Zeeman Effect of Perturbed Terms in the CO Angstrom Bands

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(Received September 29, 1932)

The Zeeman effect of the perturbed lines in the CO angstrom bands ($^1\Sigma \rightarrow {}^1\Pi$) is described. The perturbations are multiple, occur in the $^1\Pi$ state, and contain excess, much-displaced lines. New lines extending the "resonance" curves of Rosenthal and Jenkins are found. The perturbed lines show large, irregular Zeeman patterns, whereas the neighboring band lines with these intermediate and high J values are apparently insensitive to the magnetic field. Always the greater the displacement of the perturbed line, the larger its Zeeman effect. The patterns differ at each perturbation point: they are either broad, asymmetrical doublets; very broad, uniform blocks; sharp, narrow doublets; or just a shift, increasing the amount of the perturbation. An explanation is offered, assuming the perturbing state to be case a $^3\Pi$.

INTRODUCTION

THE details of the perturbations in a number of band spectra have been examined by Rosenthal and Jenkins,[1] Dieke[2] and others. These observations are in general in good agreement with the requirements of the theory as set up by Kronig[3] and by Ittmann.[4] Briefly, perturbations should occur whenever two energy levels for the molecule having the same J value approach closely to one another, the two levels having the same symmetry characteristics, Λ values the same or differing by at most 1 unit, the same multiplicity, and about the same internuclear distance. The perturbed energy levels do not cross, but rather separate from each other, so that the curves showing the departures of the perturbed band lines from the regular course of the branches to which they belong are of the "resonance" type.

Especially violent perturbations occur in the CO angstrom bands[1] ($^1\Sigma \rightarrow {}^1\Pi$), particularly in the 0, 0 band at 4511A. Rosenthal and Jenkins were the first to give a correct quantum analysis of this band, basing their assignments on the necessity of obtaining smooth deviation curves for the perturbed lines, agreement with known $\Delta_2F'(J)$ combination differences, and the abandonment of the notion that the Λ-doubling in the $^1\Pi$ state should remain small and regular. This work showed that the perturbations are in the lower $^1\Pi$ state and that they are multiple, coming in this 0, 0 band at $J=9$, 16, 17 and >30 in the P and R branches and at $J=12$, 29 and >35 in the Q branch. From the fact that these perturbations are multiple and from an examination of the nature of the near-lying levels of CO, it was concluded that the perturbing state is probably a $^3\Pi$ state, in violation of the Kronig rule that the

[1] J. E. Rosenthal and F. A. Jenkins, Proc. Nat. Acad. **15,** 381 and 896 (1929).
[2] G. H. Dieke, Phys. Rev. **38,** 646 (1931).
[3] R. de L. Kronig, Zeits. f. Physik **50,** 347 (1928).
[4] G. P. Ittmann, Zeits. f. Physik **71,** 616 (1931).

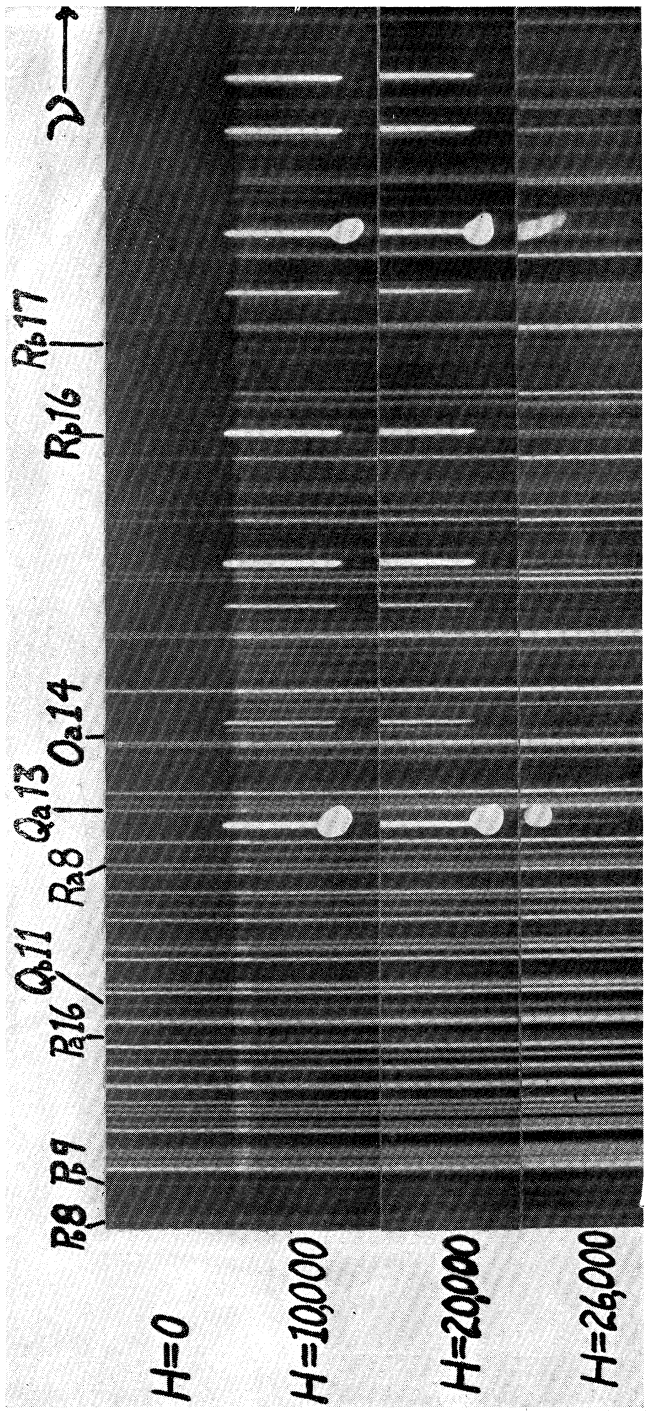


Fig. 1. The (0, 0) CO angstrom band at 4511A with magnetic field strengths up to 26,000 gauss. Several of the more violently perturbed lines are indicated, others being of too low intensity to show in the reproduction. Fe comparison lines.

perturbing terms should have the same multiplicity. We shall return to this point below.

In his work on the regular Zeeman effect in these CO bands, Crawford[5] noted the existence of large, irregular Zeeman effects for certain of the band lines which are involved in these perturbations. In the present investigation the details of these peculiar Zeeman patterns have been examined, and possible explanations are presented in connection with the facts about the perturbations and the probable nature of the interacting levels.

Experimental Procedure

Spectrograms of the 0, 0 and 0, 1 bands of the CO angstrom system were obtained in the second order of the 21-foot concave grating in a stigmatic mounting, the dispersion being approximately 2.42A per mm. The magnetic field strengths varied from 10,000 gauss to 26,700 gauss. On each plate was placed in addition to the field exposure a no-field comparison spectrum and the spectrum of the Fe arc for wave-length determinations. The source was a 15,000 volt a.c. discharge between small copper disks 3 to 4 mm apart, mounted in the gap space of a large Weiss electromagnet. These electrodes were attached to the electrode holders of a modified Back chamber, and were insulated from the pole faces with mica. CO_2 gas from a commercial cylinder was pumped slowly through the discharge chamber at a pressure of about 5 mm, in some cases directly from the cylinder, while in other cases the gas was first passed through a hot copper oxide tube and a tube filled with P_2O_5. The time of exposure was of the order of 12 hours each for the Zeeman effect spectrogram and for the no-field comparison.

This source is of course weak, but because of the increased intensity of the spectra with the grating in the stigmatic mounting, the exposure times were not excessive. Disturbing discharge in regions outside that of uniform field was effectually reduced by having copper disk electrodes but 4 mm in diameter as against a pole face diameter of 20 mm, and by taking care to see that the gas pressure never became too low. A faint background of impurity lines increasing in intensity towards the violet is present on all the spectrograms. It was found, however, that by allowing a slight leak of air into the CO_2, this unwanted spectrum was reduced in intensity to the point where it caused but little trouble in the measuring of the spectrograms. The N_2^+ bands thus introduced could be tolerated because they do not overlap the interesting perturbation points in the CO bands.[6] In Fig. 1 are to be seen Zeeman patterns of some of the perturbed lines in the (0, 0) 4511A band at the several field strengths.

Additional Lines at Perturbation Points in 0, 0 Band

A marked feature of the quantum analysis of the (0, 0) band as made by Rosenthal and Jenkins[1] is the occurrence of two lines for each of one or more

[5] F. H. Crawford, Phys. Rev. **33**, 341 (1929).

[6] These $^2\Sigma \rightarrow {}^2\Sigma$ bands of N_2^+ also display interesting Zeeman patterns for lines involved in their perturbations. These perturbations are very similar to those in the corresponding band system of the isoelectronic molecule CN, and will be the object of further study.

J values at the center of a perturbation. Furthermore, they reported the sum of the intensities of the two lines to be always about that calculated by interpolation for an unperturbed line of that J value. Also, the greater the displacement of the line the less is its intensity. According to the theory this appearance of extra lines is to be expected, for around the perturbation points the wave functions of the molecule for the two electronic states concerned become "mixed," losing their separate identity, with the result that transitions from the upper $^1\Sigma$ state to the perturbing state ($^3\Pi$?) are possible.

There are in fact more of these extra lines than are given in Table I of reference 1. The assignments of these additional lines are given in Table I,

TABLE I. *Quantum assignments of lines of intermediate J value in the (0, 0) CO angstrom band.*

J''	P		Q		R	
	a	*b*	*a*	*b*	*a*	*b*
7	22,164.60		22,191.30		22,222.99	
8	167.25	150.90*	197.10		233.45	217.08*
9	172.10	159.48	203.84		246.09	233.45
10	180.96	166.32	211.55	185.00*	d	248.11
11		171.65	220.63	200.73		261.16
12		176.87	231.85	214.38		274.08
13		182.54	246.09	227.05		287.59
14		188.97	263.48	238.77		301.79
15	179.86*	196.47		250.26	d	317.02
16	193.44	205.92		261.92	321.80	334.21
17	205.41	219.03*		274.08	341.39	355.32*
18	215.59			286.77	359.43	

where the new lines are indicated by a *. The line $P_b(8)$ lies some 12 cm^{-1} beyond the head of the band, and there is even an indication of a line P_b (7) still further to the red. The new lines are all displaced many cm^{-1} from the unperturbed points for the particular J values, and are all consequently of low intensity. The correctness of the assignments is attested however by the existence of exactly the required $\Delta_2F'(J)$ combination differences, and by the fact that they are all much affected by the magnetic field, being even broadened slightly in the no-field comparison spectrum by the field due to the residual magnetism in the magnet. Strong lines of other branches lie in the positions indicated for R_a (10) and R_a (15), making their observation impossible. The perturbations in the region of higher J values have not been examined in detail.

OBSERVED ZEEMAN PATTERNS

All of the band lines in the immediate neighborhood of the perturbations exhibit large, irregular Zeeman patterns, whereas the regular Zeeman effect for lines with these intermediate and high J values for a $^1\Sigma \rightarrow {}^1\Pi$ transition is so small as to leave the unperturbed lines totally unaffected by the magnetic field. There is a different type of Zeeman effect at each of the perturbations in the (0, 0) band, and always the perturbed lines having the greatest displacements are magnetically the most sensitive. A brief tabulation of some of the details of these patterns at three different field strengths is given in

Table II. Measurement on some of the perturbed lines is prevented either by their nearness to or fusion with other lines in the band, or by their low inten-

TABLE II. *Zeeman patterns of perturbed band lines in the (0, 0) CO angstrom band at 4511A* cm^{-1} units. + indicates a shift to the high-frequency side, − to the low-frequency side of the no-field band line.

	10,000 gauss	20,000 gauss	26,000 gauss
a. P, R branch perturbation at $J=9$.			
$P_b(8)$	Broadened +0.80 to −0.84 Min. intens. in center + side stronger	Broad doub. −0.75 to −1.35 and (stronger) +0.62 to +1.34	Broad doublet
$P_b(9)$	Broadened +0.31 to −0.49	Broadened (stronger) −0.83 to −0.36 and weaker to +1.07	Broadened, − stronger
$R_a(7)$	No effect	Slight sym. broadening	Broadened +0.38 to −0.63
$R_a(8)$ + $R_b(9)$	Slight sym. broadening	Broadened +0.42 to −0.38	Broadened +0.43 to −0.56
$R_b(8)$	Broadened +0.72 to −0.83 Min. in center, + side stronger	Broad doub. + stronger +0.48 to +1.25. −block block fuses into $P_a(18)$	Stronger +0.38 to +1.10 − block weaker
$R_b(10)$	No effect	Broadened +0.33 to −0.26	Broadened +0.40 to −0.45
b. Q branch perturbation at $J=12$.			
$Q_a(10)$	No effect	No effect	
$Q_a(11)$	No effect	Shift of +0.06. Sharp	Slight + shift
$Q_a(12)$	No effect	Shift of +0.13. Sharp	Shift of +0.15. Sharp
$Q_a(13)$	No effect	Shift of +0.51. Sharp	Shift of +0.67. Slight broadening
$Q_a(14)$	No effect	Shift of +0.89. Slight broadening	Shift of +1.06. Slight broadening
$Q_b(11)$	No effect	Shift of −0.32. Sharp	Shift of −0.58. Slight broadening
$Q_b(12)$	No effect	Slight—shift	Definite—shift
$Q_b(13)$	No effect	No effect	Shift of −0.12
$Q_b(14)$	No effect	No effect	Shift of −0.06
c. P, R branch perturbation at $J=16$.			
$P_a(16)$	Broadened +0.55 to −0.56	Broad block +1.09 to −1.03	Very broad and diffuse
$R_b(15)$	No effect	Slight sym. broadening	Broadened +0.49 to −0.27.
$R_b(16)$	Broadened +0.25 to −0.26	Broadened +0.62 to −0.66	Broadened +0.79 to −0.73
$R_b(17)$	Slight broadening	Broad doub. +0.38 to +1.14 and −0.39 to —	Broad doub +0.24 to +1.28 −block weaker
$R_a(16)$	Broad block 1.13 wide	Strong −block	Stronger at −1.04
$R_a(17)$	Broadened +0.27 to −0.26	Broadened +0.36 to −0.26	Sym. broadened
$R_a(18)$	No effect	Slight broadening	Slight broadening
d. Q branch perturbation at $J=29$.			
$Q(30)$			Sharp doub. +0.30 and (weaker) −0.20.

sity. A sufficient number of observations can be made at each perturbation, however, to enable one to say definitely the kind of pattern that is developed.

Several points about these Zeeman patterns should be emphasized. The doublets which the field produces for some of the most perturbed lines are never quite symmetrically placed with respect to the original line, the asymmetry increasing with increasing field strength. Also when a line which at low field strength is just uniformly broadened splits in stronger fields into two blocks of radiation, the two are never of the same intensity, the block on the side of increased perturbation energy being in some instances the stronger, while for other lines the reverse is true. In the Q branch around $J=12$ the displaced lines are not noticeably affected by a field of 10,000 gauss, although the perturbation is just as violent as the first two P and R branch perturbations, i.e., the two sets of interacting levels must come just as close to each other. The effect of the higher field strengths on these Q lines is merely to increase slightly the magnitude of their displacement in the perturbation, the Q_a lines being shifted to higher frequencies, the Q_b lines to lower frequencies. The most perturbed lines experience the greatest shift, and are but slightly broader than the corresponding no-field lines. A similar Zeeman effect has been observed for one of the perturbations in the (0, 1) band, but has not been worked out in detail.

The lines at the center of the P and R branch perturbation around $J=16$ mostly undergo a uniform symmetrical broadening as the field increases, but the line R_b (17) which has the largest displacement in the perturbation does become a broad doublet at the higher field strengths. And the widths of these patterns is just as large as those in the first P, R perturbation, despite the fact that the overall spread of the $2J+1$ component levels due to the field in the $^1\Pi$ state is but one half as great (varies as $1/J$), while the perturbations are of about the same degree. This would indicate that the interacting levels of the other electronic state are here more affected by the field, for instance that they are $^3\Pi_2$ levels, while for the first perturbation $^3\Pi_0$ levels are responsible. We shall mention this again in the discussion below.

Finally the character of the Q (30) line pattern at the high field strength should be mentioned. This is a narrow, sharp, but not symmetrical doublet, and the same is true of the pattern for the line Q (29) at the second Q-branch perturbation in the (0, 1) band. One would expect narrower Zeeman patterns with sharper components, other things being equal, from these perturbed lines of high J values because of the decreased width of the group of Zeeman sublevels if J is large. And for the same reason only the one or two most displaced lines at these perturbations of high rotational levels should be appreciably affected by the magnetic field. Our observations show this to be the case.

Discussion

As Rosenthal and Jenkins have shown,[1] the $a^3\Pi$ state of CO could be the state that interacts with the $^1\Pi$ levels to produce these perturbations, for extrapolation of the known vibrational levels of the a state indicates that its $v=10$ level approaches closely $^1\Pi^{(0)}$ with nearly the same ω values. Or it may be that the $d(^3\Pi?)$ level which lies below and very close to the $^1\Pi$

state is responsible for the perturbations. There is definitely no singlet level in this energy range. Also the fact that the perturbations are multiple would indicate that the perturbing terms do not belong to a singlet state. And in addition the finding of a very different type of Zeeman effect at each of the principal perturbations in the (0, 0) band seems to require different interacting levels at each of the points, in order that some variations in the arrangement of the magnetic sublevels exist. It is true that $^3\Pi$ and $^1\Pi$ levels perturbing each other constitutes a violation of the Kronig rule that the two perturbing states must have the same multiplicity. However, this rule need not be expected to hold here, for singlet-triplet transitions of fair intensity do occur in CO. And from such a $^1\Pi$, $^3\Pi$ interaction as many as six perturbations could be produced in one of the $^1\Sigma \rightarrow {}^1\Pi$ bands, since all Π terms are doubled (Λ-doubling).

It is reasonable to assume that the $^3\Pi$ state is fairly close to case *a*, for the separation[7] of the P_1 and P_3 branches near the origins of the $^3\Sigma \rightarrow a^3\Pi$ third positive CO bands is some 50 to 60 cm^{-1}. This spacing is almost entirely due to the multiplet intervals in the $^3\Pi$ level, since Dieke and Mauchly report that the triplet separation of the $^3\Sigma$ state is unnoticeable near the origin.[8] In the range of rotational energy levels in which we are interested, then, this spacing of the $^3\Pi$ levels is still probably considerably greater than the splitting produced by the magnetic field. The partial transition towards case *b* with increasing rotational energy would only tend to make the group of magnetic sublevels slightly asymmetrical with respect to the no-field level.

In case *a* states of diatomic molecules the additional energy of the component levels due to the magnetic field is given by the well-known formula[9]

$$W_{\text{mag.}} = \frac{\Lambda(\Lambda + 2\Sigma)M}{J(J+1)} \frac{eh}{4\Pi mc} |H| \tag{1}$$

where all the symbols have their usual significance. For $^1\Pi$ levels this reduces to

$$W_{\text{mag.}} = \frac{+M}{J(J+1)} \left(\frac{eh}{4\Pi mc} |H| \right) \tag{1a}$$

while for the $^3\Pi_0$, $^3\Pi_1$ and $^3\Pi_2$ levels with $\Sigma = -1, 0$ and $+1$, respectively, we have

$$^3\Pi_0 : W_{\text{mag.}} = [-M/J(J+1)](\Delta\nu_{\text{norm}}) \tag{1b}$$

$$^3\Pi_1 : W_{\text{mag.}} = [+M/J(J+1)](\Delta\nu_{\text{norm}}) \tag{1c}$$

$$^3\Pi_2 : W_{\text{mag.}} = [+3M/J(J+1)](\Delta\nu_{\text{norm}}). \tag{1d}$$

[7] R. K. Asundi, Proc. Roy. Soc. **A124**, 277 (1929).
[8] G. H. Dieke and J. W. Mauchly, Phys. Rev. **40**, 123 A(1932).
[9] Cf. for instance, R. de L. Kronig, *Band Spectra and Molecular Structure*, p. 37.

The $^3\Pi_1$ levels have exactly the same Zeeman splitting, then, as $^1\Pi$ levels of the same J value, while for $^3\Pi_0$ the splitting is of exactly the same amount but with the level $+M$ lowest and the level $-M$ highest. In $^3\Pi_2$ the overall width of the group of sublevels is three times that in the $^3\Pi_0$ and $^3\Pi_1$ levels.

As an aid in discussing the effect of the magnetic field on the perturbed levels, the possible arrangements of these levels at the intersection points is sketched in Fig. 2, only the extreme values of $M=\pm J$ being shown. If the $^3\Pi$ level lies just below the $^1\Pi$, the explanation is the same with the substitution of $-M$ for $+M$ and $+M$ for $-M$ throughout. Now the matrix elements of the perturbation energy will be different from zero only if diagonal in M as well as J; i.e., only levels of the same M will perturb each other. With a normal $^3\Pi$ the first close approach of levels with the same J will involve the $^3\Pi_0$ levels (Fig. 2a). In this case the levels with $+M$'s are thrown closer to levels of the same $+M$ value in the other group, and are thus perturbed more,

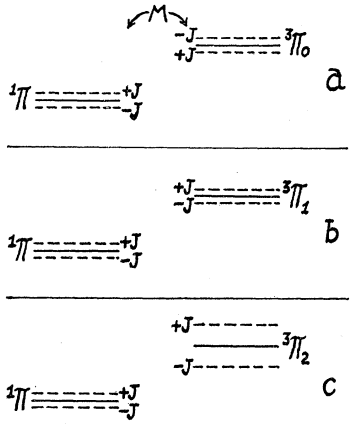


Fig. 2. Rough sketch showing the relative placing of the magnetic sublevels and widths of level patterns in case a $^1\Pi$ and $^3\Pi$ levels of the same J value. Only the no-field levels (solid lines) and the levels with extreme values of $M=\pm J$ are drawn. The other $2J-1$ sublevels will be spaced fairly uniformly between the two extreme levels in each case. The separation of the $^1\Pi$ and $^3\Pi$ levels and the scale of the splitting is quite arbitrary.

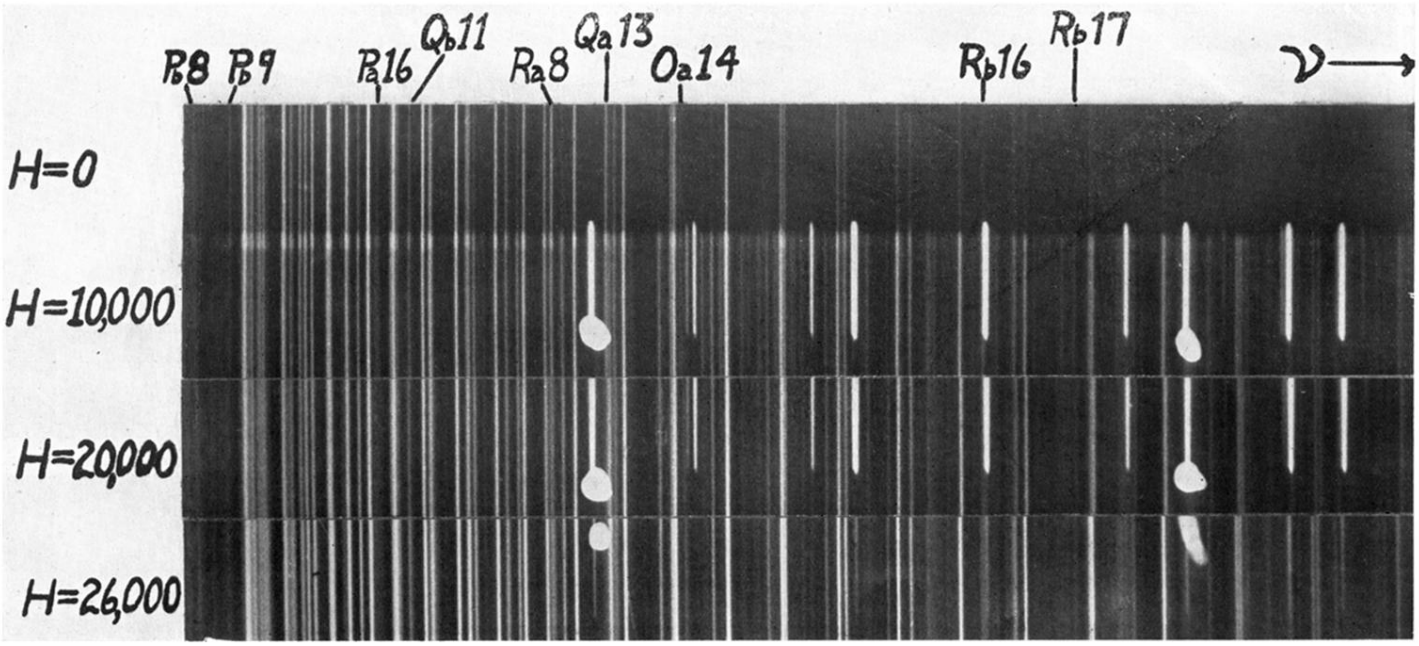
say into or beyond the normal region of $-M$ levels. The latter at the same time are forced farther apart from the $-M$ levels of the same value in the other state, and so are perturbed less than before, being thrust through or beyond the region where normally the group of $+M$ levels would be found. This effect would just tend to invert and spread out the whole pattern of magnetic sublevels in each group. The sensitiveness of the perturbation energy to slight change in the interval between the interacting levels is evidenced by the magnification of the Zeeman patterns of the lines (P_b (8) pattern spread 1.64 cm^{-1} at 10,000 gauss as compared to the regular $2\Delta\nu_{norm}/J \cong 0.11$ cm^{-1}). The occurrence of a region of zero intensity at the center of the Zeeman pattern for a much displaced line such as P_b (8) at the higher field strengths must be attributed to this sensitiveness of the perturbation energy to the size of the interval between the perturbing levels, and to the fact that in

the $^3\Pi$ groups the level $M=0$ will probably be of not exactly the same energy as the original level owing to a slight tendency to spin uncoupling by the field.

If the crossing-over occurs between the $^1\Pi$ and $^3\Pi_1$ levels (Fig. 2b), no effect of the magnetic field on the perturbed band lines should be observed if the $^3\Pi_1$ is strictly case *a*, for the field splitting in the two sets of levels is identical. But a small asymmetry with respect to the no-field levels of the block of magnetic sublevels, due to spin-field coupling, could have the effect of increasing or decreasing slightly the energy interval between the two levels having the same J value. And because this energy interval is already small (perturbation very large), the perturbation energy is appreciably increased or decreased. The type of Zeeman effect observed at the Q-branch perturbation at $J=12$ could originate in this kind of interaction.

When the levels concerned are $^1\Pi$ and $^3\Pi_2$ (Fig. 2c), the situation is somewhat like that for the $^1\Pi$, $^3\Pi_0$ interaction. Because the splitting due to the field in the $^3\Pi_2$ level is about three times that in the $^1\Pi$ level of the same J value, the $-M$ levels are forced closer together, with resulting increased perturbation, while each $+M$ level is separated further from the corresponding $+M$ level of the other group with consequent decrease in the perturbation energy. The result should be a much-broadened, solid Zeeman pattern for the perturbed band line, with perhaps a narrow minimum of intensity in the center at the highest field strengths. This is the type of pattern observed for the lines of the P, R perturbation at $J=16$.

The narrow, sharp doublets observed in the field for the $J=29$ Q-branch perturbation could originate in the $^1\Pi$, $^3\Pi_0$ type of interaction described above, the comparative narrowness being caused by the decrease in the splitting of the levels the higher the J, and the sharp doublet character originating in an asymmetry in the $^3\Pi_0$ group of Zeeman levels, caused by the ever closer approach to case *b* as J increases.



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