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Zeeman Effect for Perturbed N_2^+ Terms

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The Zeeman effects for the perturbed terms in the $v=1$ and 3 levels of the upper $^2\Sigma$ state of N_2^+ have been investigated at various field strengths up to 27,000 gauss. At the points of maximum perturbation the Zeeman patterns are doublets for the moderate and high field strengths. At high field strengths the unperturbed lines, of the same K value as the most perturbed lines, also become doublets under the influence of the magnetic field. This is attributed to a Paschen-Back effect. For K values greater than those of the maximum perturbation point, all the lines exhibit an asymmetric broadening in the field. A consideration of the interactions with the perturbing $^2\Pi$ state gives an explanation of the patterns observed.

INTRODUCTION

THE observation and discussion of the Zeeman patterns found for perturbed terms in a $^1\Pi$ state of CO by Watson[1] made it seem worth while to investigate a similar situation for a doublet state. Perturbations have been observed in the $^2\Sigma-{}^2\Sigma$ bands of N_2^+ by Fassbender,[2] by Coster and Brons[3] and by Childs.[4] The transitions which were the subject of the present investigation were the 1,3 and 3,5 bands. The perturbations found by Childs in the $v=0$ level of the upper $^2\Sigma$ state were not investigated since those perturbations occur in high rotational levels which the sources used did not excite.

EXPERIMENTAL PROCEDURE

Two sources were used for obtaining the spectrograms. The first of these was a 15,000 volt a.c. discharge between small copper electrodes in a modified Back chamber mounted on a Weiss magnet. Commercial tank nitrogen was usually flowed through the chamber. At other times a small air leak was used. The pressure in the chamber was approximately one mm as this was found to be the most suitable for enhancing the N_2^+ bands at the expense of the N_2 bands. However the latter were not entirely removed. The second source was a discharge tube similar to that used by Mulliken and Monk[5] in their investigation of the Zeeman effect for helium bands. The method of excitation was the same as before, the discharge taking place in purified helium at a pressure of 30 mm. A small trace (0.01 mm) of nitrogen,[6] obtained from sodium azide, was added to the helium. Under these conditions the N_2 bands were virtually absent.

The spectrograms were taken in the second order of a 21 foot grating mounted stigmatically. The dispersion for this order and region is 2.42 A/mm. Eastman 40 plates were used to obtain the spectrograms, the exposure time for the first source being 24 hours with the magnetic field and 24 hours without it. When using the other source 40 hours were needed instead of 24.

The field strengths used were 4,700, 9,000, 12,600, 19,700, 24,000 and 27,000 gauss. The second source was used for exposures taken at the first, third and fifth field strengths. While using the first source, the field strength was determined from the λ4680 zinc line. Since the second source contained mainly helium, the helium line at 4713A, which is a normal triplet, was available for the determination of the magnetic field's strength when this source was used. The sharpness of the atomic lines gives evidence

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[1] W. W. Watson, Phys. Rev. **42**, 509 (1932).

[2] M. Fassbender, Zeits. f. Physik **30**, 73 (1924).

[3] D. Coster and H. H. Brons, Zeits. f. Physik **73**, 747 (1932).

[4] W. H. J. Childs, Proc. Roy. Soc. **A137**, 641 (1932).

[5] R. S. Mulliken and G. S. Monk, Phys. Rev. **34**, 1530 (1929).

[6] T. R. Merton and J. G. Pilley, Phil. Mag. **50**, 195 (1925).

TABLE I. *Zeeman patterns for the 1,3 N_2^+ band.*

$\Delta\nu$ represents the magnitude of the perturbation. The field strength followed by $\Delta\nu_n$ is placed at the top of the various columns. The two measurements indicate the limits of the Zeeman pattern associated with that particular line. If three measurements are given it means that there was a definite alteration of the intensity at the middle of the three points. These measurements, as well as those in Table II, were made only on the lines of the *R* branches as the corresponding lines in the *P* branches lie in the immediate vicinity of the head of the bands, thus preventing separation of the pattern associated with one *P* line from that associated with another *P* line. — indicates a displacement to lower frequency. The other measurements indicate displacement to higher frequency. All measurements are in cm⁻¹.

K''	J	$\Delta\nu$	12,600 (0.59)	19,700 (0.92)	24,000 (1.12)	27,000 (1.26)
10	10.5	−0.80	0.70 to −0.03	0.08 to 0.02	0.78 to −0.09	0.10 to −0.72
10	9.5		0.81 to −0.10		0.79 to 0.09	0.91 to −0.10
11	11.5	−1.61	1.28 to −0.09	1.24 to 0.19 −0.98 to −1.72	1.06 to 0.35	−0.48 to 0.66
11	10.5		0.02 to −0.25	0.60 to −0.16	0.67 to −0.10	
12	12.5	−4.02	1.16 to 0.27 −0.05 to −0.93		1.21 to 0.42 −0.61 to −1.56	
12	11.5		1.10 to −0.36	1.10 to 0.37 to −1.22	1.01 to 0.21 −0.52 to −1.59	1.17 to 0.00
13	13.5	3.83	0.77 to −0.26	−0.36 to −1.10		−0.25 to −1.85
13	12.5		0.34 to −0.45	0.90 to 0.33 −0.37 to −1.06	1.39 to 0.55 −0.37 to −0.95	
14	14.5	2.23	0.25 to −0.46 to −1.27	0.25 to −0.05	−0.17 to −0.87	−0.26 to 0.00
14	13.5		0.62 to −0.16		0.01 −1.60	
15	15.5	1.63	0.30 to −0.51	0.00 to −0.03		0.01 to −0.20
15	14.5		0.54 to −0.07			
16	16.5	1.33	0.20 to −0.11	0.19 to −0.08	−0.09 to 0.09	−0.01 to −0.06
16	15.5					
17	17.5	1.18	0.27 to −0.39			0.15 to −0.14
17	16.5		0.79 to −0.09			−0.01 to −0.42
18	18.5	1.08	0.32 to −0.43	0.32 to 0.03	0.15 to 0.07	0.05 to −0.01
18	17.5		0.65 to −0.09			
19	19.5	0.95		0.01 to −0.09		
19	18.5					
20	20.5	0.94	0.12 to −0.01	0.01 to 0.01	−0.09 to −0.17	0.00 to −0.01
20	19.5					

of the constancy and uniformity of the magnetic field. An iron arc comparison spectrum was also recorded on each plate.

Observed Zeeman Patterns

The N_2^+ bands are a $^2\Sigma - {}^2\Sigma$ transition having no appreciable spin doubling for low K values (under 20). Hence we would expect that an external magnetic field would not cause any appreciable change in the band lines. Such has been found to be the case for those bands which do not contain a perturbation. The perturbing level is a $^2\Pi$ level and transitions between a $^2\Pi$ level and a $^2\Sigma$ level do give rise to Zeeman patterns of observable magnitude. Therefore we might expect that at the perturbation points in the N_2^+ bands there would be Zeeman patterns of appreciable size due to the interaction of the $^2\Pi$ and $^2\Sigma$ levels. The spectrograms confirm these expectations.

The bands studied were the 1,3 and 3,5 transitions. The patterns of the lines of only the R branches were measured as the perturbation points in the P branches occur in the vicinity of the heads of the bands and the Zeeman patterns for the P lines overlap too much to permit of determining exactly what the effect of the magnetic field is upon a particular line. Tables I and II give the observed patterns for the R branches of the 1,3 and 3,5 bands, respectively. The patterns for the lowest field strength, 4700 gauss, are not recorded as the effect of such a small field is nearly negligible. Fig. 1, which consists of two microphotometer traces, one of a portion of the R branches in a field of 12,600 gauss and one of the same lines in the absence of an external magnetic field, illustrates the results obtained. From the tables we see that the Zeeman patterns for some lines are doublets and that for many lines they consist of an asymmetric broadening.

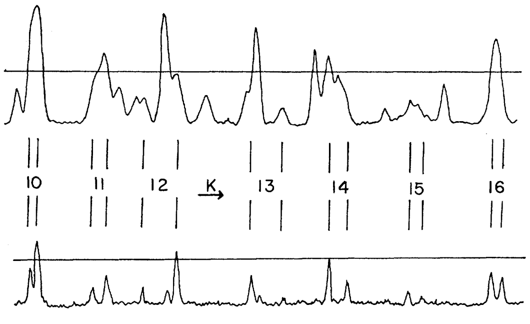

FIG. 1. Microphotometer traces of the perturbation in the 1,3 band. At left the lines are shown with an externally applied field of 12,600 gauss, at right with no external field. The position of the various lines is marked by the K value. These lines are members of the R_1 and R_2 branches.

Let us first consider the perturbation in the 1,3 band, as the situation there is much clearer than it is for the 3,5 band. Here we have but one perturbation in contrast to the two perturbations in the latter. The perturbation in the 1,3 band occurs in the T_1 terms and hence we would expect lines originating on T_1 levels to have appreciable Zeeman patterns. For while normally a $^2\Sigma - {}^2\Sigma$ transition with an inappreciable spin doubling in both electronic states would show no Zeeman effect, there is here a strong interaction of the T_1 terms of one of these states with a $^2\Pi_{1/2}$ level which has pronounced Zeeman patterns. And the transitions at the perturbation point originate in levels whose character is partially that of a $^2\Sigma$ state and partially that of a $^2\Pi$ state. Our expectations of appreciable Zeeman patterns are realized as one readily sees on glancing at either the tables or the microphotometer traces. We also see that the T_2 terms are affected by the magnetic field as well as the T_1 terms. At 9000 gauss the R_2 lines are broadened asymmetrically about the no-field position of the line, for those lines in the immediate vicinity of the maximum of the perturbation. As we progress to higher rotational quantum numbers, this broadening takes the form of a block of radiation extending from the R_2 lines to the R_1 lines and on past them for a varying amount. As the field strength is increased the patterns for these high K values more and more closely approach the width of the separation of the R_1 and R_2 lines. And at the highest field strength and highest K value, we see that the patterns are actually a filling in of this gap. The two photometer traces show this phenomenon setting in at $K=16$.

If one assumes that the separation of the T_1 and the T_2 levels is due to spin doubling and computes the Zeeman patterns to be expected on the basis of the expression developed by Hill and published by Almy,[7]

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[7] G. M. Almy, Phys. Rev. 34, 1517 (1929).

TABLE II. *Zeeman patterns for the 3,5 N_2^+ band. (See heading for Table I.)*

K''	J	$\Delta\nu$	12,600 (0.59)	24,000 (1.12)
4	4.5	−0.74	0.47 to −0.14	0.07 to −1.09
4	3.5	−2.00	1.15 to 0.00	0.15 −1.85
5	5.5	−1.03	0.30 to	
5	4.5	−2.48	0.01	
6	6.5	+0.66	1.26 to 0.21 0.09 to −0.59	1.63 to −0.44
6	5.5	−3.14	0.79 to 0.09 0.09 to −0.68	
7	7.5			
7	6.5	−4.35		1.23 to 0.25
8	8.5		1.36 to 0.59 0.59 to −0.40	
8	7.5	−6.75	1.09 to 0.21 0.13 to −0.72	1.11 to −1.13
9	9.5		2.10 to 0.14 to −0.45	
9	8.5	8.12		
10	10.5		1.14 to −0.15 −0.41 to −1.27	1.05 to −1.06
10	9.5	5.59	1.03 to 0.14 to −0.50	3.23 to 2.23 −1.90 to −3.02
12	12.5		0.58 to −0.22	0.60 to −0.34
12	11.5	3.21	0.55 to −0.73	0.25 to −0.87
14	14.5		0.67 to −0.12	
14	13.5	2.37		0.13 to −0.81
16	16.5		1.06 to −0.20	
16	15.5	1.91	0.30 to −0.85	

$$\Delta W = \pm\tfrac{1}{2}\{\nu_0^2 + 4m\nu_0\Delta\nu_n/(K+\tfrac{1}{2}+4\Delta\nu_n^2\}^{\frac{1}{2}},$$

then one finds that there is good agreement between the observed and computed patterns for K greater than 14 at the three highest field strengths.

The patterns of the most interest are those in the immediate vicinity of the perturbation. As previously remarked, the patterns in this region are doublets. At 12,600 gauss the $K=12$, $J=12.5$ line is a doublet. This is the only line which appears as a doublet in the field at this low field strength and it is the most perturbed line. At 19,700 gauss the $K=11$, $J=11.5$ line is a doublet and the $K=12$, $J=12.5$ is not measurable as there is an overlapping atomic line. Furthermore we find that the R_2 lines for $K=12$ and 13 each have patterns at this field strength which are doublets. At 24,000 gauss the lines which were doublets at the previous field strengths are doublets still and there is also evidence that the two lines with $K=14$ become doublets at this field strength. In other words in the immediate vicinity of the perturbation we find that the patterns are doublets for both the T_1 and T_2 terms, that the doubling occurs first in the T_1 (perturbed) terms and that at the higher field strengths the T_2 (unperturbed) terms likewise become doublets. This summarizes the results for the 1,3 band.

In the case of the 3,5 band the situation is complicated by the fact that there are perturbations in both the T_1 and the T_2 terms. The T_1 terms first pass through a perturbation and then the T_2 terms are perturbed. These two perturbation points are at nearly the same K value and the effects of both are present simultaneously. The observations on this band are much more meager, being mainly taken from the plates at 12,600 and 24,000 gauss, that is those taken with the second type of source.

The perturbation in the T_1 terms is relatively small while that in the T_2 terms is quite large, reaching a maximum displacement of 8.12 cm^{-1} at $K=9$. Much the same results are obtained here as for the 1,3 band. At high field strengths and high K values, the patterns tend to fill in the space between the corresponding R_1 and R_2 lines and agree with the results computed by Hill's equation. And in the immediate vicinity of the perturbation both the R_1 and the R_2 lines appear as doublets in the field.

DISCUSSION

Certain requirements have been established by Kronig[8] as necessary for the existence of a perturbation. Among them is the requirement that the two levels which perturb each other shall have the same J and the same M values. An explanation of the observed Zeeman patterns is possible with this requirement as a guide. There are three findings which need consideration. They are first the existence of doublet patterns for the perturbed terms at the points of maximum perturbation, second the asymmetric patterns of these terms throughout the remainder of the band, and third the existence of any magnetic effect for the unperturbed levels.

Fig. 2a illustrates the situation for a particular K level in the immediate neighborhood of a perturbation. The solid lines are the position of the levels in the absence of an external magnetic field. The dashed lines indicate the position of the $M=0$, $\pm J$ levels when an external magnetic field has been applied. Childs[4] has estimated the value of the B constant in the perturbing $^2\Pi$ state as approximately 1.5 cm^{-1}. We may assume an A value of 50 cm^{-1} by analogy to the similar $^2\Pi$ level in CN, as these two molecules are isoelectronic. Then by means of Hill's equation for doublet Π states,[9] we can compute the spread of the levels in this perturbing state for any field strength. Computation shows that the spread in the region of the perturbation is considerably less than $\Delta\nu_n$. We know that the spread of the levels in the $^2\Sigma$ state is from $+\Delta\nu_n$ to $-\Delta\nu_n$. Hence we see that the spread of levels for a particular K value is much greater in the $^2\Sigma$ than it is in the $^2\Pi$ state. Therefore the levels are drawn as they are. The separation of the levels in the absence of a magnetic field is not known, a fact which is absolutely essential for the quantitative treatment of the problem.

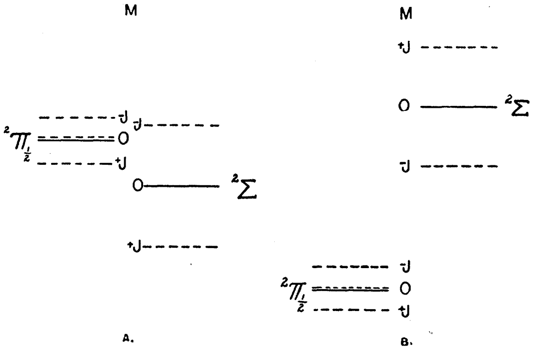

FIG. 2. Plausible positions of the $^2\Sigma$ and $^2\Pi$ levels in the immediate vicinity of a perturbation point (a) and at some distance from a perturbation point (b). The $^2\Sigma$ pattern extends from $+\Delta\nu_n$ to $-\Delta\nu_n$.

Recalling the perturbation requirement that only levels having the same M values perturb each other, we see that in the case illustrated the levels with $M=-J$ are brought closer together and hence the perturbing effect of the one on the other is greatly increased, while those for which $M=+J$ are thrown further apart and the effect is the reverse. Furthermore for the $^2\pi$ state the level $M=0$ will be slightly shifted and its perturbation will also be altered. The region of low intensity (approximately zero intensity) must be caused by the extremely close dependence of the perturbation energy on the separation between levels having the same M value. The asymmetry observed in regions where the perturbation is small is easily understandable as arising from the situation illustrated in Fig. 2b. Here we see that there is very little interaction between the levels in the absence of the field. The interaction of the $M=+J$ levels is practically unaltered by the application of an external magnetic field as the perturbation energy varies only slowly with the distance between the mutually perturbing levels when this distance is large. The drawing

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[8] R. de L. Kronig, Zeits. f. Physik **50**, 347 (1928).

[9] E. L. Hill, Phys. Rev. **34**, 1507 (1929).

together of the $M=-J$ levels is so slight as to cause but a small increase in their perturbation energy.

Now the existence of Zeeman patterns for the unperturbed levels (T_2 levels in the $v'=1$ state) following the perturbation is quite unexpected. However it may be accounted for in the following manner. There is no appreciable spin doubling in the unperturbed upper $^2\Sigma$ states of the N_2^+ molecule until quite high rotational quantum numbers are reached. This must mean that the coupling of the electron spin and the magnetic field produced by the rotation of the molecule is quite small. It is so small in fact that a perturbation is required to show the doubling of the $^2\Sigma$ state at low K values. Now the magnetic field which is applied externally is sufficient to cause a partial Paschen-Back effect and uncouple to more or less degree the spin from the magnetic field produced by the rotation of the molecule. Hence the T_1 and the T_2 terms are no longer distinct entities when an external magnetic field has been applied. And the T_2 terms (unperturbed) may share the perturbation which was previously the distinguishing characteristic of the T_1 terms. Thus we see that just as the R_1 lines are doublets in the field at the points of maximum perturbation so will the R_2 lines become doublets, though to a slightly smaller extent.

A quantitative treatment of the problem requires a knowledge of the actual position of the perturbing levels but these data are not available because of the nature and position of the perturbing state.

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