The Triplet 3*p* Complex of the Hydrogen Molecule

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Many peculiarities first observed in the Fulcher bands of the hydrogen molecule can be explained by the interaction of the $3p^3\Pi$ with the $3p^3\Sigma$ level. Such peculiarities are: irregular Λ-doublings, perturbations in the $3p^3\Pi$ and $3p^3\Sigma$ state, and the absence of *P* and *R* branches for large values of the vibrational quantum numbers. This last phenomenon is due to the predissociation of the $3p^3\Pi$ state.

§1

The present investigation is concerned with the interaction of the $3p^3\Sigma$ and $3p^3\Pi$ levels of the hydrogen molecule. The $3p^3\Pi \rightarrow 2s^3\Sigma$ bands, the so-called Fulcher bands were the first known regularities in the H_2 spectrum. Richardson and Das[1] to whom the complete analysis of the Fulcher bands is due, noted that the *P* and *R* branches of the bands showed marked irregularities and were completely absent if the vibrational quantum number of the initial state exceeded the value three, whereas the *Q* branches had a perfectly regular structure.

The study[2] of the analogous bands of HD and D_2 led to an explanation of these phenomena as being due to the interaction of the $3p^3\Sigma$ and the $3p^3\Pi$ levels and the analysis of the $3p^3\Sigma \rightarrow 2s^3\Sigma$ bands[3] confirmed this view completely. The present paper is concerned with a closer investigation of this interaction. As examples of interaction between molecular levels which give rise to perturbations in which both levels are completely known are extremely rare, the present case is of considerable general interest, especially as the same kind of interaction can be studied for the three different isotopic molecules.

The empirical material for HD and D_2 is given in two previous papers[2, 3, 4] and the data for H_2 are taken from Richardson and Das.[1]

The theoretical background for the treatment of such interaction has been summarized in a previous paper[5] to which frequent reference will have to be made as "theoretical part."

§2. Empirical Facts

It is perhaps most convenient to begin with a summary of the observed empirical facts which require an explanation. They are:

1. All the *Q* branches are quite regular.
2. The Λ-doubling of the $3p^3\Pi$ state depends in a very erratic way on the vibrational quantum number, and is quite abnormal for some vibrational levels.
3. Whereas the dependence of the Λ-doubling on the rotational quantum number *J* is only slightly abnormal in most cases, there are pronounced perturbations for certain levels.
4. The H_2, HD and D_2 levels show the same general behavior, but the irregularities are found at different places for the three molecules.
5. For $V'>3$ for H_2 and HD and $V'>4$ for D_2 the *P* and *R* branches are completely absent in the Fulcher bands.
6. The $3p^3\Sigma$ levels show also irregularities, but only the big perturbations are easily recognized, as there is no Λ-doubling which registers abnormalities with much greater precision.

§3

If we consider Fig. 1 which is a plot of the vibrational levels of the two electronic states, the explanation of many of the points mentioned above becomes apparent. In the first place we note that there are certain pairs of levels which lie very close together. Such pairs are $3p^3\Sigma$, $V=4$ and $3p^3\Pi, V=1$ for H_2, $3p^3\Sigma, V=3$ and $3p^3\Pi, V=0$ for HD, and $3p^3\Sigma, V=5$ and $3p^3\Pi, V=1$ for D_2. All these levels show big perturbations which makes it practically certain that the abnormalities listed in §2 are due to the interaction of the $3p^3\Sigma$ and $3p^3\Pi$ levels, and a closer investigation confirms this.

For the notation, etc., reference must be made to the theoretical part.[5] As the interaction is between a Π and Σ level it must be of type A, i.e.,

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[1] O. W. Richardson and K. Das, Proc. Roy. Soc. **A122**, 688 (1929).

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

[3] See the preceding article.

[4] As more extended measurements have become available the analysis of the Fulcher bands of HD and D_2 could be considerably amplified. Also the $3p^3\Sigma \rightarrow 2s^3\Sigma$ bands of H_2 could be extended.

[5] G. H. Dieke, Phys. Rev. **47**, 870 (1935).

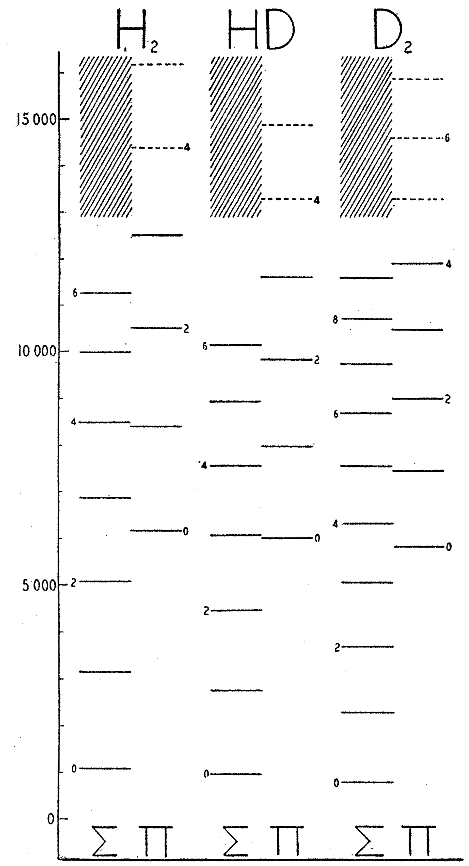

FIG. 1. The vibrational levels of $3p^3\Sigma$ and $3p^3\Pi$. The relative positions of the H_2, HD and D_2 levels are adjusted so that the vibrationless (electronic) level of $3p^3\Sigma$ has the same value for all three molecules.

the coupling of the two states is due to the rotation of the molecule.

The $p\Pi$ state is always split up into a $p\Pi^+$ and a $p\Pi^-$ state[6] due to the rotation of the molecule (Λ-doubling) and of these only the $p\Pi^+$ state can interact with the $p\Sigma^+$ levels. The $p\Pi^-$ level is the initial state for the Q branches and is completely unaffected by the interaction. This explains point 1 of §2, that all the Q branches are completely regular.

If there were no interaction the $p\Pi^-$ level would coincide exactly with the $p\Pi^+$ levels, so that the amount of the Λ-doubling is a direct measure for the magnitude of the interaction. We have seen in the theoretical part that the interaction between two levels is by far the greatest if they have the same vibrational quantum number, and we call the effect of this kind of interaction the regular Λ-doubling. If the vibrational quantum numbers differ, the interaction is much smaller and its effect on the energies is of any consequence only if the levels are close together. This gives us the irregularities in the Λ-doubling.

§4. THE REGULAR Λ-DOUBLING

According to (16) and (24) of the theoretical part the regular doubling is in first approximation given by

$$2B_v^2J(J+1)/\delta,$$

in which δ is the distance between the $p\Sigma$ level and the corresponding $p\Pi$ level with the same rotational quantum number J and the same vibrational quantum number V. As the equilibrium distances are different for the two interacting levels, a better approximation is obtained if we substitute $B_{vv}=\int RBR'r^2dr$ for $B_v=\int RBRr^2dr$. (R is the vibrational wave function.) This follows from (17) if the second small and uncertain term is omitted. This correction is very small in our case. With harmonic binding we get, e.g.,

$$B_{00}=(2a/1+a^2)^{\frac{1}{2}}e^{-b^2/2(1+a^2)}B_0,$$

in which

$$a=(\omega_e'/\omega_e)^{\frac{1}{2}},\quad b^2=4\pi^2c\omega_e'\mu(r_0-r_0')^2/h$$

and the values of the constants are for D_2

$$3p^3\Pi\quad r_0=1.047\cdot10^{-8},\quad \omega_e=1678.22$$

$$3p^3\Sigma\quad r_0'=1.096\cdot10^{-8},\quad \omega_e'=1556.64.$$

This gives for D_2 $B_{00}=0.941\ B_0$, and similarly small corrections for the two other molecules.

The regular doubling for the $V=0$ vibrational level is found to be in this way $0.321\ J(J+1)$ for H_2, $0.180\ J(J+1)$ for HD, and $0.078\ J(J+1)$ for D_2.

In Figs. 2, 3 and 4 these calculated regular doublings are compared with some of the observed values. Table I gives all the observed doublings.[7] It is seen that the order of magnitude

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[6] Usually the $p\Pi^-$ state is called $p\Pi_a$ or $p\Pi_c$ and the $p\Pi^+$ state $p\Pi_b$ or $p\Pi_d$.

[7] As a $p\Pi^+$ and a $p\Pi^-$ level with the same J never can combine with the same lower state, it is not possible to obtain the values of the doubling directly from the observations by using only the combination principle. However, as the structure of the lower ($2s^3\Sigma$) state is very regular,

TABLE I. Λ-*doubling of the* $3p^3\Pi$-*level.*

	H_2				HD				D_2				
J	$V=0$	1	2	3	0	1	2	3	0	1	2	3	4
1	0.46	−0.31	0.92	1.89	−0.04	0.48	0.29	0.67	0.13	0.09	0.18	0.13	0.23
2	1.25	−1.63	2.68	4.43	−0.43	1.34	0.84	1.89	0.35	0.20	0.62	0.37	0.74
3	2.54	−6.50	4.76	6.46	−3.26	2.45	1.46	3.34	0.50	0.21	1.23	0.70	1.36
4	3.90		6.87	8.28	+9.06	3.83	1.95	4.88	1.00	−0.17	1.97	0.98	2.04
5	5.19		8.36		7.67	5.33	1.75	6.10	1.49	−3.08	2.71	0.75	2.62
6	6.06				7.49	6.59		6.55	1.86	+8.60	3.54	−0.87	2.96
7									2.18	6.22			

of the observed doubling is well represented by the theoretical curves,[8] but that the individual values show considerable systematic deviations from the curves, positive in some cases, negative in others.

§5. Irregular Λ-Doubling

These deviations must be due, for the greatest part,[9] at least, to the interaction of the $p\Pi$ level with that $p\Sigma$ level which is its closest neighbor. We take first the case where the interacting levels are not so close that we have typical perturbations. The interaction of two levels with different vibrational quantum numbers is given in first approximation by (17) of the theoretical part in which we can omit again the uncertain second part.

The quantity $B_{vv'}$ can be calculated easily if we make use of the well-known properties of the Hermitian polynomials.[10] We get, e.g., $B_{04}=0.02B_0$ for D_2. This is much too small to account for the empirical deviations of the $V=0$ level of $3p\Pi$ from the theoretical curve (Fig. 2) which would require B_{04} to be of the order of magnitude 0.1 B_0 to 0.2 B_0.

The explanation for this discrepancy must be sought in the fact that the calculations are made under the assumption that the binding is harmonic.[11] They are, however, very sensitive for deviations from the harmonic law. The calculations could be carried out also with a general anharmonic law of force but would be much more cumbersome, and the present state of affairs would hardly justify going into them. Possibly also the neglected term in (17) may be appreciable. We hope to come back to this in a later paper but restrict ourselves now to some qualitative considerations.

Whether the Λ-doubling of a given $p\Pi$ level is diminished or increased depends on whether the $p\Sigma$ level which is its nearest neighbor lies just above or below the $p\Pi$ level. There is no simple law which governs the distance of a given $p\Pi$ level from the closest $p\Sigma$ level, therefore the relative position of such pairs can be considered to be regulated more or less by chance. This accounts for the erratic way in which the irregularities of the Λ-doubling depend on the vibrational quantum number (point 2 of §2). Also there is absolutely no connection between the relative arrangement of such pairs in H_2, HD and D_2 which can be verified by a glance at Fig. 1. This explains point 4 of §2.

If the $3p\Sigma$ level lies just *above* the neighboring $3p\Pi$ level, the effect of this will be that the $3p\Pi$ level will be depressed, i.e., the Λ-doubling diminished. We have such a state of affairs, e.g., for $V=0$ in D_2, $V=2$ in HD and $V=0$ in H_2. These are the levels represented by an x in the Figs. 2–4, and the Λ-doubling lies in all these cases below the theoretical value, as it should.

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the differences between successive rotational levels of it can be calculated with any desired accuracy. In fact it is necessary only to calculate the difference between the $J=0$ and $J=1$ levels of $2s^3\Sigma$ with the help of the term formula, and all the rest including the Λ-doublings can be calculated with the help of the combination principle only. The values in the table were obtained in this way.

[8] It may be good to emphasize that no adjustable constant was used for the calculation of the theoretical curves.

[9] There are, of course, other reasons why there should be deviations of the observed Λ-doublings from the theoretical curves. The formula used is only a first approximation and can be expected to hold only for small J. The figures show that for all levels the observed values for the larger values of J seem to have a tendency to be too low, and this kind of deviation must be due to the insufficiency of the formula used.

[10] The calculations necessary for this are of the same kind as those used for the calculations of band intensities in electronic band systems. As the calculations do not give the right magnitude anyway they are omitted here.

[11] Some of the effects of the deviations from the anharmonic binding have been taken into account; e.g., if we use $B_v=B_e-\alpha(V+\frac{1}{2})$, the empirical value of α is used. If the binding is regarded purely harmonic, α would have the same order of magnitude but opposite sign.

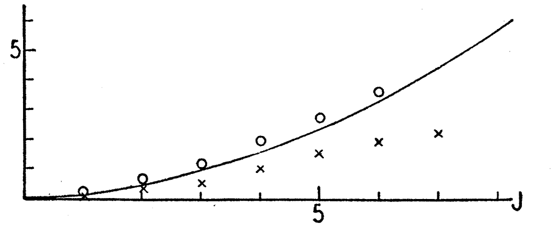

FIG. 2. Λ-doubling for $3p^3\Pi$ of D_2. Curve: calculated regular Λ-doubling for $V=0$. x Observed values for $V=0$, o for $V=2$.

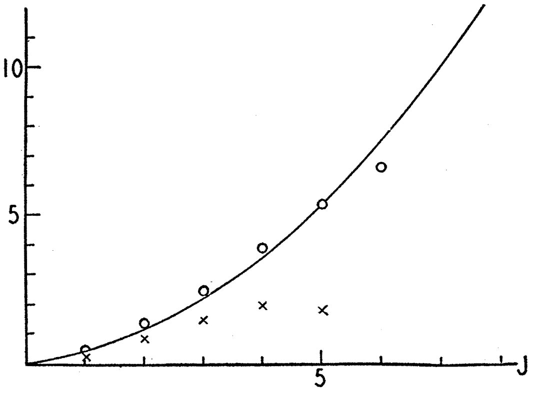

FIG. 3. Λ-doubling for $3p^3\Pi$ of HD. Curve: calculated regular Λ-doubling for $V=0$. x Observed values for $V=2$, o for $V=1$.

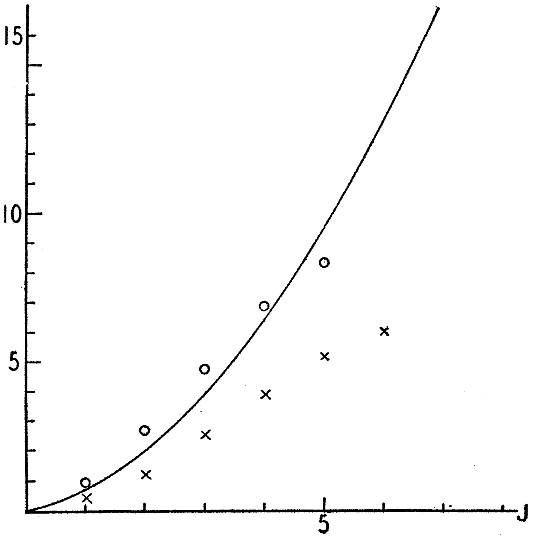

FIG. 4. Λ-doubling for $3p^3\Pi$ of H_2. Curve: calculated regular Λ-doubling for $V=0$. x Observed values for $V=0$, o for $V=2$.

It may even occur that the deviation is larger than the regular doubling in which case the total doubling becomes negative.

The opposite state of affairs exists if the $3p\Sigma$ level lies just *below* the neighboring $3p\Pi$ level as is the case for $V=2$ in D_2, $V=1$ in HD, and $V=2$ in H_2. Then the Λ-doubling should be larger than the regular doubling and that is found to be the case (see Figs. 2–4). In judging the agreement it must be borne in mind that the drawn out curve is the regular Λ-doubling for $V=0$, whereas the regular Λ-doubling for $V=1$ and $V=2$ is lower (about 25 percent lower for the $V=2$ level of H_2). The figures show that the deviations from the regular curve become relatively much larger for larger J when the doubling is *below* its regular value and the opposite is true when it is *above* its regular value.

The reason for this is that when the $p\Pi$ level lies below the $p\Sigma$ level the distance δ between rotational levels with the same J decreases with increasing J, as the spacing of the $p\Pi$ rotational levels is larger than the spacing of the $p\Sigma$ levels. This means that the higher levels are relatively more affected because of their closer proximity than the lower ones. If the $p\Pi$ state is above the $p\Sigma$ state just the opposite takes place. All this is in agreement with the experimental facts.

§6. TRUE PERTURBATIONS

We come now to the cases where the $p\Sigma$ levels lie so closely above the $p\Pi$ levels that the interaction becomes considerable and we have true perturbations. Fig. 1 shows that this is the case for $V=1$ in H_2 and D_2 and $V=0$ in HD. The data are most complete for the pair $V=1$ of $3p^3\Pi$ and $V=5$ of $3p^3\Sigma$ of D_2 and therefore we shall consider this case more in detail. The two other cases mentioned are of the same kind.

The magnitude of the perturbation can be obtained with great accuracy in the following way. The total Λ-doubling is the sum of the regular Λ-doubling which can be calculated in the way indicated in §4 and the perturbation due to the $V=5$ level of $3p\Sigma$. By subtracting therefore the calculated regular Λ-doubling from the total doubling we obtain the amount of the perturbation. According to theory the perturbation of the $V=5$ state of $3p\Sigma$ is of the same magnitude but opposite sign. By subtracting resp. adding the amount of the perturbation to the pair of the perturbed levels we obtain the unperturbed states.[12] The difference between pairs of such

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[12] Strictly speaking the interactions of the $3p\Pi\ V=1$ level with the $3p\Sigma\ V=1$ and the $3p\Sigma\ V=5$ levels are not inde-

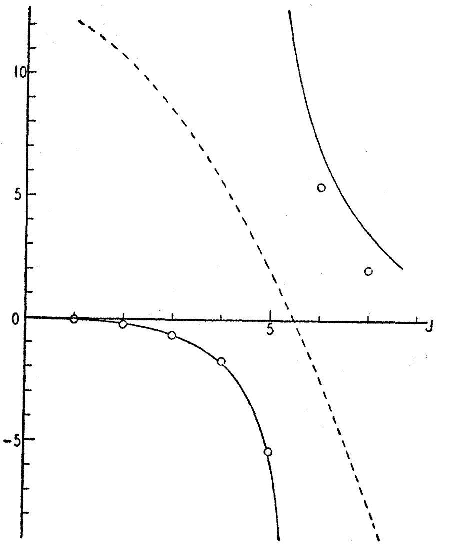

FIG. 5. The solid curve represents the calculated perturbations for the $3p^3\Pi$, $V=1$ level of D_2. o are the observed perturbations. The dotted curve gives the distance between corresponding rotational levels of $3p^3\Sigma$, $V=5$ and $3p^3\Pi$, $V=1$. (The scale for this curve is ten times smaller than that indicated by the figures on the left.)

levels with the same J is represented by the dotted curve in Fig. 5. The o mark the observed perturbations (on a tenfold magnified scale). It is seen that the perturbations become rapidly larger as the distance between the levels decreases and that they change their sign when the two levels cross over. The solid curve represents the perturbations calculated according to (13) and (18) of the theoretical part, the constant α being chosen in such a way as to give the best agreement for small values of J. It is seen that the agreement is very good for small J but that after the break there are discrepancies much larger than the errors of measurement. They are due to the approximate character of our calculations and undoubtedly the agreement could be made much better by going to higher approximations.

The value of the constant α is 4.9 from which it follows according to (17) that $B_{15}=1.5$. That is the same order of magnitude as was found for B_{04} in §5.

In all cases the perturbations of the $3p\Sigma$ state are of the same magnitude and opposite sign as those for the $3p\Pi$ state with which they interact. Only they cannot be ascertained with the same precision as those of the $p\Pi$ states as the unperturbed states are unknown whereas for the $p\Pi$ levels they are exactly given by the unaffected $p\Pi^-$ states.

There is a perturbation of smaller magnitude than those mentioned above in the $3p\Sigma\, V=7$ level of D_2. As Fig. 1 shows, this perturbation cannot be due to the interaction with a $3p\Pi$ state. It is probable that it is caused by the interaction with the $4p^3\Sigma$ level which, however, has not yet been established empirically with sufficient certainty to verify this unambiguously.

§7. PREDISSOCIATION

The vibrational levels of the $3p\Sigma$ state are discreet only up to a certain limit. Beyond this limit which is indicated in Fig. 1 the molecule is dissociated into a normal and an excited atom in the second quantum state, and the energy levels are continuous. The nature of the wave functions is not changed in such a way as to affect materially the interaction with the $3p\Pi$ state. This means that the continuous levels interact with the neighboring $3p\Pi$ levels in essentially the same way as the discreet levels. A characteristic feature of such interaction is that the molecule oscillates back and forth between the two interacting states. As the $3p\Sigma$ state is dissociated the $3p\Pi$ state will also be dissociated by the interaction (predissociated) i.e., the $3p\Pi^+$ levels above the dissociation limit of the $3p\Sigma$ state will be destroyed as discreet levels. The bands originating from these levels will therefore be absent.[13] The Fig. 1 shows that this must be the case for $V>3$ in H_2 and HD and for $V>4$ in D_2, and this agrees exactly with the experimental observations (point 5 of §2).

All this applies only to the $3p\Pi^+$ level which gives the P and R branches, as the $3p\Pi^-$ level which gives the Q branches is not affected at all by the interaction. This explains why only the P and R branches are absent, whereas the Q branches show no changes.

In a previous paper[2] this phenomenon was used to determine the heat of dissociation of H_2.

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pendent as they are caused by the same interaction force. It can be easily shown, however, that they can be treated as if they represented separate interactions, if first the regular Λ-doubling is taken into account and the new levels, shifted from their original position by the amount of the regular Λ-doubling are taken as the unperturbed states for the interaction between the close pairs.

[13] The continuous spectrum which should come in its place, is too weak to be noticed.