigma$ notwithstanding the objections which might be raised. The difficulties are of the following nature. The ${}^1X$ level shows strong irregularities which might be either due to uncoupling as in most of the other hydrogen levels or to some other kind of perturbation. Uncoupling for $2s\ {}^1\Sigma$ is out of the question, as that phenomenon is produced by the interaction with a level which differs only by the value of the quantum number Λ and such a level cannot exist for an *s* electron. Some other kind of perturbation would necessitate the presence of another level close to $2s\ {}^1\Sigma$ and, as Richardson points out, there does not seem to be any room for such a level in the energy level scheme of the hydrogen molecule. Another difficulty is that the moment of inertia calculated from Richardson and Davidson's bands is much larger than should be expected for the $2s\ {}^1\Sigma$ state. (This was one of Weizel's chief arguments in favor of his interpretation.) A further circumstance which made a definite decision difficult was the fact that the exact location of the electronic level was very uncertain. The reason for this was that there was no way of finding out whether Richardson's assignment of vibrational quantum numbers was correct or not,

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[1] O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A124**, 81 (1929). Some of the bands were also given simultaneously in a slightly different arrangement by Finkelnburg and Mecke (Zeits. f. Physik **54**, 597 (1929)). All the data are also found in Richardson, *Molecular Hydrogen and Its Spectrum* (Yale University Press, 1934).

[2] G. H. Dieke, Zeits. f. Physik **55**, 447 (1929).

[3] W. Weizel, Zeits. f. Physik **65**, 456 (1930).

[4] Richardson, *Molecular Hydrogen and Its Spectrum*, p. 308.

TABLE I. *The 2s* $^1\Sigma \rightarrow 2p\,^1\Sigma$ *bands of* H_2.

J	*P* branch			*R* branch	
	ν	*I*		ν	*I*
	0→0				
0	—	—		9 024.68	5
1	8 922.38	3		112.16	4
2	908.51	5		223.06	7
3	919.82	3		356.57	3
4	956.37	5		511.82	6
5	9 017.90	5	blend	687.71	1
6	104.22	4			
7	214.74	1			
8	348.80	1			
9	505.49	00*d*			
	1→0				
0	—	—		11 350.51	9*b*
1	11 250.34	4		429.32	8
2	234.37	9		529.75	10*b*
3	236.99	7		646.32	6
4	263.11	10*b*		780.85	8
5	307.67	5		919.60	5
6	373.17	6			
7	447.78	1			
	2→0				
0	—	—		13 402.09	10*b*
1	13 317.22	10		447.76	10
2	285.91	10*b*		470.33	10
3	255.43	10			
4	203.59	10			
	2→1				
0	—	—		12 083.82	10*b*
1	12 000.89	9		131.44	7
2	11 973.41	10		157.81	9
3	948.54	8			
4	903.93	9			
	2→2				
0	—	—		10 802.36	1
1	10 721.05	0		851.72	0
2	696.83	4		881.21	0
3					
4	638.35	0*d*			
	3→0				
0	—	—		15 211.79	6
1	15 142.64	7			
2	095.67	8		237.22	?
3	039.34	5			
4	14 970.53	6			
	3→1				
0	—	—		13 893.44	10
1	13 826.20	10		915.23	9
2	783.00	10		924.66	10
3	732.32	10			
4	670.75	10			
	3→2				
0	—	—		12 611.92	1
1	12 546.36	0		635.39	1
2	506.50	4		648.03	2
3	460.55	2*c*			
4	405.23	2			
	3→3				
0	—	—		11 365.27	5
1	11 301.11	4		390.16	3
2	264.10	5		405.66	4
3	222.43	4			
4	172.64	4			
	4→1				
0	—	—		15 927.80	4
1	15 867.12	3		937.80	2
2	817.47	5		933.16	3
3	754.91	5		912.62	1
4	679.29	5			
5	590.02	1			
	4→2				
0	—	—		14 646.38	5
1	14 587.32	4		658.02	4
2	540.88	8*r*		656.59	6
3	483.16	5		640.91	4
4	413.75	9			
5	331.98	4			
	4→3				
0	—	—		13 399.61	4
1	13 342.00	1		412.70	2
2	298.34	7		414.14	9
3	244.94	3		402.76	0
4	181.28	10	blend		
	4→4				
0	—	—		12 186.60	4
1	12 130.38	1		201.03	1
2	089.44	4		205.08	3
3	039.86	1*c*		197.55	0
4	11 980.98	3			
5	912.22	0			
	4→5				
0	—	—		11 006.61	00
1	10 951.68	1			
2	913.07	5		028.78	00
3	867.07	3			
4	813.00	3			
5	749.89	2			

in other words, whether what according to Richardson's numbering should be the vibrationless electronic state had not perhaps several quanta of vibrational energy. In that case there should be additional bands in the hitherto photographically inaccessible infrared, and the position of the ^1X level would have to be lowered by several thousand wave numbers.

With this state of affairs it seemed desirable to see whether an investigation of the HD and D_2

TABLE II. *The* $2s\,^1\Sigma \rightarrow 2p\,^1\Sigma$ *bands of HD.*

J	ν (*P* branch)	I (*P* branch)		ν (*R* branch)	I (*R* branch)	
			0→0			
0	—	—		8 949.49	0	
1	8 872.37	0		9 015.49	2	
2	861.73	0		099.24	3	
3	869.86	1		200.34	3	
4	896.80	3	$+D_2$	318.29	0	
5	942.59	1		452.55	0	
6	9 006.99	1				
7	089.80	1				
8	190.64	0	?			
			1→0			
0	—	—		10 988.26	3	
1	10 913.66	3		11 049.10	5	
2	900.44	4		125.10	6	
3	903.43	5		216.06	6	
4	922.67	5		321.18	6	
5	958.29	4	$+H_2$	439.87	5*c*	
6	11 009.87	4		571.67	5	
7	077.15	4				
8	159.77	3				
9	257.11	00				
			2→0			
0	—	—		12 862.28	6	
1	12 791.84	7		913.96	7	
2	774.47	9		971.14	2	
3	768.10	10	$+D_2$			
4	768.80	4				
			2→1			
0	—	—		11 714.25	5	$+H_2$
1	11 645.87	5		767.96	7	
2	631.03	7		827.76	3	
3	628.65	7				
4	634.01	4				
			2→2			
0	—	—				
1	10 527.87	0		10 595.93	0	
2	515.27	1		649.95	0	
3	516.09	2				

spectra would not overcome the difficulties mentioned above. Since the early studies on the spectra of isotopic molecules, it has been known that any ambiguity in the assignment of vibrational quantum numbers can be removed if two or more isotopic forms of the same molecule are available. The results obtained with other band systems of H_2, HD, and D_2 seemed to make it rather probable that a study of the $^1X \rightarrow 2p\,^1\Sigma$ bands of HD and D_2 would also lead to a solution of the other difficulties. It was fortunate that in the meantime the new plates had become available which allowed the photography of the spectrum beyond 10,000A. This allowed a direct check of some of the results obtained. It will be seen that all the results support the identification of the initial state of the bands with $2s\,^1\Sigma$.

§ 2. EXPERIMENTAL PROCEDURE

The procedure for obtaining and measuring the plates was essentially the same as described previously.[5] In collaboration with Drs. C. R. Jeppesen and D. H. Rank the spectrum was extended to about 11,700A. Details of these measurements will be published shortly. A part of the wave numbers given in the subsequent tables is subject to small systematic corrections of a few hundredths of a cm^{-1}. The writer is at present engaged in a complete revision of the entire wave-length material, and different parts of the spectrum are at present at different stages of completion. The corrections are of such a nature that they will affect only inappreciably or not at all the values of the constants given in this paper.

Tables I–III give the wave numbers and intensities of the bands in question for H_2, HD and D_2. It will be seen that the data are most complete for D_2. That is partly due to the fact that because of the larger moment of inertia of D_2, the bands will be better developed so that the lines go to higher values of J. Also, in general, it can be expected that there will be more bands in a given system. In our particular case more care has been taken to obtain plates of great intensity for D_2 than for H_2. For HD it is in general more difficult to obtain as complete data, as the HD spectrum cannot be obtained without the lines of H_2 and D_2 being present at the same time and confusing the HD spectrum.

For H_2 the 2→0, 2→1, 3→0, 3→1, and 3→2 bands agree with Richardson's analysis except that Richardson's values of OV' are raised by one. Richardson gives some lines with higher J values than those included in the table, but their reality seems doubtful, and therefore they have been omitted. I have some alternative lines to

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

TABLE III. *The 2s* $^1\Sigma \rightarrow 2p\,^1\Sigma$ *bands of* D_2.

J	*P* branch			*R* branch		
	ν	*I*		ν	*I*	
	0→0					
0	—	—		8 859.83	00*d*	
1	8 808.23	00		904.24	1	
2	800.96	0		960.53	1	
3	806.16	1		9 028.67	3	
4	823.91	0*d*		108.44	2	+HD
5	854.06	1		199.45	2	
6	896.78	2	+HD	301.61	0	
7	951.73	1		414.60	1	
8	9 018.92	0		414.60		
9	098.19	0*d*				
	1→0					
0	—	—		10 546.91	5	
1	10 496.50	5		588.40	7	
2	487.85	5		640.59	5	
3	490.30	7		703.23	7*b*	
4	503.90	6	blend	776.02	4*b*	
5	528.65	7		859.03	6	
6	564.33	4		951.70	4	
7	611.34	7		11 053.82	5	
8	669.05	4		164.96	3	
9	737.48	5		284.		
10	816.28	6				
11	905.38	3				
	1→1					
0	—	—				
1	9 554.83	1		9 646.75	00	
2	547.64	0			*c*	
3	552.24	2		765.23	2	
4	568.65	1		841.11	0	
5	596.86	2		927.35	1	
6	636.67	00*d*		023.92	0	
7	688.15	2		130.56	1	
8	750.95	0				
	2→0					
0	—	—		12 137.31	4	
1	12 088.46	6		175.71	6	
2	078.25	6		223.21	6	
3	077.59	7		279.44	7	
4	086.51	6		340.76	3	
5	104.88	7		418.44	5	
6	129.13	3				
7	170.73	5				
	2→1					
0	—	—		11 195.02	2	
1	11 146.89	3		234.15	3	
2	138.10	3		283.06	2	
3	139.45	5*b*		341.47	4	
4	151.33	3		405.61	3	
5	173.12	4		486.72	4	
6	201.43	2				
7	247.57	2				
	2→2					
0	—	—		10 272.12	3	
1	10 224.61	5		311.86	5	
2	217.10	4		362.05	4	
3	220.46	6		422.32	4	
4	234.62	4		488.94	1	
5	259.44	5		573.03	4	
6	291.25	1				
7	341.47	4				
	2→3					
0	—	—				
1	9 320.54	00		9 407.63	00	
2				458.99	0	
3	319.34	2	blend?	521.05	0	
4	335.49	00*d*		589.81	0	
5	363.07	0		676.89	0	
6	398.12	1				
7	451.90	0				
	3→0					
0	—	—		13 589.02	2	
1	13 543.44	4		620.60	4	
2	529.95	3		656.66	3	
3	522.53	10		693.71	4	
4	520.06	9*c*				
5	519.17	9*c*				
	3→1					
0	—	—		12 646.71	3	
1	12 601.83	8		679.01	7	
2	589.82	6		716.52	5	
3	584.47	7		755.73	5	
4	584.78	6				
5	587.37	7				
	3→2					
0	—	—				
1	11 679.83	0		756.69	(3*d*)	+HD
2				11 795.55	1	
3	665.10	4*c*	blend			
4						
5	673.76	1*d*				
	3→3					
0	—	—		10 819.21	2	
1	10 775.54	2		852.71	3	
2	765.99	5		892.61	1	
3	764.12	4		935.36	2	
4	769.08	2				
5	777.40	2				
	3→4					
0	—	—		9 932.11	00	
1	9 889.12	0		966.21	2	
2	880.24	1*v*		10 007.05	0	
3	880.24	1*v*		051.35	1	
4	887.12	0				
5	897.96	00				
	3→5					
0	—	—				
1	9 019.67	00*d*		9 096.64	00	
2						
3	012.95	00*d*		084.19	00	
	4→0					
0	—	—		14 950.72	1*b*	
1	14 878.80	0		929.27	1	
2	856.31	0		939.54	00	
3	831.14	1		944.72	1*c*	
4	802.80	0				
5	770.07	0*c*				

TABLE III.—*Continued.*

J	ν	I	ν	I
	P branch		R branch	
		4→1		
0	—	—	13 973.04	2
1	13 937.13	4	987.65	5
2	916.10	2	999.36	3
3	893.11	5	006.64	5
4	867.60	3		
5	838.28	4		
		4→2		
0	—	—	13 050.10	2*d*
1	13 014.90	1	065.41	3*c*
2	12 995.16	1	078.40	1
3	974.02	3	087.53	2
4	950.96	2		
5	924.68	3		
		4→3		
0	—	—	12 145.51	1
1	12 110.82	2	161.32	2
2	092.22	2	175.45	0
3	072.73	3	186.28	1
4	051.94	2		
5	028.31	2		
		4→4		
0	—	—	11 254.12	0*d*
1	11 224.31	1	274.81	2
2	206.74	0		confused
3	188.79	3	302.31	3
4	169.97	2		
		4→5		
0	—	—	10 384.50	1
1	10 354.75	3	405.32	3
2	338.13	2	421.39	1
3	321.61	2	435.18	2
4	304.70	4		
5	285.95	3		

substitute for them, but they are not very satisfactory either and therefore are not included in the table. The bands with the initial vibrational quantum number 4 have been greatly extended. Of the 1→0 band Richardson gives only the pair $R0$ and $P2$. The 0→0 band lies in a region for which hitherto no measurements existed.[6] Naturally all the HD and D_2 bands are new.

§ 3. THE FINAL STATE $2p\,{}^1\Sigma$

We shall not discuss in this paper the properties of the final state of the bands. This state is also the final state of a number of other bands in the visible and it will be discussed together with those bands in another paper. When it was necessary to use the constants of that state as, e.g., for the calculation of the zero lines of the bands, use has been made of the results of the analysis of the $3d \rightarrow 2p\,{}^1\Sigma$ systems of HD and D_2 by M. Lewis and the author which will be published soon.

§ 4. THE VIBRATIONAL QUANTUM NUMBERS

If there are two isotopic molecules the correctness of the assignment of vibrational quantum numbers can be ascertained in a very simple way. If the electronic frequency of the band system is calculated it should have approximately the same value for the two molecules. If that is not the case the vibrational quantum numbers have to be adjusted in such a way that the changed new electronic frequencies satisfy the condition. If we use just the quadratic approximation $\omega(V+\frac{1}{2})-x(V+\frac{1}{2})^2$ for the vibrational energies of H_2 and D_2 we obtain the values 8368.6 and 8426.5 for the values of the electronic frequencies, which can be regarded as agreement in a case like ours. For the comparatively large discrepancy of about 58 cm^{-1} there are two reasons. In the first place in a molecule like the hydrogen molecule relatively large electronic shifts must be expected. The largest shift so far observed is 25.5 cm^{-1},[7] and it is likely that it is larger for our system. In the second place it is certain that the simple quadratic formula used to extrapolate to the electronic frequency is inadequate, but it is useless to try a more elaborate formula because of the irregularities in the initial state. Nevertheless the agreement can be regarded as conclusive proof for the correctness of the vibrational quantum numbers, as increasing the vibrational quantum numbers of the upper state by one[8] would produce a discrepancy of more than 900 cm^{-1}, in the electronic frequencies. Instead of comparing H_2 with D_2 we could just as well have compared HD with H_2 or D_2 with the same result.

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[6] Richardson (Nature **135**, 99 (1935)) announces the discovery of bands which have the $V=0$ level of ${}^1X$ as final state. Whether this level is identical with our $V=0$ or $V=1$ level cannot be ascertained from his description.

[7] G. H. Dieke, Phys. Rev. **47**, 661 (1935).

[8] Decreasing the vibrational quantum numbers is not possible because otherwise there would be no place for the bands around 8900 (0→0 bands with the correct numbering).

TABLE IV. *Rotational differences of the 2s* $^1\Sigma$ *level.*
$R(J)-P(J)$

$J \diagdown V$	0	1	2	3	4
			H_2		
1	189.76	178.98	130.54	89.04	70.68
2	314.55	295.38	184.41	141.54	115.70
3	436.47	409.33			157.72
4	555.45	517.74			
5	669.81	611.93			
			HD		
1	143.12	135.44	122.11		
2	237.51	224.66	196.70		
3	330.48	312.63			
4	421.49	398.51			
5	509.96	481.58			
6		561.80			
			D_2		
1	96.01	91.91	87.25	77.17	50.50
2	159.57	152.73	144.96	126.70	83.24
3	222.52	212.93	201.85	171.22	113.54
4	284.59*	272.31	254.30		
5	345.13	330.41	313.58		
6	404.86	387.37			
7	462.90	442.44			
8		495.91			

§ 5. ROTATIONAL STRUCTURE OF 2s $^1\Sigma$

Table IV gives the rotational differences $R(J)-P(J)=F(J+1)-F(J-1)$ of the upper level. These values can be used to represent the rotational levels by the usual formula

$$F_V(J)=B_VJ(J+1)-D_VJ(J+1). \quad (1)$$

It is found that this formula is quite adequate for the lowest values of the vibrational quantum number V, but that for the higher values of V there are marked deviations from the regular formula. The rotational constants are collected in Table V. Those values for which the formula is inadequate are marked by an asterisk. They were calculated from the first *two* differences of Table IV only and cannot be regarded as having much significance. The others were calculated by a least-square formula from the first *three* differences.

The most striking feature about the constants in Table V is the rapid decrease of the value of B_V with the vibrational quantum number. The decrease is too irregular to be represented by the usual formula

$$B_V=B_e-\alpha(V+\tfrac{1}{2})+\beta(V+\tfrac{1}{2})^2. \quad (2)$$

As the rapid decrease of B_V and its irregularity are obviously connected with the perturbations, and the $V=0$ and $V=1$ level are practically free of them, we can apply the above formula, with neglect of β to B_0 and B_1 and calculate an approximate value of B_e. The values so obtained and the moments of inertia I calculated from them are

	H_2	HD	D_2
B_e	32.679	24.568	16.373
$I\cdot 10^{40}$	0.8464	1.1258	1.6892

The values for D_2 are probably most reliable, as it is less affected by the perturbations than the two other molecules and also the formulas used are a better approximation. The value of the equilibrium distance is found to be $r_e=1.0087\cdot 10^{-8}$ cm. That this value and the values of B_e from which it is derived are not far from the correct ones can be ascertained by a comparison of the three isotopic molecules. The ratios of the B_e values are

	HD : H_2	D_2 : H_2	D_2 : HD
empirical	0.7517	0.5010	0.6664
theoretical	0.7502	0.5005	0.6671

The discrepancies between the empirical and the theoretical ratios are small and of the same order of magnitude as for other states of the hydrogen molecule.[5]

The values of D_0 are of the right order of magnitude which can be seen again by observing that the isotopic ratios have about the correct values. The empirical ratios 0.556, 0.233, 0.419 are all slightly smaller than the theoretical values 0.563, 0.250, 0.445. This means that the values for the lighter molecules are too big in proportion and is an indication that the per-

TABLE V. *2s* $^1\Sigma$. *Rotational constants.*

$V=$	0	1	2	3	4
H_2 B_V	31.770	29.952*	24.23*	15.35*	11.930
D_V	0.0228	0.0277*	0.414*	0.086*	0.0256
HD B_V	23.924	22.636	20.863*		
D_V	0.0123	0.0118	0.085*		
D_2 B_V	16.032	15.350	14.583	13.01*	8.49*
D_V	0.0053	0.0054	0.0063	0.0240*	0.0116*

turbations which affect so strongly the higher vibrational levels have also a very slight influence on the $V=0$ level. The D_V values for the higher V are abnormally large, and, as mentioned before, this must not be taken that the actual D_V have these values but rather as an indication that the simple formula for the rotational energy breaks down. The value of D_V can be taken as a direct indication for the degree to which the level is perturbed.

§ 6. THE VIBRATIONAL CONSTANTS

Table VI gives the origins of all the bands found so far calculated in the usual way. The values marked by an * again refer to the perturbed bands. These latter values have been calculated from the $P(1)$ line only by adding to it the rotational energy $F(1)$ of the final state. Table VII gives the vibrational differences of the $2s\,^1\Sigma$ state. The vibrational differences of the $2s\,^3\Sigma$ state as a representative of a normal state are included in small print for comparison.

The table shows immediately the difference between the $2s\,^3\Sigma$ and the $2s\,^1\Sigma$ states. For the former the second differences are approximately constant and the small variations which do occur are very regular. For $2s\,^1\Sigma$, however, the second differences are very irregular, so that the formula

$$F_V=\omega(V+\tfrac{1}{2})-x(V+\tfrac{1}{2})^2+\cdots \tag{3}$$

for the vibrational energy is no more a good approximation. Nevertheless, for lack of anything better, we can use the formula to calculate from the first two differences the constants ω and x. The values for ω are 2588.9, 2204.4, and 1784.5, respectively, and the values for x are 130.5, 81.6 and 48.1. As could be expected the isotopic ratios show that the values of x must be considerably wrong and that the values of ω are less though quite appreciably affected.

		HD : H_2	D_2 : H_2	D_2 : HD
ω	empirical	0.8514	0.6893	0.8095
	theoretical	0.8662	0.7074	0.8168
x	empirical	0.625	0.369	0.590
	theoretical	0.750	0.501	0.667

The values of all these constants are too low, but the values for D_2 must be more nearly correct than those for the two other molecules.[9]

TABLE VI. *Origins of the $2s\,^1\Sigma\rightarrow 2p\,^1\Sigma$ bands.*

V'/V''	0	1	2	3	4	5
			H_2			
0	8 961.23					
1	11 289.19*					
2	13 356.07*	12 037.81*	10 756.33*			
3	15 181.49*	13 863.12*	12 581.64*	11 334.93*		
4		15 904.02	14 622.58	13 375.79	12 162.85	10 982.86
			HD			
0	8 901.72					
1	10 943.02					
2	12 821.18*	11 673.91*	10 554.86*			
3						
			D_2			
0	8 827.98					
1	10 516.22	9 573.86				
2	12 108.17	11 165.88	10 242.34	9 338.28		
3	13 563.16*	12 620.82*	(11 698.18*)	10 793.21*	9 906.22*	9 036.18*
4	14 898.52*	13 956.12*	13 033.25*	12 128.59*	11 241.60*	10 371.56*

TABLE VII. *First and second vibrational differences of $2s\,^1\Sigma$ and $2s\,^3\Sigma$.*

		H_2		HD		D_2	
	V	Δ_1	Δ_2	Δ_1	Δ_2	Δ_1	Δ_2
$2s\,^1\Sigma$	1	2 327.96		2 041.30		1 688.24	
			260.98		163.14		96.26
	2	2 066.98		1 878.16		1 591.98	
			241.64				137.01
	3	1 825.34				1 454.97	
			−215.56				119.64
	4	2 040.90				1 325.33	
$2s\,^3\Sigma$	1	2 524.35		2 202.75		1 814.97	
			136.03		102.72		69.15
	2	2 388.32		2 100.03		1 745.82	
			132.10		100.08		67.56
	3	2 256.12		1 999.95		1 678.26	
			129:22		97.92		66.18
	4	2 126.90		1 902.03		1 612.08	

The electronic frequencies of the bands systems have been discussed in § 4.

§ 7. THE PERTURBATIONS

It was mentioned in the introduction that there was considerable doubt whether the irregularities observed in many of the bands were due to decoupling or ordinary perturbations. This question can be answered now satisfactorily. If the irregularities were due to decoupling they should be the same or even larger for the $V=0$ level,

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[9] For this reason, if the exact value of, e.g., ω for H_2 is desired, it would be more nearly correct to take the D_2 value and multiply it with the correct isotopic factor than to use the value derived from the H_2 bands. This is true for most of the constants of the hydrogen molecule, and the cause is that all interactions which are usually difficult to express in a satisfactory formula are much less for D_2 than for the other two molecules.

TABLE VIII. *Differences between observed and calculated rotational 2s $^1\Sigma$ levels of D_2.*

	$J=0$	1	2	3	4	5	6	7
$V=0$	−0.04	0.01	−0.01	0.02	0.00	0.04	0.00	−0.04
1	0	.01	.00	.01	.04	−.05	.16	.39
2	0	−.01	−.02	.00	.01	−2.41	1.41	
3	0	−.19	−.28	.11	−.32			
4	0	−.11	−.12	.02	−.18			

whereas it was seen in § 5 that that level is perfectly normal. This shows that they must be produced by the accidental presence of another level in the vicinity of 2s $^1\Sigma$. Much can be learned of the nature of this level by a careful scrutiny of the perturbations. However, it is likely that bands coming from this perturbing level can be found empirically which will allow a much more thorough discussion of the perturbations and therefore only the most outstanding features of the perturbations will be mentioned now and the rest reserved for a future paper.

In order to give an idea of the kind and magnitude of the perturbations the differences between the observed rotational levels and those calculated by formula (1) are given for D_2 in Table VIII. The level $J=0$ is taken to be zero except for $V=0$ where it comes from an obviously poor line. The table shows that the agreement for $V=0$ is as good as can be expected. The discrepancy for $V=1$, $J=6$ and 7 may be the beginning of a weak perturbation or it may be due to the fact that the constants B and D do not have quite the correct values, as they were calculated from the first few rotational levels only. The first view is more likely correct as there is definitely a weak perturbation in the $V=1$ level of H_2. $V=2$ is quite regular up to $J=4$. $J=5$ and 6 however show marked perturbations. $V=3$ and 4 behave both very similarly. They show marked irregularities but the actual value of the perturbations must be larger than the values in the table as the constants were calculated so as to give as good an average fit of the rotational differences as possible and probably are very different from the unperturbed constants. The values for $J=5$ and 6 must be expected to be much more strongly perturbed, but unfortunately they have so far escaped discovery.

The $V=0$ level of H_2 is regular. The $V=1$ level seems to have a definite perturbation for small J. $V=2$ is very strongly irregular as indicated by the abnormally large value of D in Table V, the $V=3$ level less so, and the $V=4$ level seems again to be quite regular.

There are two types of perturbations which have widely different characteristics and causes.[10] Class A perturbations arise from the interaction between rotation and electronic motion, and therefore the nonrotating molecule cannot be perturbed. The two levels influencing each other have values of the quantum number Λ different by one.

On the other hand class B perturbations arise from the interaction of vibration and electronic motion, and the two levels perturbing each other must have the same value of Λ. In both cases the perturbations appear primarily as irregularities in the rotational structure, as the relative distance of the perturbing levels which enters quite prominently into the magnitude of the perturbations is dependent on the rotational quantum number.

We see immediately that the perturbations in our case must belong to class B. For the irregularities in the vibrational differences of Table VII shows that we have here vibrational perturbations, i.e., that even the rotationless molecule is affected, and this can happen only for class B. This is the first case of this type of perturbation in the hydrogen molecule. We know now that the level causing the perturbations must also be a $^1\Sigma$ level which must besides have the same symmetry properties as the 2s $^1\Sigma$ level.

All the perturbed vibrational levels are lower than their expected position except the $V=4$ level of H_2 which is higher. This means that the perturbing level must now lie below it. The perturbing level has probably a much larger moment of inertia than 2s $^1\Sigma$ and therefore no typical rotational perturbations can arise, which is just what is observed. However, the possibility that the $V=4$ vibrational level belongs perhaps to a different electronic state cannot be entirely disregarded. Further experimental evidence will clear up this point.

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[10] G. H. Dieke, Phys. Rev. **47**, 870 (1935); J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936).

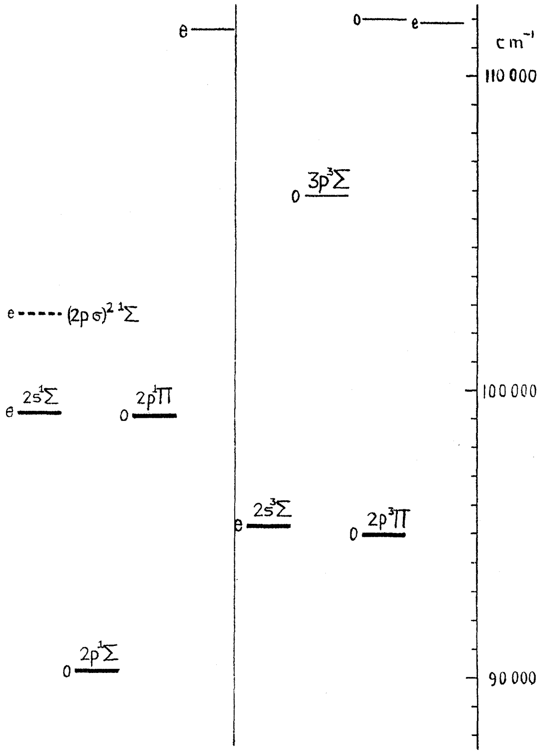

FIG. 1. The two quantum states of the hydrogen molecule. A few of the next higher levels are also given.

§ 8. THE NATURE OF THE UPPER STATE

If we review the facts presented in the preceding paragraphs we see that all the evidence against identifying the upper level of our bands with $2s\ {}^1\Sigma$ has disappeared. The internuclear distance $1.0087 \cdot 10^{-8}$ is only slightly larger than $0.9868 \cdot 10^{-8}$, that of $2s\ {}^3\Sigma$. The relative magnitudes of the vibrational constants of these two states shows that the binding of the singlet level is less strong than that of the triplet level which is undoubtedly due to the fact that the former is influenced by the perturbing level and takes some of its characteristics. Fig. 1 shows that the position of all the known two quantum levels. It is seen that the position of the $2s\ {}^1\Sigma$ level is just where it would be expected from analogy with the triplet system.

Finally there remains the identification of the perturbing level. From the facts of the preceding paragraph it follows that it must be a ${}^1\Sigma_g$ state, and there is no possibility for such a state with only one electron excited. We must therefore look for a state with two excited electrons and among these $(2p\sigma)^2\ {}^1\Sigma$ is the most probable one. All the arguments which Weizel[3] brought forward to show that this state can be expected to lie in the right region and to be a discrete state notwithstanding the fact that the $2p\sigma$ state of the H_2^+ ion is continuous still hold. The $2p\sigma$ state of the H_2^+ ion is for not too small internuclear distances a very low state. It is not discrete, however, but a continuous, repulsive state. This is not necessarily a difficulty, as the interaction energy of two such electrons might produce a minimum in the potential energy curve and give thus a discrete state. It must be assumed, that the equilibrium distance for such a state is quite large. Of course, none of these arguments are conclusive, and they make only plausible the existence of this state with the required properties. A more direct calculation would be highly desirable, but, unfortunately, is far from simple.

There is an additional argument in favor of $(2p\sigma)^2\ {}^1\Sigma$ as the perturbing state. All the electronic states of the hydrogen molecule occur in pairs, one each for the triplet and one for the singlet system, except when the two electrons have identical quantum numbers. In that case the triplet level is missing. The $2s\ {}^3\Sigma$ state which is the lower level of the Fulcher bands shows no trace of any perturbation whereas we have seen that the $2s\ {}^1\Sigma$ state is strongly perturbed. This difference in the behavior of the two analogous states is perfectly explained by the assumption that $(2p\sigma)^2\ {}^1\Sigma$ is the perturbing level. For there is no analogous level in the triplet system and therefore no possibility for any perturbations of $2s\ {}^3\Sigma$.

The position of the perturbing level can be roughly estimated from the character of the perturbations. It should be about 3 500 cm⁻¹ above the $2s\ {}^1\Sigma$ level although this figure is not very trustworthy as it involves several assumptions. In any case the $(2p\sigma)^2\ {}^1\Sigma$ state should lie in this general neighborhood.