The Structure of the Third Positive Group of CQ Bands

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The third positive group of CO was photographed under high dispersion. The bands are ${}^{3}\Sigma \rightarrow {}^{3}\Pi$ transitions. The ${}^{3}\Sigma$ state shows many strong perturbations. The triplet separation is very small. Of the 15 branches which must be expected under these conditions, 14 are found and traces of the fifteenth. Nine of these branches are strong and can be traced to $K = 55$. The others are weak and present only for small values of the rotational quantum number K . The five edges which are characteristic for the. bands of the third positive group are formed by the two 0-branches and

§1. INTRODUCTION

HE band spectrum of the CO molecule belongs to the most often studied band spectra. A number of diferent band systems are known and their vibrational analysis satisfactorily completed. But the rotational analysis of' only the Angstrom bands and some bands associated with them is known. For that reason the CO spectrum was photographed in this Iaboratory under high dispersion in order to obtain a rotational analysis of some additional band systems. The present paper contains the results on the structure of the third positive group of Deslandres. Work on other band systems is in progress.

The third positive group was discovered by Deslandres' in discharge tubes which contain carbon and oxygen. That these bands are due to CO was established definitely by Johnson' who showed their connection with the Cameron bands. The Cameron bands in turn are absorbed by cold CO and are, therefore, undoubtedly due to this gas.

the three P -branches. The character of the Λ -doubling and the number of missing lines near the origin shows that the 3 II state is a normal 3 II state.

The values of the rotational constants are $B' = 1.89$ for the initial and $B'' = 1.686$ cm⁻¹ for the final state from which follows that the values for the moments of inertia are $F' = 14.7 \cdot 10^{-40}$ and $F'' = 14.43 \cdot 10^{-40}$. Complete details are given for the $0 \rightarrow 0$ (2833), $0 \rightarrow 1$ (2977), $0 \rightarrow 2$ (3134), and $0 \rightarrow 3$ (3305) bands.

There have been several previous attempts at analyzing the third positive group. Wolter' photographed the band at 2977A under high dispersion. But it is not surprising that he did not get far with the analysis, as he did not have the modern theory of band spectra at his disposal, and it seems quite impossible to analyze such a complicated band system without it. Later Asundi⁴ published a rotational analysis of the bands 2833 and 2977. He believed to have shown that the bands are ${}^5\Sigma \rightarrow {}^5\Pi$ transitions. There were, however, some inconsistencies in Asundi's analysis which made it very doubtful whether his results were right, and accordingly many observers did not accept them. The results of the present paper do not conhrm Asundi's analysis but give the bands as ${}^{3}\Sigma \rightarrow {}^{3}\Pi$ transitions. The general appearance of the bands had already induced Birge' and Mulliken' to assume the bands to be ${}^{3}\Sigma \rightarrow {}^{3}\Pi$ transitions.

§2. EXPERIMENTAL PROCEDURE

The CO bands are produced very easily in any discharge tube which contains carbon and oxygen. After some preliminary experiments it was found most convenient to use commercial $CO₂$ directly from a tank supplied by the Pure Carbonic Company of America. It was not

¹ H. Deslandres, Ann. Chim. Phys. 15, 5 (1888); C.R. 106, 842 (1888). Deslandres called "third positive group" all bands of CO in the ultraviolet not belonging to the fourth group or the second group (Angstrom bands). More recently it has become customary to separate two progressions from it, the so-called $3A$ and $5B$ -bands and consider only the strong bands which form the $0 \rightarrow n''$ progression as the third positive group. We are following this custom here.

² R. C. Johnson, Nature 117, 376 (1926).

⁸ P. Wolter, Zeits. f. Wiss. Phot. 9, 361 (1911).

⁴ R. K. Asundi, Proc. Roy. Soc. A124, 277 (1929).

⁵ R. T. Birge, Phys. Rev. 28, 1172 (1926).

R. S. Mulliken, Phys, Rev. 28, 481 (1926).

necessary to use any device for purifying the gas, as no lines or bands of impurities could be detected. The gas was allowed to stream continuously through a capillary into the discharge tube and was pumped out by means of an oil pump.

The Pyrex discharge tube was of the ordinary type consisting of a horizontal tube about 50 cm long, with two side tubes which contained the aluminum or. nickel electrodes. In order to obtain the maximum intensity, the cross section of the horizontal part of the tube had the form of a slit. This allowed one to make a more efficient use of the light coming out of the tube. The whole tube, except the quartz window, was immersed in running water, so that currents of 1.6 amperes or more could be passed through the tube without damaging it.

The electrical energy for the uncondensed discharge was supplied by a 13,200 volt, 15 kw transformer. By means of an auto-transformer the main transformer could be used for any voltage below its maximum.

Except for the preliminary investigations, all plates were obtained with the 21 ft. concave grating spectrograph of the Johns Hopkins University.^{7} The mounting of the grating is a Paschen mounting, and the temperature of the grating room is kept constant by a thermostat. In the first part of the investigation a grating with 20,000 lines per inch ruled by Anderson was used. It gave excellent definition when used under the most favorable conditions, but it had a slightly warped surface which made working with it rather tedious. However a number of good second order plates with a dispersion of about 0.97A per mm were obtained with this grating.

It was replaced later by a new grating with 30,000 lines per inch ruled by Professor Wood in April of this year. This grating proved to be excellent for our purpose and gave very good definition in the first and second orders. A number of second order plates obtained with it (dispersion 0.66A per mm) were also used for the measurements.

Ihe exposure times ranged from one hour to 48 hours. As a rule good second order plates could be obtained with about a seven hour exposure.

It was found that the appearance of the bands could be modified considerably by changing the pressure of the gas. The modifications can be easily understood, if one realizes that in the discharge tube with CO at a fairly high pressure the current heats the gas to a higher temperature and accordingly brings out the lines with a higher rotational quantum number. At pressures of about 2.5 cm, so high that the full voltage of 13,200 volts is needed to maintain the discharge, the tails of the bands, especially 2977, show very characteristic triplets (see Fig. 2). These triplets which show immediately that the bands are triplet and cannot be quintet trarisitions cannot be brought out at lower pressures. An increase in the exposure time does not help, for then the general background comes out so strongly, that the triplets cannot be recognized.

§3. GENERAL DESCRIPTION OF THE BANDS

The following bands appear most strongly on the plates. They are given with their vibrational quantum numbers.

These five bands are investigated in detail in the present paper. Deslandres also gives a band at 3699A, the existence of which is denied by Wolter, nor does Asundi mention it. It is present on our plates though it is not nearly as conspicuous as the other bands because of the fact that it is weaker than the other bands, and does not stand out well from the background which consists of a very large number of faint unresolved lines. This background extends from about 3500 toward longer wave-lengths. Its origin is not quite certain, but it is probably due to $CO₂$. The band at 3699A is the $0 \rightarrow 5$ transition. We have not yet attempted to analyze it.

On the short wave-length side of each of the main bands, there is a band which has under small dispersion the same appearance as one of the main bands. These bands which were also

⁷ We acknowledge gratefully a grant to one of us from the National Research Council and one from the Rumford Committee of the National Academy of Sciences which made the construction of the spectrograph possible.

found originally by Deslandres have the same set of final states as the main bands. Their initial state was originally believed to be the state with the vibrational quantum number $V'=1$ of the same electronic state as that which gives rise to the main bands. Asundi noticed, however, that these bands seem to have quite a different structure under high dispersion, and therefore he thought it necessary for them to have a different electronic state. He called the bands accordingly " $5B$ "-bands, and this name has been used by most authors since. We shal1 retain it also in this paper, although it is almost certain that the bands are not quintet but triplet bands and we think it very probable that the original assumption that they form the $V'=1$ progression belonging to the main bands is correct. We hope to be able to demonstrate this conclusively when the rotational analysis of the 58-bands which has been started has been finished. In the meantime the analysis of the main bands has already shown that Asundi's argument for assigning a new electronic initial state to the $5B$ -bands, namely, that their appearance is quite different from that of the main bands, does not necessarily prove anything.

The general appearance of the bands of the third positive group is largely determined by the per'turbations of the initial state. These perturbations which are very large and numerous cause the characteristic intensity Huctuations which become at once apparent even under moderate dispersion, and which were already noticed by Wolter. In the zero vibrational state the first big perturbation occurs for about $K = 19$. This. means that the immediate neighborhood of the heads is not affected and, therefore, presents a normal appearance. Only farther towards the tail the perturbations cause a massing together of lines in some places and gaps in other places. It is very likely that rotational levels with smaller values of K will be perturbed for the next higher vibrational level. That may completely disarrange the region of the heads and may give an entirely different appearance to the bands which have this vibrational level as initial level. Of course, only the complete rotational analysis of these bands can settle this point.

FIG. 1. Portion near the head of the $0\rightarrow 3$ band at 3305A. The figure shows the arrangement of the branches for low quantum numbers.

FIG. 2. The tail of the 2977 (0-1) band. The figure shows clearly the triplets which are characteristic for high rotational quantum numbers. It also can be seen easily that successive triplets do not follow each other in regular intervals, but that there are perturbations.

Under small dispersion the bands of the third positive group show five heads. More or less regular series of rotational lines can be seen in the vicinity of these heads. These series can, however, only be followed for a short distance into the bands, as the perturbations destroy the regularity completely. In the middle of the band there is no apparent regularity at all. Also the fact that the 58-bands are mixed up with the main bands in this region complicates matters still further. On plates taken with a relatively high pressure in the discharge tube the tails of the bands show very characteristic triplets. These come out especially well in the 2977 band as the 58-band at 2930 is comparatively weak, and therefore does not obstruct the structure of the main band. (See Fig. 2.) In front of the heads a few faint lines are visible which form a very weak series. Further on it will be shown that these lines are due to $K\rightarrow K+3$. transitions.

$$
\begin{array}{ccccccccc}\n\text{Hilag} & \text{Hilag} & \text{Hilag} & \text{Hilag} & \text{Hilag} & \text{Hilag} \\
\text{Hilag} & \text{Hilag} & \text{Hilag} & \text{Hilag} & \text{Hilag} & \text{Hilag} & \text{Hilag} \\
\text{Hilag} & \text{Hilag} \\
\text{Hilag} & \text{Hilag} \\
\text{Hilag} & \text{Hilag
$$

Whether these are the lines which Asundi observed in front of the head cannot be made out with certainty. The lines mentioned above never come to a head on our plates. Sometimes other lines of unknown origin are found which may be due to impurities.

§4. ANALYSIS OF THE BANDS

The bands of the third positive group have a very complex structure. It has been mentioned already that the complete absence of any apparent regularities in the middle of the bands is largely due to the perturbations of the initial state. But even in the neighborhood of the heads the structure is far from simple, as there is a large number of branches, most of which do not follow Deslandres' law very closely. In the present paper mainly the empirical aspects of the structure will be discussed. A more theoretical discussion of some of the properties of the terms will follow in another paper.

As the analysis shows that the bands are due to ${}^{3}\Sigma \rightarrow {}^{3}\Pi$ transitions, it is best to start with a brief statement of the properties of such transitions. ' At the same time the meaning of the symbols used will become clear. The nomenclature is the one generally adopted.

The quantities which are important for a discussion of the term properties are mainly: The resultant electronic spin $S(S=1$ for triplet terms); its component Σ along the internuclear axis; the component Λ of the total orbital angular momentum L along the internuclear axis $(\Lambda = 0$ for Σ -terms; 1 for II-terms, 2 for Δ -terms; etc.). $\Omega = \Lambda + \Sigma$. *J* is the total angular momentum of the molecule, and K is the angular momentum due to the rotation of the nuclei.

For the ${}^{3}\Sigma$ terms $\Lambda=0$, and therefore there can be no interaction between S and ^A which usually gives rise to a big triplet separation. However, S will be slightly coupled to the rotational axis which has the result that the terms with $J=K+1$, $J=K$, and $J=K-1$ will have slightly different magnitudes. A detailed discussion of the properties of ${}^{3}\Sigma$ terms has been given by Kramers.⁹ But we do not need to consider the exact theoretical structure here, as the triplet separation, which is small in general, is negligible for the initial state of the third positive group, at least for small values of X.

For all terms with $\Lambda \neq 0$, the properties of the rotational levels depend very largely on whether the spin S is coupled to the internuclear axis (*case a*) or to the rotational axis (*case b*).

For case a the projection Σ of S on the internuclear axis can have the three values -1 , 0 and $+1$ for triplet terms, and therefore for a ³II term there will be for small rotations three different components with $\Omega = 0$, 1, 2. With increasing rotation each of the three components is split up into a doublet (A-doubling). The character of the doubling is different for the three components. Hill and Van Vleck¹⁰ found that (1) if $\Omega = 0$, there is an appreciable Λ doubling also for very small values of J. The Λ -doubling does not vary much with J . (2) if

⁸ A fuller account of the general theory of complex band can be found, e.g., R. S. Mulliken, Rev, Mod. Phys. 2,

^{60 (1930); 3, 89 (1931).&}lt;br>⁹ H. A. Kramers, Zeits. f. Physik 53, 422, 429 (1929).

¹⁰ E. L. Hill and J. H. Van Vleck, Phys. Rev. 32, 261 (1928).

 $\Omega = 1$, the A-doubling is proportional to $J(J+1)$ (3) if $\Omega = 2$, the A-doubling is very small and increases proportional to $J^2(J+1)^2$.

A spin multiplet can be either normal or inverted. It is called normal, if the term with the smallest value of Ω has the lowest energy.

If we go to the other extreme $(\text{case } b)$ in which the spin is completely coupled to the rotational axis, Σ and Ω have no physical meaning. We can then characterize the rotational levels by J and the angular momentum K of the nuclear rotation. The rotational energy is in first approximation equal to $BK(K+1)$. Mainly because an inHuence of the spin coupling to the internuclear axis still remains every rotational term with a given K is split up into a triplet, the components of which are characterized by $J=K+1$, $J=K$, $J=K-1$. It is customary to indicate the three triplet components of a given term F by indices 1, 2, 3 so that F_1 has $J=K+1$, $F_2: J=K$ and $F_3: J=K-1$.

Usually the observed terms are neither exactly case a nor exactly case b but are in a transition case between case a and case b . That is also the case for the final terms of the third positive group. The rotational energy levels do not follow a simple formula then. For small values of J the terms are closer to case a ; for large values, closer to case b . To label the terms it is, of course, advisable to use a uniform notation for all values of J. In our case it is most convenient to use the notation of case b throughout. Therefore throughout this paper 3 Π_1 means that triplet component for which $J=K+1$, ${}^{3} \Pi_{2}$ that for which $J=K$, and 3 II₃ that for which that for which $J = K$, and ³II₃ that for which $J = K - 1$.¹¹ The values of *K* (*not* those of *J*) are used to number the rotational levels.

It is always easy to go over to the notation of case a , if one remembers that if the coupling to the internuclear axis is made stronger, so that we come to case a , we get the following values of Ω

case
$$
b \begin{cases} \n3\text{H}_1 & 3\text{H}_2 & 3\text{H}_3 \\
J = K + 1 & K - 1\n\end{cases}
$$
\n
\ncase $a \begin{cases} \n\Omega = 0 & 1 & 2 \\
\Omega = 2 & 1 & 0\n\end{cases}$ (normal triplet).

The lines which are obtained from all the ${}^{3}\Sigma \rightarrow {}^{3}\Pi$ transitions which are allowed by the selection rules form 27 branches. (See Fig. 4.) If the 3 II state is exactly case b only nine of

FIG. 4. The 27 branches resulting from a $\Sigma \rightarrow \S II$ transition. The dotted lines represent satellites which cannot be separated from the main lines if the Σ — triplet separation is negligible.

these remain. The fact that the initial ${}^{3}\Sigma$ state has a negligible triplet separation causes a number of branches to coincide. The following little table shows the expected branches. The nomenclature here also is that which is suitable for case b . Therefore we call a branch an N branch, if the transition is $K-3\rightarrow K$, O-branch, if $K-2\rightarrow K$, P-branch, if $K-1\rightarrow K$, etc. The

¹¹ Usually the value of Ω is designated by the subscript. But as we employ the notation of case b , Ω would have no physical meaning.

¹¹a Note added in proof: In order to make sure, whether irregularities which occur now and then in the estimated intensities are real or only produced by errors in judging due to the fact that the lines lie far apart in a very crowded region, microphotometer records were made of several plates. We are very grateful to Mr. A. L. Loomis for the opportunity to use in his Tuxedo Laboratory a microphotometer constructed by him. The microphotometer records confirmed the statement made in the text that some of the lines show anomalous intensities. Details about

this will be given in a forthcoming paper on the perturbations. However it became also apparent that some of the irregularities in the tables were due to errors in estimating, and these were corrected in the first part (up to P_{41} , Q_{35} , R_{32}) of λ 3305 and in the tail of λ 2977. The records also showed that the expected intensity relations between the branches hold, namely that the Q-branches are the strongest and the R-branches the weakest branches.

 K value of the *final* state is always used to number the lines. Each branch will have to have two indices. The first one indicates the index of the initial, the second one that of the final, state. The allowed branches are then

P ₁₁	Q ₁₁ , Q ₂₁	
O_{12}	P_{22} , P_{12}	Q_{22} , Q_{12} , Q_{32}
N_{13} , O_{22} , O_{12}	P_{33} , P_{23} , P_{13}	Q_{33} , Q_{23}
R_{11} , R_{21} , R_{31}	S_{21} , S_{31} , T_{31}	
R_{22} , R_{32}	S_{32}	
R_{33}		

Those nine branches which are printed in heavy type are the only ones present if the final state is in the rigorous case b . As case b is approached better and better for higher values of K , those nine branches are the only ones which can be expected for high values of the rotational quantum number. All other branches will fade out if the coupling to the internuclear axis is no longer appreciable, especially those for which K changes by two or three.

When the triplet separation of the ${}^{3}\Sigma$ state is negligible, the notation can be still further simplified, as all the branches with the same final but different initial index coincide. The initial index can then be dropped entirely, and this is done in the present paper. We expect under these conditions therefore the following fifteen branches

$$
\begin{array}{ccccccccc}\nP_1 & Q_1 & R_1 & S_1 & T_1 \\
0_2 & P_2 & Q_2 & R_2 & S_2 \\
N_3 & O_3 & P_3 & Q_3 & R_3\n\end{array}
$$

The N_3 and T_1 -branches will be extremely weak and present only for very small values of X. The 0 and S-branches will be weak and be absent for high values of K. The remaining nine P, Q, and R-branches will be strong.

It is necessary now to show that the observed empirical structure of the bands agrees with the theoretical scheme for a ${}^{3}\Sigma \rightarrow {}^{3}\Pi$ transition outlined above. An inspection of the plates shows that a number of branches can be traced near the heads of the bands. It is possible to establish combination relations between these branches by which the numbering of the lines can be fixed. At the same time it is possible to find out which

branches belong together. In this way it becomes apparent that the first two rather weak heads of the bands are formed by the O_3 and O_2 -branches. The three strong heads arise from the P-branches. The three Q and R -branches are also easily found. The branches can be traced. to about $K=19$. The intensities of the different branches behave exactly as we must expect. The P , Q , and R-branches gain constantly in intensity and are very strong where they break off. The two O-branches, however, start with a fair intensity, becoming weaker with increasing K , and the last few lines are just at the limit of visibility. The intensities therefore confirm the classification of the branches.

Table I gives the wave numbers of the O, P , Q and R-branches of the four bands at 2833 2977, 3134 and 3305. The data for the band $0 \rightarrow 4$ at 3493A will be given in a later paper. Its analysis has been also carried through, but there are still a few doubtful points due to the fact that for this band also the final state is perturbed. Most of the lines were measured on two different plates and for good lines the agreement is within a few hundredths of a wave number. The intensities^{11a} are rough visual estimates. The column to the right of the intensity column shows whether the line coincides with another classified line. The wave-lengths of the lines which are used more than once are not as reliable as those of the single lines, as such lines are formed by two or more lines very close together. This usually shows in the intensity, and very often such lines are broad or diffuse. It must be borne in mind that many lines may coincide with other not yet classified lines, e.g., those of the 5B-bands.

About the remaining four branches which ought to be expected for a ${}^{3}\Sigma \rightarrow {}^{3}\Pi$ transition, the following can be said.

N_3 -branch

There are some very weak lines in front of the first head which apparently form a series. They are the lines of the N_3 -branches as shown by Table II which gives their calculated¹² and observed frequencies. The branches are ex-

 12 The N-branches can be calculated with the help of the combination relations discussed farther below. In the same way also the S and T-branches can be calculated.

TABLE I. The bands $0\rightarrow 0$ ($\lambda 2333$); $0\rightarrow 1$ ($\lambda 2977$); $0\rightarrow 2$ ($\lambda 3134$); and $0\rightarrow 3$ ($\lambda 3305$).

In the intensity column the symbols have the following meaning: b , Line broad. c , Line confused with other line. Wave-length may be affected by this. d , Line diffuse. D , Unresolved doublet. r , Line degraded towa

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TABLE I. (Continued). λ 3134; 0-2.

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24 ~ 10

 $\Upsilon_{\rm ABLE}$ 11.

tremely weak and would have escaped observation if they were not in front of the head, where there are no other lines which might obscure them.

The S-branches

The S-branches fall into the region in which many strong lines are crowded together. As they consist of weak lines, it is not surprising that many of them are obscured by the stronger lines of the main branches. Therefore they are much less completely observed than the 0 branches (especially the weaker S_2 -branches). The S-branches are also given in Table II. The T-branch is so weak that only uncertain traces of it can be found.

There is no evidence of any other branches besides those mentioned. Therefore the bands can be only ${}^{3}\Sigma \rightarrow {}^{3}\Pi$ transitions, as it is easy to see that any other kind of transition would lead see that any other kind o
to a different structure.¹³

It was mentioned above that in the branches of all bands the lines can be followed to about $K=18$. After this the branches seem to stop. The last few lines present in every branch show perturbations of increasing magnitude. This shows that a big perturbation of the initial state cuts off the regular sequence of lines. Usually if there is a perturbation in a sequence of rotational lines the lines come back to a regular sequence after the perturbation is past, but as there could not be detected anywhere in any of the bands a regular sequence of lines, it became very probable that there must be more than one perturbation. Although this considerably complicates the analysis of the rest of the bands, it is possible nevertheless, by looking for analogous groups of lines in all five bands and by comparing them carefully to arrange the rest of the lines as well into branches. The spacing of the lines in each branch is very irregular (see Fig. 3), and cannot be used at all to decide whether a line belongs to the branch or not. Nevertheless we are convinced that the classification of the lines given in Table I is correct, perhaps with the exception of a few difficult lines. The following criteria can be used to test the correctness of the classification:

(1) The perturbations are in the initial state. There is one line in each of the nine branches which comes from a given initial state, and as all five bands have the same initial state, one perturbation must affect 45 lines. This is always found to be so and excludes almost completely the possibility of an accidental agreement which might be found if the number of necessary coincidences were smaller.

(2) All properties of the final terms such as triplet separations, A-doublings, and final term differences are entirely unaffected by the perturbations. The final term differences allow the numbering of the lines to be fixed unambiguously.

(3) The intensities of the lines in each branch run smoothly. There are exceptions from this rule which will be given in a forthcoming paper on the perturbations, as the perturbations affect sometimes also the intensities of the lines. But in such a case the intensity anomaly occurs 45 times and can easily be identified.

(4) The perturbations which at first sight seem to be entirely without regularity follow a definite scheme. The structure of the perturbations will, however, be discussed in a separate paper.

(5) The differences $R(K) - P(K) = F(K+1)$
- $F(K-1)$, if $F(K)$ represents the initial rotational terms, are given in Table III. These differences ought to be equal for all five bands and the tables show that this is actually the case within the limits of experimental errors. In judging the agreement one must take into account that there are many lines which are blends or unresolved doublets for which the accuracy of the measurements is much less than for a good line. Differences which involve lines which can be recognized to be bad lines are marked by an *. The absence of an * does not necessarily mean that the lines involved are

¹³ One might ask how Asundi could obtain such a completely diferent analysis of the same bands. He classified the bands as ${}^5\Sigma \rightarrow {}^5\Pi$ bands and obtained five P, five Q, and R-branches. A comparison of his data with ours shows that most of his branches are not real and that the successive lines in these branches have no relation at all with each other. Also his branches are very short, the intensities irregular, and only a small percentage of the total number of lines in the bands is accounted for by his analysis. The agreement of the combination relations seems to us entirely accidental or probably caused by Asundi's method of analysis. All these and. many other minor details seem to us sufficient evidence against Asundi's classification.

TABLE III.

without suspicion. For instance, in the tails of the bands there will be many coincidences with lines of the 58-bands which, as a rule, cannot be recognized easily, as the SB-bands have not been analyzed yet.

$$5.$ The ${}^{3}\Sigma$ Terms

It was already anticipated that the ${}^{3}\Sigma$ terms must have very small triplet separations. If that were not the case, most of the main lines ought to be accompanied by satellites of the kind which are found, for example, in the NH or OH bands. The table on page 16 shows for which lines satellites must be expected. .There is, however, no trace of such satellites and the lines do not show even any perceptible asymmetrical

broadening, but appear to be completely sharp. The triplet separation ought therefore to be less than about 0.2 cm^{-1} . This reasoning does not hold for high values of K (about >20) where the satellites would be too weak to be noticeable.

But the identity within the limits of experimental errors of the three sets of initial term differences $F_i(K+1) - F_i(K-1)$ (Table III) shows that if there is a triplet separation for high K it cannot be large, although this criterion is not nearly as sharp as the absence of satellites for the lines with small K . There is a possibility that the strongly perturbed terms have an anomalous triplet separation.

It will be noticed in Table II that there is a systematic difference between the calculated and observed wave numbers of the N and S -branches.

The observed values of the N-branches appear to be higher and those of the 5-branches lower than their calculated values. As this is true for all bands, it is highly improbable that it can be ascribed to a systematic error in the wavelengths. If the difference is real, it means that there is a triplet separation of the order of magnitude of 0.1 cm⁻¹ and that F_1 is the highest and F_3 the lowest term. The data are too inaccurate for further conclusions.

The presence of the strong perturbations does not allow an accurate evaluation of the rotational constants. Even the lowest levels show definite deviations from the simple quadratic formula which ought to be valid for Σ terms. These deviations for small K probably arise from the fact that the lowest levels are on the edge of an additional perturbation.

The value of B calculated from the term differences for $K=7$ to $K=15$ which are fairly normal¹⁴ is $B = 1.89$ cm⁻¹. From $B = h/8\pi^2 cJ$ we get the moment of inertia of the initial state $J=14.7 \cdot 10^{-40}$ g cm².

$§6.$ THE 3 II TERMS

The question whether a multiplet term of a molecule is a regular or inverted term can often be settled easily by observing how many lines are missing in the vicinity of the band origin. For as $J \geq \Omega$ there will be more lines missing for a larger value of Q.

In our bands this criterion is of not much value as the origin falls into a crowded region and the lines in the vicinity of it are very weak so that it is very difficult to decide whether a particular line is entirely missing or merely so weak that it escapes observation. The only branch which allows a definite conclusion is the O_3 -branch. The first line of this branch is $O_3(3)$ in all bands. It has a fair intensity but there is no trace of $O_3(2)$, although the place where it ought to appear is relatively free from other lines. This can only mean that the level with $K=3$ is the lowest rotational level for 3 II₃. It must have then $J=2$ from which it follows that $\Omega = 2$ (see p. 16). As 3 H₃ is the highest triplet component the triplet must be a normal triplet.

A confirmation of this conclusion can be obtained from the Λ -doubling. In Fig. 5 the A-doubling of the three triplet components is

plus from λ 3134 ($V=2$).

plotted. It is obtained from the lines in the following way. If we designate the rotational terms of the initial state by $F(K)$ and those of the final state by $f_a(K)$ and $f_b(K)$ in which f_a are the terms which are responsible for the Q-branches and f_b those of the P and R-branches, we have $P(K) = F(K-1) - f_b(K); Q(K) = F(K)$ $-f_a(K); R(K) = F(K+1) - f_b(K).$

 $R(K) + P(K+1) - Q(K) - Q(K+1) = f_a(K+1)$ $-f_b(K+1)+f_a(K)-f_b(K)$. This gives us the sum of the Λ -doublings of two successive levels. If we call this quantity $2\Delta' \nu$, $\Delta' \nu$ is the average of two successive Λ -doublings $\Delta \nu$. The variation of the Λ -doubling with K is so slow that the difference between the real Λ -doubling $\Delta \nu$ and the average A-doubling $\Delta' \nu$ is smaller than the errors of measurement.

In Fig. 5 the crosses represent the values obtained from the band $0 \rightarrow 1 +$ those from $0 \rightarrow 2$. Those of the other bands have been omitted in order to avoid confusion. It appears that $\Delta \nu_2$ and Δv_3 are practically independent of the vibrational state. The figure shows, however, that for $\Delta \nu_1$ the plusses lie systematically above the crosses. The values for $V''=2$ are still higher and those for $V''=3$ are very much higher so that the sign of $\Delta \nu_1$ is reversed for $K > 10$.

In comparing the empirical data of Fig. 5 with the theoretical predictions given on page 16,

¹⁴ Note added in proof: A further investigation of the perturbations showed that there are no levels which are completely free from the inhuence of the perturbations. The value of B given is probably somewhat too small.

it must be born in mind that departures from case a take place already for small values of K , which affect the Λ -doubling considerably, so that a quantitative agreement cannot be expected. It is apparent, however, that Δv_1 which is appreciable for very small values of X must belong to $\Omega = 0$. Δv_3 is much smaller for small K than $\Delta \nu_2$. $\Delta \nu_2$ must have, therefore, $\Omega = 1$, and $\Delta \nu_3$, $\Omega = 2$. This shows again in agreement with what was found before, that the triplet is a normal triplet and that the numbering of the branches is correct.

The rotational constants of the 3 II level are best calculated from the middle triplet component as this is not affected by the change in coupling.

We find

The moment of inertia of the state $V=0$ is $J=16.43\cdot 10^{-40}$ g cm

FIG. 1. Portion near the head of the $0\rightarrow 3$ band at 3305A. The figure shows the arrangement of the branches for low quantum numbers.

FIG. 2. The tail of the 2977 $(0\rightarrow 1)$ band. The figure shows clearly the triplets which are characteristic for high rotational quantum numbers. It also can be seen easily that successive triplets do not follow each other