The Zeeman Effect in the Molecular Spectra of Hydrogen*

G. H. Dieke, S. P. Cunningham, and F. T. Byrne
Johns Hopkins University, Baltimore, Maryland
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The Zeeman effect in the molecular spectrum of hydrogen was observed for all six isotopic species for a field strength of nearly 35 000 gauss. Several thousand lines show modification in the field with many completely resolved patterns. When there is no L decoupling, the splittings are represented by the simple theory. When there is L decoupling, the splittings may be helpful for the evaluation of the degree of L decoupling and other interactions. Abnormal effects occur for some lines which are related to the Paschen-Back effect in atomic spectra.

In a molecular spectrum of this type the observed Zeeman effects are a valuable aid for the classification and interpretation of the lines fully as much as in atomic spectra.

I. INTRODUCTION

RELATIVELY little is known experimentally about the behavior of molecular spectra when the light source is placed in a magnetic field. Because the molecular spectrum of hydrogen has a great variety of different types of energy levels it appears particularly well-suited for a study of the molecular Zeeman effect. Such a study was undertaken in this laboratory on the spectra of all six isotopic species, H_2, DH, D_2, TH, TD, and T_2, primarily to obtain evidence which might help in the interpretation of as yet unclassified lines. The present paper presents the experimental details and data on some known bands which are of interest as they show a greater variety of effects and more complete resolution than have been observed in any other molecular spectrum.

In the past the Zeeman effect of the H_2 spectrum was studied by Dufour[1] and Croze.[2] These investigators worked with relatively weak magnetic fields and spectrographs of only moderate resolving power. Furthermore the technique of exciting the spectrum with great intensity was unknown to them. They reported that most of the H_2 lines were unaffected by the magnetic field but found together about 68 lines which appeared as doublets of up to normal separation. Lack of knowledge of the structure of the spectrum made an interpretation impossible at the time. It now turns out that these old observations gave an entirely inadequate picture of the Zeeman effect of H_2.

2. EXPERIMENTAL PROCEDURE

The magnet used for this work, a Bitter magnet manufactured by A. D. Little,[3] was able to give a field strength of about 35 000 gauss with pole pieces of one-inch diameter and an air gap of about 23.8 mm width, with a power input of 25 kilowatts. For some exposures 5-inch pole pieces were used in order to get uniformity over a larger area, or wider gaps were used when it was necessary to accommodate wider discharge tubes. The field strength under those conditions was not much above 30 000 gauss. In the beginning a few exposures were made with narrower gaps and field strengths up to 40 000 gauss. In all cases measurement of the field strength was possible with the help of atomic lines with known Zeeman effects. In particular, the singlet lines of helium were found convenient.

In the past the greatest drawback for getting satisfactory Zeeman effects from gas discharges has been the difficulty of maintaining the discharge in a strong magnetic field, particularly when the discharge is perpendicular to the lines of force. For direct current or low-frequency alternating current discharges the ions are forced against the walls and the tube will be destroyed in a very short time. Much better results are obtained with high-frequency discharges, particularly at fairly high gas pressures. There is a tendency even under those conditions for the discharge to go out when the field is turned on. Moreover, it is considerably more difficult to maintain a discharge in hydrogen than in most other gases. Attempts to use neon or helium as a carrier gas did not give any noticeable improvements, for at hydrogen pressures sufficient to bring out the molecular spectrum strongly the discharge would be inhibited in a magnetic field.

Successful spectra were obtained with a 200-megacycle triode generator and external electrodes and with a 2500-megacycle magnetron generator with a tuned cavity. In the latter case the fields were limited because of the necessity of wider gap spacings in order that the cavity could be accommodated between the pole pieces. With the 200-megacycle discharge observations were made first by observing perpendicularly to the axis of the tube. The discharge was forced through perpendicularly to the field by placing external electrodes a suitable distance apart. Although we obtained a number of satisfactory exposures with this arrangement, it had several disadvantages. The gas pressure had to be fairly high, which resulted in broader lines. The light silver coating of the inside walls of the tube, necessary to bring out the molecular spectrum with satisfactory intensity, attenuated the light. Moreover the discharge

* This work was carried out with the support of the U. S. Atomic Energy Commission.
[1] A. Dufour, J. de phys. **8**, 237 (1909).
[2] F. Croze, Ann. phys. **1**, 35 (1914).
[3] F. Bitter and F. E. Reed, Rev. Sci. Instr. **22**, 171 (1951).

in the magnetic field heated the gas and the tube walls considerably. This reduced the life of the tube.

After experimenting with several tubes of special construction which seemed to give no particular advantages the bulk of the exposures were made with the following procedure which, although it probably does not present the optimum condition, had the advantage of allowing us to use the discharge tubes already available for the general photography of the spectrum. These tubes[4] are simple and cheap and can easily be replaced when damaged.

The axis of the tube was placed horizontally, directed toward the slit of the spectrograph. It was normal to the direction of the magnetic field but the discharge was parallel to the field between external electrodes placed between the tube and the pole pieces (Fig. 1). The latter were protected by thin mica sheets. The size of the electrodes guaranteed that the discharge would take place only where the field was constant. The observations were made end on. With maximum power, when the discharge was quite bright, frequent breakdowns (after one to 20 hours of operation)

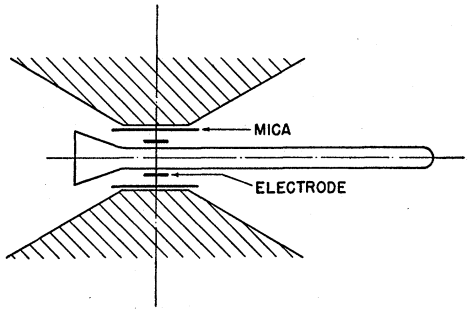

FIG. 1. Placement of the discharge tube between the pole pieces of the magnet.

occurred even with this arrangement. We believe that this was due to dielectric heating of flaws in the quartz or Pyrex walls. This resulted in weakening of these spots, which were then punctured by the discharge. With Pyrex, a local softening of the glass could be observed although there was no excessive general heating of the tube walls in the discharge region. An air jet directed at the tube provided enough cooling.

In order to avoid the chances of breakdown, particularly for the tubes containing tritium, the discharge was run at reduced power. Exposure times for the visible were then of the order of ten hours without a polarizer.

In the visible satisfactory exposures of even the faintest lines could be obtained up to about 6300A. The limitations on weak lines were imposed by the complexity of the spectrum in the magnetic field, which was liable to make weak lines disappear in the patterns of the stronger ones. Also the continuous background was more unfavorable as it retained its full strength while the intensity of the lines was distributed over numerous components. In the infrared up to about 9000A satisfactory exposures were obtained showing all the stronger lines. Work is being continued to extend the observations to longer wavelengths. The number of lines that are noticeably affected by the magnetic field probably runs into thousands. The present paper gives only the observations on a few of the most fundamental band systems.

All exposures were made in the first or second order of a 21-foot grating in a Paschen mounting with a dispersion of about 1.2 and 0.6A per mm, respectively. The polarizations were separated with a calcite rhomb except for the fainter discharges or except for instances when the weak lines in unfavorable regions were desired. In such cases the polarizations were not separated. Exposure times lasted up to 12 hours. The constancy of the field was adequate without any special precautions since the voltage fluctuations in the power supply usually did not exceed one percent. The resolution of the patterns was limited in most cases by line widths due to pressure broadening. The field strength for all the measured plates was 34 500 gauss.

3. THEORETICAL BACKGROUND

The molecular spectrum of hydrogen consists of singlet and triplets. The triplet separation in the most favorable cases is only about 0.20 cm^{-1}. It cannot be resolved under the discharge conditions prevailing in a magnetic field. Complete Paschen-Back effect would result anyway even at moderate fields. For our purpose the behavior of all lines is that of singlet lines, and the electron spin can be left completely out of the discussion. The general structure of the H_2 spectrum is discussed in Richardson's monograph,[5] that of the other isotopic species in previous publications from this laboratory.[6]

Unless interactions between close levels complicate the picture, the energy change due to the magnetic field is given by

$$E=gMa_0H, \tag{1}$$

where H is the strength of the magnetic field, $a_0=e/4\pi mr=4.67\times10^{-3}$ cm^{-1}/gauss the normal splitting, M the magnetic quantum number ($-M\leq K\leq M$), and g the ratio between the average magnetic moment (averaged over the rotation) of the molecule (in Bohr magnetons) to the total angular momentum K (in

[4] G. H. Dieke and S. P. Cunningham, J. Opt. Soc. Am. **42**, 187 (1952).

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

[6] G. H. Dieke and R. W. Blue, Phys. Rev. **47**, 261 (1935), $3p\,^3\Pi\rightarrow2s\,^3\Sigma$, D_2 and DH; G. H. Dieke, Phys. Rev. **48**, 606 (1935), $3p\,^3\Sigma\rightarrow2s\,^3\Sigma$ of D_2 and DH; G. H. Dieke, Phys. Rev. **50** 797 (1936), $2s\,^1\Sigma\rightarrow2p\,^1\Sigma$ of H_2, DH and D_2; G. H. Dieke and M. N. Lewis, Phys. Rev. **52**, 100 (1937), $3d\,^1\Sigma$, $\Pi\rightarrow2p\,^1\Sigma$ of DH and D_2; G. H. Dieke, Phys. Rev. **54**, 440 (1938), $3d\,^1\Sigma$, Π, $\Delta\rightarrow2p\,^1\Pi$ of H_2; G. H. Dieke and F. T. Tomkins, Phys. Rev. **76**, 283 (1949), $3p\,^3\Pi\rightarrow2s\,^3\Sigma$ of TH and T_2; G. H. Dieke and F. T. Tomkins, Phys. Rev. **82**, 796 (1951), $3p\,^3\Sigma\rightarrow2s\,^3\Sigma$ of TH and T_2. Classifications of a number of other band systems are completed but not yet published.

units $\hbar$). As in the case of atomic levels, g measures the separation between the $2K+1$ magnetic levels.

If L is coupled to the internuclear axis (case b), we have[7]

$$g=\Lambda^2/[K(K+1)], \quad (2)$$

while in the other extreme, when L is coupled to the axis of rotation (case d) and has a component r along this axis,

$$g=[L(L+1)+r(2K+1)-r^2]/[2K(K+1)]. \quad (3)$$

The relative intensities are also given by Millis.[7] The first three lines in each branch are shown in Fig. 2.

For the molecular hydrogen spectrum, the p levels are the only levels with $L\neq 0$ which have good case b coupling and can be expected to satisfy formula (2). The other levels show strong though not complete L decoupling. The expected separations will then lie much closer to (3) though the actual values can be obtained only by rather tedious perturbation calculations.

4. RESULTS

In the magnetic field the molecular hydrogen spectrum is greatly modified. Although some lines remain single and show no appreciable broadening, many others have well-resolved Zeeman patterns. Between these two extremes there are intermediate cases, such as broad unresolved patterns or broadened or diffuse lines. Naturally the resolved patterns are of greatest interest. We have been able to resolve lines with as many as 17 components. In general the patterns are symmetric and in many cases consist of equidistant lines. The latter situation occurs when one of the two states, usually the final state, is not split. The pattern then represents the splitting of the initial state. We shall deal with this case in greater detail below. In general the relative intensities and the polarization of the lines are in agreement with the simple theory.

Occasionally asymmetrical patterns are observed. These are due to interactions related to the Paschen-Back effect in atomic spectra. Perturbations in the original spectrum may also give rise to anomalous effects.

When the spectra with and without field are compared, often a number of intensity changes are observed. These are particularly noticeable when the discharge is perpendicular to the magnetic field. Although genuine changes in intensity, because of an influence of the magnetic field on the transition probability, are entirely possible, it turns out that the most obvious changes observed here are only indirectly connected with the magnetic field. With the field on the gas is very much more heated by the discharge than without the field. That the intensity distribution in the spectrum is quite sensitive to temperature accounts for most of the observed changes. Only a detailed study will show whether there is a direct influence of the magnetic field on the intensities.

[7] J. S. Millis, Phys. Rev. **38**, 1148 (1931).

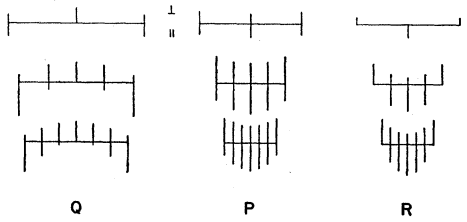

FIG. 2. Calculated Zeeman patterns of the first three lines in the Q, P, and R branches of a $\Pi\rightarrow\Sigma$ transition. The spacings are given for a completely uncoupled $d\Pi$ state. The intensities and polarization are independent of the coupling.

5. LEVELS WITHOUT L DECOUPLING

The $3p\,^3\Pi\rightarrow 2s\,^3\Sigma$ bands are the best example of a case where no L-decoupling is involved. The situation is similar to that of the $^1\Sigma\rightarrow{}^1\Pi$ bands of CO investigated by Crawford, Kemble, and Mulliken.[8] The first lines in all three branches are completely resolved triplets with the characteristic polarizations (see Fig. 3). The second lines are just barely resolved, whereas the higher lines are only partially resolved. In the Q branches the lines appear as narrow doublets in the parallel polarization, and the total width can be measured with fair accuracy. The g factors for the $3p\,^3\Pi$ levels of H_2 and D_2 found from such measurements are listed in Table I.

In judging the accuracy of these values and those of Table II the following remarks may be useful. For good lines free from interference the g values should be accurate to a few units in the third decimal. Measurements of the same line on different plates confirm this. The accuracy of the measurements is, however, greatly affected by even slight interferences from other lines. In a spectrum of this complexity such interferences are not rare. The accuracy is, of course, also lowered in measurements of only partly resolved patterns and is

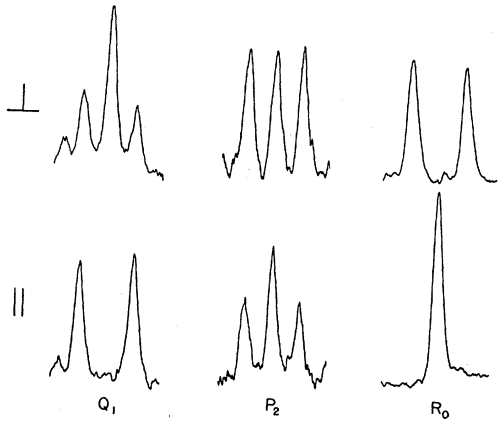

FIG. 3. Observed Zeeman patterns of the first line in each branch of the Fulcher bands ($2\rightarrow 2$ band of D_2).

[8] F. H. Crawford, Phys. Rev. **33**, 341 (1929); Kemble, Mulliken, and Crawford, Phys. Rev. **30**, 438 (1927).

TABLE I. g factors of the $3p\ ^3\Pi$ state.

	H_2					D_2							
K	$v=0$	1	2	3	4	$v=0$	1	2	3	4	5	Av	Theor
1	0.510	0.501	0.496	0.500	0.499	0.507	0.504	0.505	0.514	0.503		0.504	0.500
2	0.179	0.171	0.167	0.166	0.168	0.172	0.173	0.176	0.168	0.158	0.173	0.170	0.167
3	0.085	0.080	0.078	0.079	0.079	0.078	0.083	0.086	0.081	0.083		0.081	0.083
4	0.047	0.048	0.047			0.049	0.050	0.050	0.049	0.048	0.047	0.048	0.050
5	0.029	0.029	0.028			0.029	0.034	0.033	0.035			0.031	0.033
6						0.021	0.023	0.024	0.022			0.023	0.024
R_0	0.485	0.503	0.495	0.500		0.480	0.495	0.495	0.497	0.497		0.494	0.500
P_2	0.490	0.502	0.493	0.505		0.492	0.502	0.500	0.466	0.495			
R_1	0.171	0.163	0.128										0.167
P_3		0.154	0.143	0.128									

much less when only the edges of unresolved patterns can be measured. g values derived from such measurements are given in parentheses (see Table II).

It is seen that the observed g values in Table I are in excellent agreement with the theoretical ones. The mean of 10 observed g values for the Q_1 lines is 0.504, well within the limits of experimental errors of the theoretical value 0.500. The agreement for the higher K values is equally good even though most of these values were obtained from only partly resolved lines. One may say therefore that the p levels split exactly as the simple theory prescribes.

There are bigger fluctuations in the values for the $3p\ ^3\Pi^+$ state derived from the P and R branches. Most values that depart considerably from the theoretical ones are smaller than expected, the average being 0.494. We know that the $3p^3\ \Pi^+$ state interacts with the $3p\ ^3\Sigma$ state which has $g=0$. Such interaction would lower the g values for $3p\ ^3\Pi^+$. A complete analysis of this case, however, requires further data.

The bands from the higher $np\ ^3\Pi$ levels and the analogous singlet bands show exactly the same behavior in the magnetic field, but the data are less complete.

When both upper and lower levels are Σ states and when no L decoupling is involved, there should be no noticeable splitting of the resulting lines. In such cases the lines are observed to remain single and sharp. This is the case for the extensive $3p\ ^3\Sigma \rightarrow 2s\ ^3\Sigma$ and $2s\ ^1\Sigma \rightarrow 2p\ ^1\Sigma$ systems as well for others where only s and p electrons are involved. Because of the predominance of these systems in the near infrared, beyond 8300A the spectrum appears unaffected by the magnetic field.

6. LEVELS WITH PARTIAL L DECOUPLING

All levels with a d electron show strong L decoupling. This phenomenon, which is very pronounced in H_2, occurs also, but to a smaller extent, in other light molecules, notably He_2. The Zeeman effect in the He_2 spectrum was investigated by Millis,[7] who found general

TABLE II. g values of the $3d\ ^1\Sigma(3D)4d\ ^1\Sigma(4D)$ and $3d\ ^1\Pi(3E)$ states. The subscripts indicate the values of the vibrational quantum number v.

			H_2			DH	TH	D_2	TD	T_2		
$2\mu=$			1.00			1.33	1.50	2.00	2.40	3.00	Theoretical	
K	$3D_0$	$3D_1$	$3D_2$	$3D_3$	$4D_0$	$3D_0$	$3D_0$	$3D_0$	$3D_0$	$3D_0$	d	b
1	0.901	0.606	0.293	0.663	1.178	0.475	0.789	0.628	0.569	0.488	1.500	0
2	0.571	0.358		0.281	0.565	0.431	0.610	0.533	0.487	0.422	1.000	0
3	0.445	0.275	(0.180)	(0.217)	0.597	0.265	0.486	0.444	0.418	0.371	0.667	0
4	0.387	0.257		(0.142)		0.319	0.395	0.361	0.355	0.323	0.500	0
5	0.331	0.222	(0.150)	(0.076)	0.383	0.323	0.333	0.320	0.305	0.288	0.400	0
6	0.287					0.287	0.287	0.277			0.333	0
7	(0.111) (0.122)	0.164	(0.077)				0.249	0.240		0.225	0.286	0
8	(0.227)							0.217			0.250	0
9	(0.203)									(0.156)	0.222	0
	$3E_0^-$	$3E_1^-$	$3E_2^-$	$3E_3^-$	$4E_0^-$	$3E_0^-$	$3E_0^-$	$3E_0^-$	$3E_0^-$	$3E_0^-$		
1	0.496	0.492	0.492		0.490	0.500	0.495	0.480	0.500		0.500	0.500
2	0.412	0.341	0.281	0.236	0.729	0.338	0.322	0.272	0.258	0.23	0.833	0.167
3	0.317	0.269		(0.168)		0.276	0.250	0.210	(0.209)		0.500	0.083
4	0.256	0.214		(0.145)				0.169	(0.163)	0.152	0.350	0.050
5	(0.204)	(0.197)							(0.141)		0.267	0.033
6	(0.182)	(0.140)								(0.110)	0.214	0.024
	$3E_0^+$	$3E_1^+$	$3E_2^+$	$3E_3^+$		$3E_0^+$	$3E_0^+$	$3E_0^+$	$3E_0^+$	$3E_0^+$		
1	0.500	0.354	0.379	0.267		0.356	0.307	0.163		0	1.500	0.500
2	(0.140)	(0.169)				0.236	0.244	0.243			0.500	0.167
3	*bb*	(0.050)				(0.091)		0.198		(0.163)	0.250	0.083

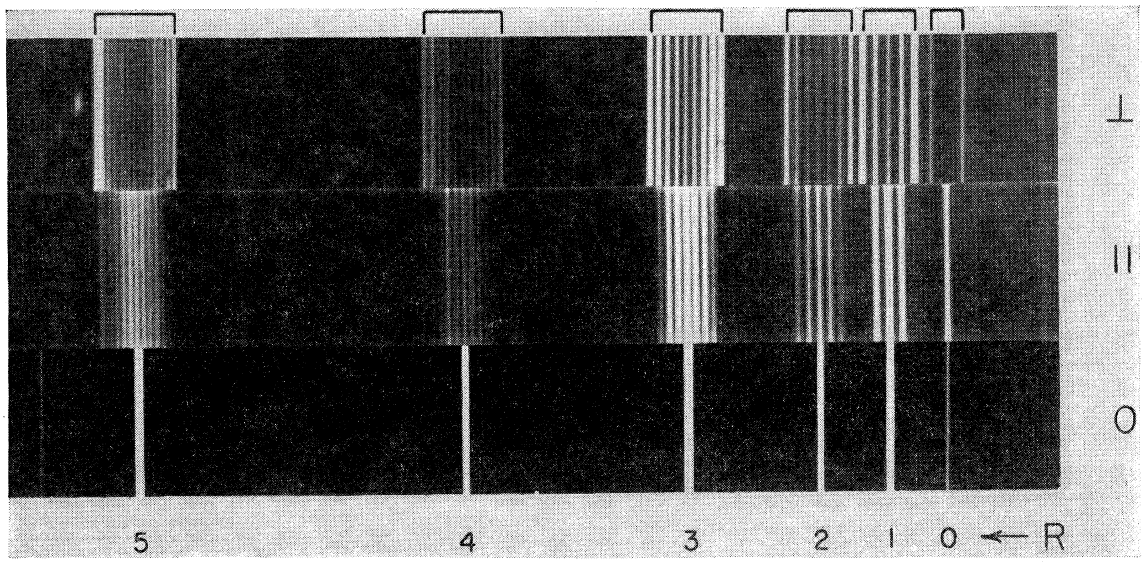

FIG. 4. The first few lines of the R branch of the $3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Sigma(0\rightarrow 0)$ band of D_2.

qualitative agreement with the theoretical expectations. The conditions in He_2 are, however, considerably less favorable than for any of the hydrogen molecules, partly because the L decoupling is less, partly because the strong bands are transitions to a Π state, and therefore the observed Zeeman effects have more complicated patterns as both initial and final state are split.

For hydrogen, even a casual inspection of the plates shows that there are many lines with splittings much larger than possible for normal (nondecoupled) levels. Figure 4 shows part of the R branch of the $3d\,{}^1\Sigma_0 \rightarrow 2p\,{}^1\Sigma_0$ transition in D_2. The lines show all clearly resolved patterns while a normal Σ state should show no splitting. It is also apparent that the number of components is $2K'+1$, where K' is the rotational quantum number of the initial level. Figure 5 shows microphotometer traces of typical lines. Table II presents the measured g values for $d\Sigma$ and $d\Pi$ levels of all six species. For H_2 also higher-vibrational states are listed in order to show how the vibration affects decoupling.

A complete quantitative analysis of the data in Table II would necessitate the calculation of the g values by the very tedious perturbation method. This has not been done so far since the data are not complete enough to justify it. The following qualitative conclusions can be drawn from the data:

1. The $K=1$ state of the $d\Pi^-$ level should not show any L decoupling since it cannot interact with any other state of identical symmetry with the same K. We see that the observed values are very close to the normal values $g=0.500$.

2. All other values show the influence of L decoupling even for the smallest K values. This influence is particularly large for the $d\Sigma$ states, in accord with the expectations [see formula (3)].

3. A comparison of the observed g values with theoretical ones which are valid for a complete L decoupling shows that the ratio $g_{\text{obs}}/g_{\text{theor}}$ approaches one with increasing rotation.

4. In general the amount of L-decoupling as expressed by the approach of the observed g values to the theoretical ones is largest in H_2 and decreases with increasing reduced mass μ. This is as to be expected since the rotational angular velocity, which determines the amount of L decoupling, is roughly proportional to K/μ.

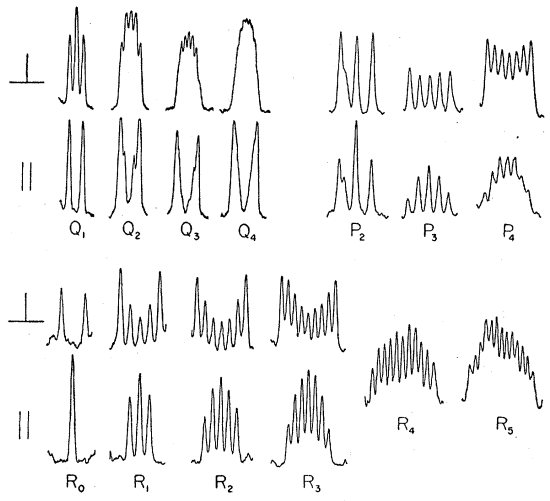

FIG. 5. Observed Zeeman patterns in the $3d\,{}^1\Sigma$ and $3p\,{}^1\Pi \rightarrow 2p\,{}^1\Sigma$ transition. All are polarized except R_4 and R_5. There is noticeable interference with extraneous lines in P_2, R_4, and R_5. Identity of the lines as follows: Q_1-Q_4: $1\rightarrow 0$ band of $3d\,{}^1\Pi \rightarrow 2p\,{}^1\Sigma$ of H_2, R_0 to R_3, P_3: $3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Sigma(0\rightarrow 0)$ of D_2; R_4, R_5 same of TH; P_2, P_4 $3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Sigma$ of H_2.

5. The degree of L decoupling is larger for $4d\Sigma$ and $4d\Pi$ than for $3d\Sigma$ and $3d\Pi$. This agrees with the fact that the larger orbit ($n=4$) is less closely coupled to the internuclear axis. On the other hand, the degree of L decoupling decreases with increasing vibrational quantum number V. This is also expected since for the greater vibrational amplitudes the influence of the internuclear axis is larger, which means a stronger coupling of L to it.

6. There are pronounced deviations from the rules expressed under (4) and (5). These must be explained by particular interactions. For instance, the g values for $v=3$ in H_2 are larger than those for $v=2$, contrary to what should be expected. The $v=3$ level of $3d\Sigma$ lies very close to the much more strongly decoupled $4d\Sigma$ and presumably is influenced by it, which would result in larger apparent decoupling. The g values of $3d\Sigma$ for DH are smaller than one should expect from its reduced mass. There appears no obvious reason for this. On the other hand, there exist many interactions for this type of level, some of them only imperfectly known. A more detailed study of these interactions will undoubtedly clear up the reasons for the anomalous g values.

7. PERTURBATIONS

Whenever interacting energy levels lie close together irregular shifts in the levels may occur, which usually are called perturbations. Such perturbations may occur in a molecular spectrum without a magnetic field or new ones may be introduced by the field. There are examples of both types in the molecular hydrogen spectrum.

Ordinary perturbations may show anomalous Zeeman effects because the wave function of the perturbed state has intermixed with it the wave function of the perturbing state. This may result in anomalous Zeeman splittings which are not necessarily between those of the two interacting states since the amplitudes of the wave functions are added with the proper phase factors. An example of this type of perturbation occurs evidently in the $3d\Sigma_0$ state of H_2. The R_6 line is displaced and instead of one line at the expected place there are two, one at longer, the other at shorter, wavelengths. Both show a partly resolved Zeeman splitting, but smaller than that extrapolated from the preceding lines.

An example of an interaction caused by the magnetic field occurs in the $3d\,{}^1\Pi \rightarrow 2p\,{}^1\Sigma$ bands. This type of effect does not seem to have been observed previously. It is closely analogous to the Paschen-Back effect in atomic spectra.

In the Paschen-Back effect the coupling between the orbital angular momentum and the electron spin is small compared to the coupling of these two vectors with the magnetic field. This means that they orient themselves in the magnetic field independently of each other. This results in the well known Paschen-Back effect, the chief feature of which is a great reduction in the number of observed Zeeman components.

The effect observed here is similar to the Paschen-Back effect except that the two angular-momentum vectors involved are the angular momentum R of the rotation of the nuclei and the orbital angular momentum L of the electrons. Ordinarily R and L are coupled together and the resultant K orients itself in the magnetic field. The degree of coupling manifests itself by the closeness of certain levels. If the separation of the magnetic levels becomes of the same order of magnitude as the natural separation, we begin to have an incipient Paschen-Back effect, which usually presents a very complicated picture of spacings and intensities. If the natural spacing is negligible compared to the magnetic splitting, the extreme simplification of the pattern occurs.

For complete L decoupling, when the rotational energy is proportional to $R(R+1)$ and essentially independent of the orientation of L, we would expect this effect since the coupling to the rotational or internuclear axis would be negligible to the interaction with the magnetic field even for moderate field strength. We have seen that the L decoupling is not complete even for H_2. We expect, however, a partial effect whenever two levels which differ only by the orientation of L nearly coincide. This happens in the $3d$ complex for $3d\Pi^-(K)$ and $3d\Pi^+(K-1)$ which satisfy the condition. For low values of K the Π^+ level which gives rise to the P and R branches is lower than the Π^- level which produces the Q branch. For high values of K the situation is reversed. For an intermediate value of K the levels cross over. The cross-over point, of course, does not necessarily occur at an integer value of K, but the possibility for a very close approach is present. The cross-over point is different for the different isotopic species. It takes place between $K=2$ and $K=3$ in H_2 and near $K=8$ in T_2. There is a very close approach for $K=4$ in TH and $K=8$ in T_2 which show well the simplified pattern, whereas in the other species the incomplete transformation can only be observed.

Figure 6 shows part of the observational data. Figure 6(a) shows Q_5 and P_5 of the $3d\,{}^1\Pi_0 \rightarrow 2p\,{}^1\Sigma_0$ band of D_2. The $\Pi^+(4)$ level is 3.01 cm^{-1} below $\Pi^-(5)$. In the parallel polarization the Q_5 line shows the typical pseudo-doublet structure but with greatly distorted intensities. Also the asymmetry in the pattern for P_5 can be seen. In Fig. 6(b), the $\Pi^+(5)$ level is 5.96 cm^{-1} above $\Pi^-(6)$. The asymmetries are again visible and it is evident that in both cases the inner components are weakened. In Fig. 6(c), $\Pi^-(8)$ of T_2 is only 0.68 cm^{-1} below $\Pi^+(7)$. In the magnetic field, the transformation is nearly complete. The inner components have nearly all disappeared and only two somewhat asymmetrical lines separated by 3.03 cm^{-1} remain. The case is even more extreme in Fig. 6(d), where $\Pi^-(4)$ of TH is only 0.31 cm^{-1} below $\Pi^+(3)$. In the magnetic field, two sharp lines separated by 1.70 times the normal Zeeman splitting remain with only very slight traces of asymmetry. If the levels had coincided exactly and if the

L decoupling had been complete, the separation should have been two times the normal separation.

Quantitative details of this kind of transformation can only be understood with a complete perturbation treatment of the problem. Experimental studies at different field strengths will be helpful as well. We hope to come back to this in a subsequent paper.

8. ISOTOPE EFFECT

For normal (case *b*) states the magnetic splitting should be independent of the mass and Table I shows that this is borne out by the observations. On the other hand, the degree of L decoupling depends directly on the angular rotational velocity and this is roughly inversely proportional to the reduced mass for a given K. Since the g factors depend strongly on the L decoupling, they must differ for different masses. This is exactly what was found (see Table II).

Finally, perturbations which depend on the accidental closeness of two sensitive levels are quite different for the different isotopes. Moreover, the interaction matrices depend on the angular velocity of rotation or the amplitudes of vibration, which are different for the isotopic species. Therefore any perturbation or interaction effects must be quite different for the different isotopic species, and this also agrees with the observations.

9. LINE CLASSIFICATION AND ZEEMAN EFFECT

In a spectrum of the complexity of the molecular hydrogen spectrum, there are two major problems of classification and interpretation. The first is to find the often widely scattered lines that form a particular band. This may not be easy, as the regularities are often not obvious and many lines of different origin intervene. The second problem concerns the interpretation of a given band, that is, the identification of the electronic levels which are responsible for the transition. Both problems are made very considerably easier when the Zeeman effects of the lines are known. If the splitting can be resolved, the classification of the line can be ascertained without ambiguity. The information is less complete when the pattern is only partly resolved, but may be decisive for clearing up uncertainties. From the size of the splitting, conclusions may be drawn as to the nature of the electronic state. It is, for instance, immediately obvious, even if the pattern is only very imperfectly resolved, whether a line is a Q or an R line, for the former forms a close doublet in the parallel but not in the perpendicular component, whereas the situation is just the reverse for an R line. (Compare for instance Q_4 and R_3 in Fig. 5.) A distinction between a P and an R line can be made easily through observations parallel to the lines of force. It can easily be seen from the intensity relations that for positive g, the unresolved doublet of an R line must show circular polarization in the same sense as a normal triplet, a P line, however, in the opposite sense. The situation would be just the reverse for negative g values. The presence of both "regular" and "irregular" doublets when observations are made parallel to the lines of force was discovered in the early observations of Dufour.[1]

Much of the classification of the molecular hydrogen spectra is well established. The Zeeman effect gives a complete and detailed confirmation. There are a number of bands which are either dubious in their structure or where the interpretation is uncertain. In particular, there are many bands found by Richardson and his co-workers which do not seem to fit into the general energy-level scheme of the molecule and have therefore been attributed to initial levels with both electrons excited. The status of most of these is still very uncertain.

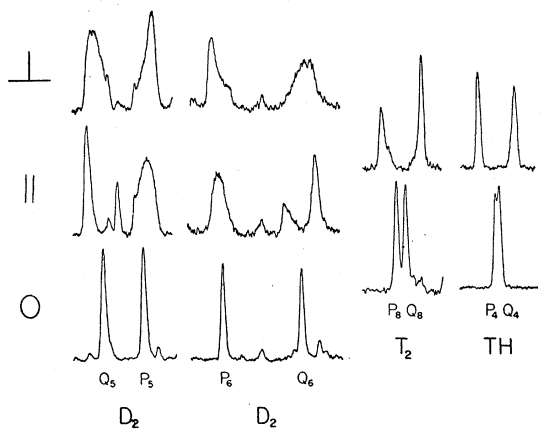

FIG. 6. Magnetic Interaction between the $3d\Pi^-(K)$ and $3d\Pi^+(K-1)$ levels. $Q(K)$ and $P(K)$ lines polarized for D_2, unpolarized for TH and T_2.

At the present stage we can say the following about these levels which are all $^1\Sigma$ levels:

$3\,^1K$ shows a small but distinct Zeeman splitting for the lower K values, and at least one of the electrons must have $l \neq 0$.

The following levels, on the other hand, show no appreciable splitting and therefore cannot show any L decoupling, the 4142.8 progression, ^1L, ^1M, ^1N, $3\,^1O$.

It is not surprising that we have found a few cases where the Zeeman effects do not confirm the accepted classification. In a number of cases the behavior in the magnetic field has made it possible to identify some as yet unclassified lines.

Most of the wavelength measurements on which this paper is based were very ably made by Miss Dorothy Taylor.

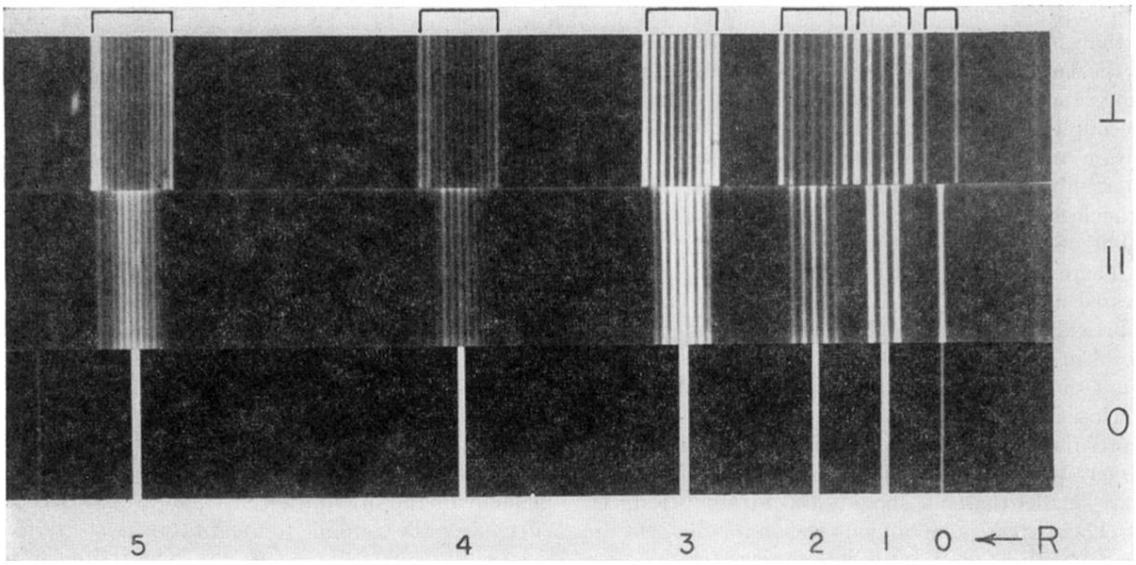

FIG. 4. The first few lines of the R branch of the $3d\,{}^1\Sigma \rightarrow 2p\,{}^1\Sigma (0 \rightarrow 0)$ band of D_2.