(Eq. (55)), the function φ has a minimum at

$$r_{\min}=\tfrac{1}{2}De^{-\zeta}=0.216\times10^{-13}\text{ cm}, \tag{73}$$

where

$$\zeta=C+\tfrac{1}{2}f(0). \tag{73a}$$

The result(73) is about the Compton wave-length of the proton, $\hbar/Mc$. At its minimum, φ has the value

$$\varphi_{\min}=1-e^{-\zeta}=0.9925, \tag{73b}$$

which is very close to unity.

The two functions φ and ψ are very close together for all values of r inside the range of the nuclear forces. Neglecting higher terms,

$$\psi=1+(2r/D)(\zeta+\ln 2r_1/D), \tag{74}$$

$$\varphi=1+(2r/D)(\zeta+\ln 2r/D-1), \tag{74a}$$

and the ratio is

$$\psi/\varphi=1+(2r/D)(\ln r_1/r+1). \tag{75}$$

As is clear from the definition of r_1 in (59), the ratio ψ/φ has a maximum at $r=r_1$ whose value is

$$\begin{aligned}\psi(r_1)/\varphi(r_1)&=1+2r_1/D\\&=1.040\text{ for square well}\\&=1.032\text{ for Yukawa potential.}\end{aligned} \tag{75a}$$

At other values of r, the functions are closer together. This shows that it must be a very good approximation to replace φ and w by ψ and u, respectively, in calculating r_1. Also it shows that for a given nuclear potential, r_0 and the correction P (see Section IV) must have substantially the same values as in the absence of the Coulomb potential.

VIII. ACKNOWLEDGMENTS

I am indebted to Dr. Blatt for valuable discussions, and to him and Mr. Jackson for sending me the manuscript of their paper before publication; it was most valuable to have their numerical results to test and guide the theory. My thanks are also due Dr. Longmire for several calculations, in Sections IV and VI, and for important suggestions (see Section IV).

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Bands from Doubly Excited Levels of the Hydrogen Molecule*

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A band system of H_2 is described which has as upper state $(2p\sigma)^2\,{}^1\Sigma$. Although this state has two electrons excited, its energy is about the same as that of the states with only one electron excited to a two-quantum state. The position of the lines and their intensities are very irregular. These irregularities, however, can be satisfactorily explained as being due to the interaction with the $(1s\sigma)(2s\sigma)\,{}^1\Sigma$ state.

I. INTRODUCTION

IN a previous paper[1] the system $2s\,{}^1\Sigma\rightarrow 2p\,{}^1\Sigma$ of the hydrogen molecule was discussed. The analysis of the upper state $2s\,{}^1\Sigma$, or more completely $(1s\sigma)(2s\sigma)\,{}^1\Sigma$, revealed strong perturbations which could only be accounted for by the presence of another electronic state slightly above the $2s\,{}^1\Sigma$ state. The nature of the perturbations showed that the perturbing state must be a ${}^1\Sigma_g^+$ state, with the same symmetry properties as the $2s\,{}^1\Sigma$ state. As all the low lying states of the molecule with one electron excited were already accounted for, this had to be a state with both electrons excited, and some arguments were given which made it probable that this hypothetical state was $(2p\sigma)^2\,{}^1\Sigma$.

The existence of a doubly excited stable state with such low energy seems at first sight rather surprising, and it is, therefore, highly desirable to obtain further information concerning this state. So far the only evidence for its existence has been furnished by the perturbations in the $2s\,{}^1\Sigma$ state. Naturally the situation would be strengthened a great deal if bands could be found coming from this $(2p\sigma)^2\,\Sigma$ state. Such bands have been available since 1937, but inconsistencies in their structure made some of them rather uncertain, so that they were not published. In the meantime, quantitative intensity measurements[2] in the infra-red have become available which make it possible in many doubtful cases to judge whether the bands are genuine or not. In this way the regularities previously found were sifted and amplified and they are now believed to be correct at least in their essential points, and they form the basis of the present paper. The evidence is derived entirely from the H_2 spectrum. The analysis of the analogous bands of the HD and

* This paper was written in 1941, but its publication delayed because of the war. It is presented in the original form with only minor revisions.

[1] G. H. Dieke, Phys. Rev. **50**, 797 (1936).

[2] N. Ginsburg and G. H. Dieke, Phys. Rev. **59**, 632 (1941).

TABLE I. The $(2p\sigma)^2\,{}^1\Sigma \rightarrow 2p\sigma\,{}^1\Sigma$ bands.

	P Branch					R Branch				
K	ν	D	L	Int. N	H	ν	D	L	Int. N	H
					2→0					
0						13 654.36	−0.01	6.3	(4)	
1	13 596.22	−0.01		0.74	1.8*c*	660.68	−0.01		(5)	*c*
2	538.30	+0.08	17.7	7.8	6.4*c*	470.36	+0.01	37.5	13.7	10.8
3	468.33	0.00	7.9	2.5	2.8	432.36	+0.19		4.1	*c*
4	203.63	+0.02	51.6	22.3	18.1					
5	093.58	+0.05		1.8	9.4					
					2→1					
0										
1	12 279.80	−0.02		(00)						
2	225.62	−0.05		0.49		12 157.77	−0.03	79.3	31.6	19.1
3				0.43						
4	11 903.93	+0.01	112	45.3	30.3					
5	802.56	+0.02		2.0						
					2→2					
0						11 054.57	+0.02	93.3	(10)	
1	11 000.02	+0.04		(5)		064.42	−0.02	45.2	(8)	
2	10 949.11	+0.04	193	(10)		10 881.15	−0.05		(0)	
3	889.58	+0.01		(5)		853.44	+0.03		(1)	
4	638.34	+0.01		(00*d*)						
5	544.42	−0.08		(00)						
					3→0					
0						14 543.91	+0.04		(3)	
1						537.97	+0.08		(00*c*)	
2	14 427.74	+0.02		(5)		508.57	−0.20		(5)	
3	345.48	−0.05		(4)						
4	242.02	−0.01		(1)						
5										
					3→1					
0						13 225.51	−0.02	21.7	7.6	4.2
1	13 171.89	0.00	10.8	3.5	*c*	221.63·	+0.15	32.2	14.3	8.0*c*
2	115.15	−0.02	45.2	13.9	4.5	196.21	−0.01		3.8	3.9
3	038.58	−0.01		(3*d*)	3.5					
4	12 942.39	+0.05		5.9*c*	5.0*c*	085.97	−0.03		7.9	
5	827.40	+0.03		1.0	2.2					
6	697.10	+0.06		0.90	1.5					
					3→2					
0						11 944.05	0.00	35.5	11.3	3.1
1	11 892.05	0.00	9.1	4.6	1.4	941.64	0.00	20.0	9.3	5.2*c*
2	838.58	+0.01	72.6	24.0	6.3	919.62	0.00	16.4*c*	8.0*c*	5.6*c*
3	766.81	+0.04	12.5	5.2	2.4	878.28	−0.06		1.0	1.9
4	676.77	+0.02	21.5	10.0	7.4	820.39	−0.92		1.7	4.7
5	569.37	+0.04		1.2	1.8					
6	447.78	−0.06	*c*	*c*	*c*					
					3→3					
0										
1	10 646.78	−0.02		(8)*c*						
2	596.17	−0.03		(0)						
3	528.65	0.00		(00)						
4	444.20	+0.06		(00)						
					4→0					
0						15 787.78	+0.02		(3)	
1	15 723.84	−0.01	3.0	0.70						
2	671.59	−0.02	11.8	3.0	1.7	802.73	−0.01	3.7	1.7	2.0*c*
3	607.90	−0.01		1.4	1.0	798.25	−0.02	1.2	0.68	
4	536.11	+0.11	*c*	*c*	*c*	787.78	−0.07		(3)	*c*
5	459.58	−0.05	2.0	0.74	1.7					
6	380.15	+0.01		(1)						
					4→1					
0						14 469.44	+0.02	13.0	3.1	
1	14 407.45	+0.01	5.6			483.86	0.00	6.3	6.3	2.0
2	359.06	−0.02	24.3	5.1		490.21	+0.02	10.9	3.9	
3	300.97	0.00	7.2	2.5		491.35	+0.02		1.8	
4	236.31	0.00	12.5	4.7		488.14	0.00		2.2	
5	186.66	+0.02		1.7						
6	099.17	−0.03		2.6						

TABLE I.—*Continued.*

	P Branch					R Branch				
K	ν	D	L	Int. N	H	ν	D	L	Int. N	H
					4→2					
0						13 187.95	+0.01	13.2	3.8	
1	13 127.59	−0.01		2.3						
2	082.44	−0.02	32.1	8.1		213.58	−0.01		1.3	
3	029.18	+0.03		2.1						
4	12 970.65	−0.07		2.7						
5										
6										
					4→3					
0						11 941.21	−0.02	63.4	14.3	3.5
1	11 882.36	+0.01	19.7	4.8	0.97	958.75	−0.02	13.1	4.6	1.6
2	840.07	−0.01	109	24.5	4.2	971.23	+0.02	26.3	10.5	7.1
3	791.00	−0.03	18.7	6.3	2.0	981.38	−0.01	6.4	2.9	2.7
4	738.17	+0.06	32.0	11.1	6.8	989.93	−0.03	3.6	2.4	6.0
5	684.77	+0.06	4.0	2.0	2.3					
6	631.89	+0.03		2.2	6.3					
					4→4					
0						10 728.23	+0.01		(5)	
1	10 670.63	+0.04		(3)		747.08	+0.07		(1)	
2	630.98	−0.04		(7)		762.16	+0.01		(3)	
3	585.78	−0.08		(3)		776.20	−0.20		(00)	
4	538.01	0		(6)						
5	490.78	+0.07		(1)						
6	445.10	−0.01		(0)						
					5→2					
0						13 930.92*c*	−0.01	12.1	12.9	4.9
1	13 874.47	−0.04	16.4	3.8	1.6	937.85	+0.05	6.2	7.2	1.6
2	825.40*c*	+0.03	142	25.8	6.4	930.92*c*	−0.02	12.1	12.9	4.9
3	763.04	−0.01	12.6	4.1	2.0	911.13	−0.03		(0)	1.6
4	688.05	−0.02	18.0	6.8	4.2	881.42	+0.03		(1)	2.0
5	602.23	−0.04		(4)						
6	508.78	−0.02		1.1	2.7					
					5→4					
0						11 471.22	0.03	60.2	15.0	2.8
1	11 417.54	0.04	28.6	5.8	1.2	480.94	0.05	13.5	3.9	1.5
2	374.00	0.01	134	30.6	5.3	479.44	−0.02	28.1	9.2	5.0
3	319.72	−0.02	22.8	5.8		467.80	−0.01		1.4	1.7
4	255.37	0.05	41.1	(10*c*)		448.68	−0.06		1.9	3.4
5	182.40	−0.04		(5)						
6	104.03	0.04		(3)						
					5→5*					
0						10 291.29	+0.05		(0*d*)	
1	10 238.86	−0.13		(0)						
2	197.70	0.04		(0)		303.32	−0.19		(00)	
3	147.12	0.12		(0)						
4	087.39	0.10		(1)						
5										
6	9 948.23	0.19		(0*b*)						
					6→0					
0										
1										
2	17 802.57	+0.02	1.7							
2										
4										
					6→1					
0						16 600.34	+0.02	4.5	(0)	
1	16 539.87	+0.03	2.4			610.85	−0.01		(0)	*c*
2	489.99	−0.01	11.0	3.2	1.5	608.44	−0.03	2.5	(00)	
3	427.94	−0.01		(00)						
4	354.65	+0.06	4.2	2.3	6.4					
					6→2					
0						15 318.89	+0.01	1.8	0.56	
1	15 259.98	−0.02		(00)						
2	213.37	−0.03		(2)		331.87	0.00	1.9	0.74	*c*
3	156.19	+0.04		(1)						
4	089.04	+0.04	1.5	0.64						

TABLE I.—*Continued.*

	P Branch					R Branch				
K	ν	D	L	Int. N	H	ν	D	L	Int. N	H
					6→3					
0						14 072.15	−0.02	15.9	3.4	
1	14 014.75	0.00	8.0	2.0		085.73	−0.04	4.8	1.5	
2	13 971.02	0.00	6.2*c*	7.2*c*		089.44	−0.85	8.5	2.1	
3	918.06	+0.03	6.9	2.1						
4	856.41	+0.02	11.4	4.1						
					6→4					
0										
1										
2										
3										
4										
					6→5*					
0						11 679.15	−0.06	34.2	6.9	1.5
1	11 624.19	−0.03	10.7	2.6	1.2	695.31	+0.06	6.7	2.9	1.5
2	585.61	−0.02	63.8	13.9	2.6	704.06	−0.04	13.0	6.4	2.9
3	540.12	0.00	8.0	3.3	1.1					
4	488.30	+0.04	14.5	5.2	2.8					
					6→6*					
0										
1										
2	10 441.55	−0.08								
3										
4										

Note: The initial vibrational quantum numbers are uncertain.

* Not used for calculation of averages.

D_2 molecules will probably clear up the points of uncertainty which still exist.

In the meantime, shortly after the $2s\ ^1\Sigma$ state had been analyzed, Richardson[3] published a number of bands lying in approximately the right region of the spectrum, which he identified with the desired $(2p\sigma)^2\ ^1\Sigma \rightarrow 2p\ ^1\Sigma$ bands. In fact, he found two systems, the initial states of which he called $\Sigma(a)$ and $\Sigma(b)$. Both these systems were highly irregular, a fact which had to be expected, but which made it rather hard to judge whether the systems were genuine or spurious, especially when the only measurements available to him were rather inaccurate. To have two electronic levels appear where only one is theoretically expected is, as Richardson points out, somewhat embarrassing, but since nothing is known with certainty about the position of most of the levels with two electrons excited, both levels might well be genuine. Of the 8 vibrational levels which comprise Richardson's two electronic states, one ($V=x+2$ of $\Sigma(a)$) is identical with one of the vibrational states ($V=4$) of the present $(2p\sigma)^2\ ^1\Sigma$; the rest are different. A careful scrutiny of the other seven vibrational levels with the help of more accurate wave-length and intensity measurements renders it probable that they are all spurious.

[3] O. W. Richardson, Proc. Roy. Soc. **A164**, 316 (1938).

II. GENERAL FEATURES

The observed frequencies and intensities of the lines in the band system in question are given in Table I. The intensities are quantitative measurements[2] taken at pressures of 0.06 mm (L), 0.2 mm (N), and 20 mm (H). When these were not available, the usual estimated values are given between parentheses in column N.

In order to ascertain whether the regularities are real or perhaps only due to the accidental presence of several lines in approximately the right places, we can employ several criteria, of which the most direct and most accurate is the test of the combination principle.

The final state of the bands, $2p\ ^1\Sigma$, is very well known from several band systems lying chiefly in the blue and violet.[4] The relative spacing of the various rotational and vibrational levels of this state is, therefore, known with great accuracy (to within a few hundredths of a wave number).

As each rotational-vibrational level of the new electronic state combines with a number of $2p\ ^1\Sigma$ levels, and the values of these $2p\ ^1\Sigma$ levels are exactly known, except for a common additive constant, we can calculate a value for the upper level from each line. If all the lines originating from one upper level yield values for this upper level which

[4] See O. W. Richardson, *Molecular Hydrogen and Its Spectrum* (Yale University Press, New Haven, 1934).

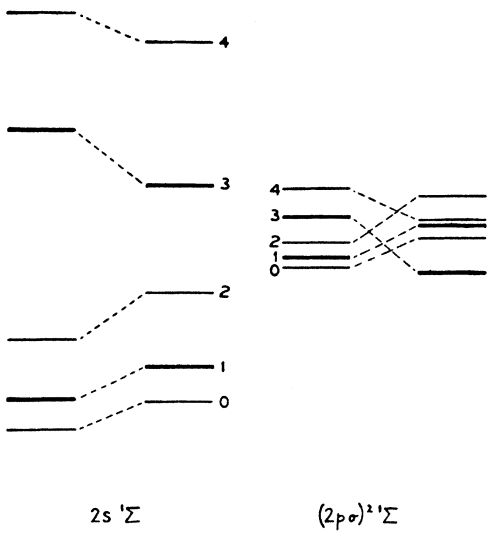

FIG. 1. Rotational levels of the $V=2$ states of $2s\ ^1\Sigma$ and $(2p\sigma)^2\ ^1\Sigma$. The inner columns represent the unperturbed levels, the outer ones the empirical perturbed levels. Note that the order of the rotational levels in $(2p\sigma)^2\ ^1\Sigma$ is now 3, 0, 1, 4, 2.

are identical within the limits of experimental errors, we have a good indication for the correctness of the classification. The greater the number of lines involved and the greater the accuracy of the measurements, the more certain one can be that no accidental coincidences play a role.

From the average of the calculated values for the upper level, the individual lines originating from this level can then be recalculated and compared with the observed values. The differences between the observed and calculated wave numbers are listed in column D in Table I. It is seen that the agreement is very satisfactory throughout; the two lines for which the difference exceeds 0.1 cm^{-1} are clearly blends.[5]

The fulfillment of the combination relations is practically conclusive proof for the genuineness of the regularities. The interpretation of these regularities must be obtained from an analysis of the structure of the upper state and from the observed intensities. If both can be satisfactorily correlated with the known facts of the structure of the molecule, this forms additional evidence for the correctness of the classification.

As we anticipate that the bands are strongly perturbed, we cannot expect that the lines in one band will be very regularly spaced nor can we assume that the intensity distribution will be regular.

III. PERTURBATIONS

The presence of the new bands was suggested by the perturbations which the $(2p\sigma)^2\ ^1\Sigma$ level produces in the $2s\ ^1\Sigma$ state. The first test we should make, therefore, is whether the perturbations are actually accounted for by the interaction of these two levels.

The type of perturbations with which we have to deal here has been called type B or vibrational perturbations.[6] The latter name is somewhat misleading, as in this type of perturbations, irregularities in the spacing of the rotational lines may also occur, and, as in the present case, may be the most conspicuous feature. Type B perturbations occur when the value Λ of the electronic moment along the internuclear axis is the same in both levels. The perturbations are due to the interaction of vibration and electronic motion.

The perturbation function, i.e., the term in the Hamiltonian omitted in the approximate treatment of the problem is given by

$$H^{(4)}\psi = B\left[(M_\xi^2+M_\eta^2)\Phi - 2r\frac{\partial\Phi}{\partial r} - r^2\frac{\partial^2\Phi}{\partial r^2} - \frac{2r^2}{R}\frac{\partial R}{\partial r}\frac{\partial\Phi}{\partial r}\right]RU, \quad (1)$$

where M_ξ and M_η are the components of the electronic angular momentum perpendicular to the internuclear axis and Φ, R, U the electronic, vibrational, and rotational wave functions, respectively.

The part inside the bracket is not a function of the rotational coordinates. Therefore, we can integrate with respect to them and leave the rota-

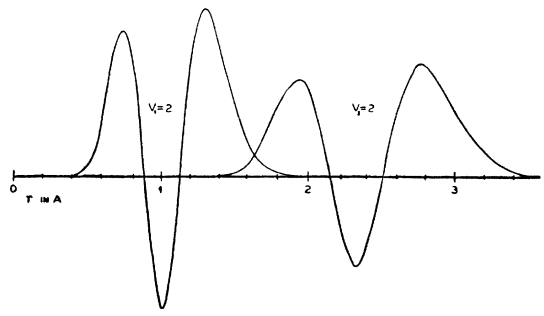

FIG. 2. Overlapping of the vibrational wave-functions for the two states with $V=2$ of $(1s)(2s)\ ^1\Sigma$ (left) and $(2p\sigma)^2\ ^1\Sigma$ (right).

[5] We can test in the same way the seven vibrational states of Richardson which do not fit into our scheme. Most of the wave-lengths which Richardson used are not accurate enough to make the agreement or lack of it mean very much. If, however, we substitute our own more accurate wave-lengths, big discrepancies show up. This, together with the erratic intensities and the unproportionately large number of blends, supports the view that these bands are not genuine.

[6] The general theory of perturbations has been developed by Kronig and Van Vleck. For our present case see G. H. Dieke, Phys. Rev. **47**, 870 (1935), where the same notation is used as here and where references to other papers on this subject are given.

tional part out of further consideration. The perturbation matrix elements will not depend on the rotational quantum number.

However, the dependence on the internuclear distance r is quite complicated, as besides R also Φ and B are functions of r. Little can therefore be said about the value of the interaction except in a few extreme cases. Let us call the interaction element

$$S=\int \bar{\psi}_1 H^{(4)} \psi_2 d\tau$$

which does not depend on the rotational quantum number K but very decidedly on the vibrational quantum numbers V_1 and V_2 of the two perturbing states.

If A is the distance between the two unperturbed states for $K=0$ then

$$2\delta=A+(B_2-B_1)K(K+1)$$

is in first approximation the separation of the unperturbed rotational levels. The energy shifts due to the perturbation referred to the lower of the pair of unperturbed levels is

$$\epsilon=\delta\mp(S^2+\delta^2)^{\frac{1}{2}}, \qquad (2)$$

and therefore the distance between the perturbed levels

$$d=2(S^2+\delta^2)^{\frac{1}{2}}.$$

The value of d can be obtained as function of K from the empirical data as it is the distance between the actually observed levels. Therefore from three pairs of rotational levels the three constants A, B_1-B_2, and S can be obtained. If we take the values for $K=1$, 2, 3, which are best established, we obtain

$$A=196.10, \quad B_1-B_2=20.33, \quad S=141.15.$$

With these values of the constants the relative distances of the levels for $K=0$ and $K=4$ can be computed and compared with the observed data.

	$K=0$	$K=4$
Calc.	279.82	−290.15
Obs.	279.01	−292.93

Considering the approximations made in the calculations the agreement is very good.

Knowing now the constants for the perturbations we can calculate the unperturbed rotational levels of both states. The distances between the first four successive unperturbed levels of the $V=2$ state of $2s\ ^1\Sigma$ turn out to be

53.33 105.17 157.05

which are as regular as can be expected. From these differences the values of B and D for the $V=2$ state of $2s\ ^1\Sigma$ are

$$B=26.57 \qquad D=0.023.$$

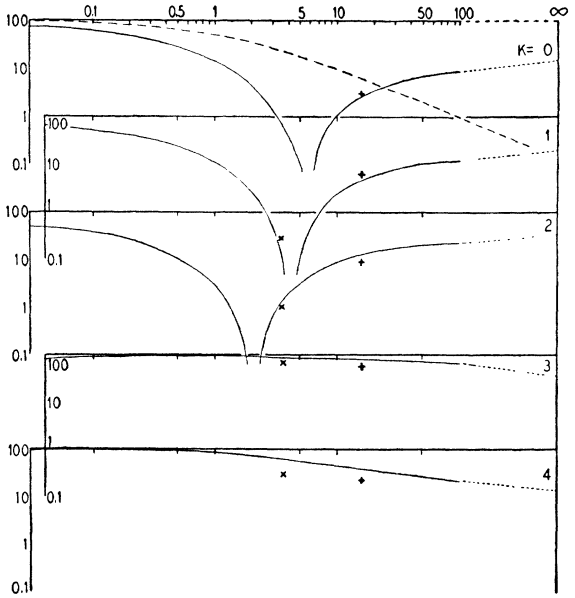

FIG. 3. Calculated intensities for the lines originating from the first five rotational levels of the $V=2$ vibrational state of $(2p\sigma)^2\ ^1\Sigma$. Abscissae are the unperturbed intensity ratios of the perturbing pairs. Ordinates give the perturbed intensities of one band in percent of the total of the perturbing pair. Experimental values + for 2→0, x for 2→1 band.

Not much importance should be attributed to the value of D, although it agrees exactly with the value derived from the unperturbed $V=0$ state. However, the value of B should be fairly accurate.

Figure 1 gives the relative positions of the perturbed and unperturbed rotational levels of the two electronic states. Note that in the perturbed $(2p\sigma)^2\ ^1\Sigma$ state the order of the rotational levels is quite anomalous, namely $K=3$, 0, 1, 4, 2. For an electronic state which interacts as much with other electronic states as the $2s\ ^1\Sigma$ state we must be careful what significance we should attach to the value of B found above, and in general to the rotational and vibrational constants.

Such constants are commonly used to calculate a potential curve, and such a curve is then compared with theoretical calculations done, e.g., after the method of James and Coolidge. This calculated potential curve is found by neglecting completely the influence of rotation and vibration of the nuclei, i.e., the interaction of different electronic states which is caused by the presence of rotation or vibration. If we want, therefore, to compare the empirical with the theoretical curve, we must be sure that all influence of the interaction is eliminated from the former. That has been done for the large interaction of the $2s\ ^1\Sigma$ ($V=2$) with the $(2p\sigma)^2\ ^1\Sigma$ ($V=2$) level. However, this level is also influenced, though to a much smaller extent,

by the other vibrational levels of $(2p\sigma)^2\,{}^1\Sigma$. The magnitude of this influence can be roughly estimated in the following manner:

If $\delta \gg S$ we obtain for the perturbation

$$\epsilon = -\frac{S^2}{2\delta} = -\frac{S^2}{A+(B_2-B_1)K(K+1)}$$

$$= \frac{S^2(B_2-B_1)K(K+1)}{A^2} - \frac{S^2}{A}.$$

The change in the apparent value of B is, therefore, $S^2(B_2-B_1)/A^2$ which will give about 0.4 cm^{-1} with the values found for S and B_2-B_1 and with $A=1000$. The levels which lie even higher will contribute less. If we had a series of levels at equal distances of 1000 cm^{-1} above the level under consideration the result of the joint action would be obtained by multiplying the influence of the nearest level by $\Sigma(1/n^2)=(\pi^2/6)=1.64$.

This calculation can, of course, give only a rough idea of the influence of the other vibrational states. The value of S may be quite different for the individual pairs of interacting vibrational states, but the order of magnitude will probably remain the same. We may expect, therefore, that the value of B_2 for $2s\,{}^1\Sigma$ is correct to within about one wave number and that the true value for the unperturbed state will be probably slightly higher.

The value for B for $(2p\sigma)^2\,{}^1\Sigma$ is $B=6.24$ which is the smallest ever observed for a H_2 state. The effective internuclear distance is $r=2.31$A (normal state 0.749A). This large internuclear distance agrees very well with the interpretation of the new state as one for which both electrons are excited to a $2p\sigma$ state. The order of reliability is the same or better than that for the $2s\,{}^1\Sigma_2$ state.

The perturbations of the higher vibrational levels cannot be evaluated so easily as they cannot be considered in first approximation as arising from only one pair of perturbing levels.

IV. THE VIBRATIONAL QUANTUM NUMBERS OF $(2p\sigma)^2\,{}^1\Sigma$

As it is almost certain that the matter of the assignment of vibrational quantum numbers to the new state can be settled definitely with the help of the equivalent bands of HD and D_2 which are not yet sufficiently analyzed, only a few remarks may suffice here.

The most obvious thing would be to assign to the lowest observed vibrational level of $(2p\sigma)^2\,{}^1\Sigma$ the quantum number $V=0$. However, there are several objections to this.

1. In the first place there seems to be a small though distinct perturbation in the $V=1$ level of $2s\,{}^1\Sigma$ which would remain unexplained if there would be no vibrational level of $(2p\sigma)\,{}^1\Sigma$ below the lowest observed one. As the spacing of the vibrational intervals of $(2p\sigma)^2\,{}^1\Sigma$ is much narrower than that of $2s\,{}^1\Sigma$ we must expect that the vibrational level of $(2p\sigma)^2\,{}^1\Sigma$ with V two units lower than the lowest observed one must be responsible for this perturbation. If we assume this is actually the lowest vibrational level we obtain the vibrational numbering employed in this paper. However, there is no certainty that even what is called here the $V=0$ level is actually the lowest vibrational level, so that the vibrational quantum numbers might have to be revised by one or two units.

2. I have searched for bands arising from the $V=0$ and $V=1$ levels of $(2p\sigma)^2\,{}^1\Sigma$ but without success. This is not surprising as according to the Frank Condon principle these bands should have a very low intensity. The fact that the bands originating from $V=2$ are so relatively strong is entirely due to the fact that the interaction of this state with $2s\,{}^1\Sigma$ gives to this level some of the properties of the $2s\,{}^1\Sigma$ state which combines very strongly with the final state $2p\sigma\,{}^1\Sigma$. That this interaction is responsible for this is proved by the very abnormal rotational intensity distribution (see Section V).

3. Although a quantitative evaluation of the perturbation matrix (1) is not feasible, we can say that, unless there is a definite overlapping of the vibrational wave functions of the two states, there can be no appreciable perturbation. The approximate vibrational wave functions have been drawn in Fig. 2 under the assumption that the perturbing $(2p\sigma)^2\,{}^1\Sigma$ state has $V_2=2$.

Figure 2 shows that if we would disregard the evidence of the small perturbations[7] in $2s\,{}^1\Sigma$ ($V=1$) and take the lowest observed level of $(2p\sigma)^2\,{}^1\Sigma$ to have $V=0$, the overlapping of the two wave functions would be insufficient to account for the very strong perturbation. Of course, the figure cannot be trusted quantitatively but should give an adequate qualitative picture. The overlapping increases as the vibrational quantum numbers increase.

Figure 2 shows that both the facts that we have a very small perturbation in the $V=1$ level of $2s\,{}^1\Sigma$ ($V_1=1$, $V_2=0$) and a strong perturbation in the $V=2$ level ($V_1=2$, $V_2=2$) are in agreement with our choice of vibrational quantum numbers.

V. INTENSITIES

The intensities in the new bands appear to be very irregular but we shall see that these irregu-

[7] It is true that this level is involved only in one observed band ($1\rightarrow 0$) which makes it less easy to be sure of the correctness of the rotational levels than if several bands issuing from this level could be observed. However, the $1\rightarrow 0$ band is very strong and there seem to be no alternate lines in the region in question. Therefore, the existence of the perturbation in the $V=1$ level of $2s\,{}^1\Sigma$ must be considered as well established.

larities can be entirely accounted for by the influence of the perturbations at least for the bands having $V'=2$. As only for this level the perturbations can be regarded on first approximation as being due to a pair of interacting states, we can make reasonable calculations only for the bands originating from it. Even in this case we must not expect exact quantitative agreement because of the approximations discussed in Section III.

If I_1 and I_2 are the intensities of a pair of unperturbed lines the intensities of the perturbed lines are

$$\left.\begin{aligned} I_a &= \frac{S^2}{S^2+\epsilon^2}\left((I_1)^{\frac{1}{2}} - \frac{\epsilon}{S}(I_2)^{\frac{1}{2}}\right)^2 \\ I_b &= \frac{S^2}{S^2+\epsilon^2}\left((I_2)^{\frac{1}{2}} + \frac{\epsilon}{S}(I_1)^{\frac{1}{2}}\right)^2 \end{aligned}\right\} \qquad (3)$$

if $W_1^0 < W_2^0$. The signs of the second term are reversed if $W_1^0 > W_2^0$.

In this expression all quantities are known, except I_1/I_2. For comparison with the experimental data the dimensionless quantity

$$\frac{I_b}{I_a+I_b} = \frac{S^2}{S^2+\epsilon^2}\,\frac{1 \mp \frac{\epsilon}{S}(I_1/I_2)^{\frac{1}{2}}}{1+I_1/I_2}$$

is more convenient. It is represented in Fig. 3 as function of I_1/I_2 on a double logarithmic scale for the first five lines of the P-branch. The five values lying along one vertical represent the intensity distribution in a band with that particular value for I_1/I_2. Without a perturbation the five values should be identical and equal to $(1+I_1/I_2)^{-1}$. The dotted curve in the upper part of the diagram represents this distribution. We see that for some values of I_1/I_2 the actual intensities are lower than the unperturbed ones, for others they are higher. The intensity changes produced by the perturbations are by no means small. Changes by a factor 100 or more may easily occur.

The difference of the curves for $K=0$, 1, 2 with those for $K=3$, 4 is very striking. The former go down to zero for a definite value of I_1/I_2 due to the fact that the amplitudes are subtracted, whereas the $K=3$, 4 curves have their amplitudes added and reach 100 percent for certain I_1/I_2 values. The curves here drawn are those for one of the perturbed levels. According to (3) the other members of the pair will be always of the opposite type.

When curves like Fig. 3 are drawn the experimental values can be plotted in the curves so that they give the best agreement. This will determine the values of I_1/I_2 for the band in question. For the $2\rightarrow0$ band we obtain $I_1/I_2=15$, for the $2\rightarrow1$ band $I_1/I_2=3.5$. The order of magnitude of these values is in agreement with the Franck Condon principle. The agreement between calculated and observed intensities is as good as can be expected from the approximations made in the calculations and the uncertainties of the experimental values. Most of these are derived from only one measurement and there is always the danger of blends.

We notice the following peculiarities:

1. Two *ordinary* bands originating from the same upper level should have the same intensity distribution, i.e., we should be able to obtain the intensities of the second band by multiplying those of the first by a constant factor. We see that there is nothing like this here. Whereas $P(2)$ and $P(3)$ are much stronger in $2\rightarrow0$; $P(4)$ is about twice as strong in $2\rightarrow1$. In fact we see that the intensity distribution in neither band is anything like normal.

2. The intensity ratios $R(K-1)/P(K+1)$ are within the limits of experimental errors the normal values for a $\Sigma\rightarrow\Sigma$ transition no matter how irregular the intensities of the individual lines themselves are. This must be the case for all vibrational perturbations.

3. The intensity distribution of I_a+I_b is more or less that of a normal band as it should be as this sum, according to (3), must be independent of the influence of the perturbations.

4. While, therefore, the intensities within one band are very irregular, they can be perfectly explained theoretically. This adds weight to the interpretation of the bands advanced in this paper.