INTERPRETATION OF THE ATMOSPHERIC ABSORPTION BANDS OF OXYGEN

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Abstract

It is shown that the atmospheric oxygen absorption bands can be attributed to a $^3S \rightarrow {}^1S$ transition from the normal (^3S) to a metastable ^1S excited state of O_2. This accounts for all the strong lines, and explains missing lines, without conflict with existing theory. Certain very weak series such as the A' band are, however, not yet explained. Of the three rotational levels for each value of j_k in the ^3S normal state, the two for which $j = j_k \pm 1$ show only a very small separation, which increases slowly with j_k, while the third is separated from the other two by an interval of about 2 wave-numbers which does not change with j_k (cf. Fig. 2 and Table I). The ^3S and ^1S states involved in the atmospheric bands may perhaps be attributed both to the same electron configuration, in agreement with a suggestion made in a previous paper. If this is the case, it is likely that a metastable ^1D state derived from the same configuration also exists, and that infra-red atmospheric bands corresponding to the transition $^3S \rightarrow {}^1D$ should be found.

Introduction

ALTHOUGH the atmospheric absorption bands of O_2 have been much studied,[1] and although their obvious structure appears very simple (cf. Fig. 1), no satisfactory explanation of this structure has yet been given. Valuable progress has, however, been made by Mecke, Dieke and Babcock,
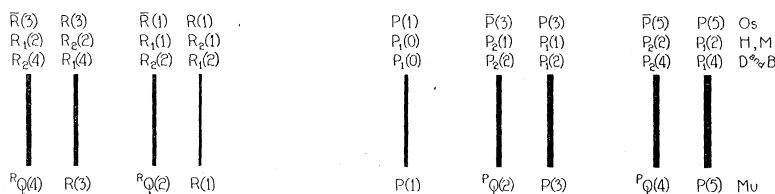

Fig. 1. *Arrangement and intensities of lines near center of A band. Comparison of notations of various investigators.* The lines are plotted on a frequency scale. The widths of the lines as drawn correspond to the widths or "intensities" of the lines as given by Dieke and Babcock. The designations of the lines are those given by various investigators (D. & B. = Dieke and Babcock, H. = Heurlinger, M. = Mecke, Os. = Ossenbrüggen, Mu = Mulliken). The line given above as $P_1(0)$ of D. & B. is really listed in their tables, evidently inadvertently, as $P_2(0)$.

and Ossenbrüggen. It is generally agreed that these bands form a progression with $n'' = 0$, and $n' = 0, 1, 2, 3, \cdots$, this conclusion being supported by combination relations between the bands.

For convenience in the following discussion, the arrangement and intensities of the central band lines in the A band ($n' = n'' = 0$) are shown in Fig. 1,

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[1] R. Mecke, Phys. Zeits. **26**, 233 (1925); G. H. Dieke and H. D. Babcock, Proc. Nat. Acad. Sci. **13**, 670 (1927); W. Ossenbrüggen, Zeits. f. Physik **49**, 167 (1928); and a large number of earlier papers to which references may be found in the papers just cited.

together with the notation used by various investigators. In the present paper, a new notation is adopted for systematic reasons.

The following combination relations (re-expressed in the present notation) have been given by Mecke, and later by Dieke and Babcock:

$$R(j-1)-P(j+1)=\phi_1(j,n'')\tag{1}$$

$$^RQ(j)-{}^PQ(j)=\phi_2(j,n'')\tag{2}$$

Equations (1) and (2) mean that the differences of suitably chosen R and P, or ^RQ and ^PQ, lines are functions only of the quantum numbers of the lower electronic state, and are therefore the same for the entire series of atmospheric bands; this relation is demonstrated with great accuracy for the stronger bands by the data of Dieke and Babcock. Equation (1) is given also by Ossenbrüggen, who shows, furthermore, that the ultra-violet Schumann absorption bands of O_2 share $\phi_1(j, n'')$ with the atmospheric bands.

All these investigators interpret $\phi_1(j, n'')$ as a $\Delta_2 F''$, and all (except Ossenbrüggen) interpret $\phi_2(j, n'')$ as another $\Delta_2 F''$: $\phi_i(j)=\Delta_2 F_i''(j)=F_i''(j+1)-F_i''(j-1)$, $i=1$ or 2. All agree with the assumption, first made by Mecke, that alternate lines are missing in each branch (as in most of the He_2 bands); this assumption is necessary to avoid the assumption of half integer jumps in the rotational quantum number.

Mecke, and Dieke and Babcock, interpret Eqs. (1) and (2) by means of the following assumed relations, involving a double set of rotational terms in both upper and lower electronic states:[2]

$$R(j)=F_1'(j+1)-F_1''(j)\tag{3}$$

$$^RQ(j+1)=F_2'(j+1)-F_2''(j)\tag{4}$$

$$P(j)=F_1'(j-1)-F_1''(j)\tag{5}$$

$$^PQ(j-1)=F_2'(j-1)-F_2''(j)\tag{6}$$

Granting the correctness of Eqs. (3)–(6), the terms $F_1'(j)$, $F_2'(j)$, $F_1''(j)$, $F_2''(j)$ can be completely determined to within additive constants. Results are given in the references cited.[1] But the correctness of these equations is not assured, since all the measured bands have $n''=0$, so that it is not possible to obtain combination relations for the upper electron level. A very serious objection to Eqs. (3)–(6) is the fact that—at least for a molecule which, like O_2, is homopolar—they would almost necessarily correspond to a $^2S \rightarrow {}^2S$ transition;[3,4] this, however, is impossible for neutral O_2, because the latter has an even number of electrons.

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[2] The parameter j in the *right* hand sides of Eqs. (3)-(6) is not supposed to be *necessarily* identical with the true quantum number j. In the symbols $R(j)$, etc., on the *left* of the equation, however, j *is* the supposed true j corresponding to the present interpretation.

[3] The fact that only P-form and R-form branches are observed probably shows that $\Delta\sigma_K=0$, and probably also that $\sigma_K=0$ (if $\sigma_K>0$, weak Q-form branches would also be expected and would almost certainly have been observed). The alternate missing lines show *definitely* that $\sigma_K=0$, since otherwise, as e.g. in a $^1P \rightarrow {}^1P$ transition, alternate lines would at most be displaced, but not missing. Hence it is practically certain that the transition is $S \rightarrow S$. If Eqs.

Supposing Eqs. (3)–(6) to be correct, we should have for the doublet separations in the R and P branches,

$$^RQ(j+1)-R(j)=D_R(j)=[F_2{}'(j+1)-F_1{}'(j+1)]-[F_2{}''(j)-F_1{}''(j)]$$

$$=D_R{}'(j+1)-D_R{}''(j) \tag{7}$$

$$^PQ(j-1)-P(j)=D_P(j)=[F_2{}'(j-1)-F_1{}'(j-1)]-[F_2{}''(j)-F_1{}''(j)]$$

$$=D_P{}'(j-1)-D_P{}''(j) \tag{8}$$

The quantities $D_R{}''(j)$ and $D_P{}''(j)$ should be the same for all the bands,[4a] since $n''=0$ for all, but $D_R{}'(j)$ and $D_P{}'(j)$, and therefore $D_R(j)$ and $D_P(j)$, would be expected to depend at least slightly on n', which differs from band to band. But it is found experimentally (as the reader can verify from the data of Dieke and Babcock) that $D_R(j)$ and $D_P(j)$ are with great accuracy the same for all the bands, that is, *independent* of n'. This suggests that, contrary to Eqs. (3)–(6), $D_R{}'(j)\equiv 0$ and $D_P{}'(j)\equiv 0$, i.e., that the rotational levels of the upper electron state are truly single.[4] If this is the case, it becomes necessary to suppose at the same time, in order to account for the observed fact that corresponding doublet widths $D_R(j)$ and $D_P(j)$ are slightly different, that the final levels are at least triple.[4a]

The fact that $D_R(j)$ and $D_P(j)$ are both independent of n' can be stated in another way by saying that the following combination relations, in addition to those expressed by Eqs. (1)–(2), hold with an accuracy as great as the latter.

$$^RQ(j)-P(j+1)=\phi_{21}(j,n'') \tag{9}$$

$$R(j-1)-{}^PQ(j)=\phi_{12}(j,n'') \tag{10}$$

New Interpretation of Atmospheric Bands

We know definitely from Ossenbrüggen's work that the lower electron level of the atmospheric bands is identical with that of the ultra-violet (Schumann) bands, and therefore that it is an S level, since the Schumann bands consist of P-form and R-form branches only, corresponding to an $S{\rightarrow}S$, in all probability a $^3S{\rightarrow}^3S$ transition.[5] The rotational levels should then be triple for the lower electronic state of the atmospheric bands. Also, the upper electronic state of the atmospheric bands must almost certainly be an S state.[3]

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(3)-(6) are correct, it must almost certainly be $^2S{\rightarrow}^2S$; $^3S{\rightarrow}^3S$ in which two of the three levels of each triplet are accidentally coalescent would also be a remote possibility.

[4] Another indication that Eqs. (3)-(6)—cf. Fig. 1 for key to earlier designations—are incorrect is the fact that they give doublets of almost exactly similar type for the upper and lower rotational states; i.e. for both $F_1{}'$ and $F_1{}''$ the effective quantum numbers T are almost exactly half integral, while for both $F_2{}'$ and $F_2{}''$, the T values fall approximately 0.05 units below half integers. Such very close similarities between two different electronic states would be surprising.

[4a] If Eqs. (3)-(6) are accepted, $D_R{}''(j)\equiv D_P{}''(j)$; also $D_R{}'(j)\equiv D_P{}'(j)$. Separate designations $D_R{}''$ and $D_P{}''$ are used here because, in the new interpretation given below, the corresponding quantities are *not* identical: cf Eqs. (16)-(17).

[5] Cf. R. S. Mulliken, Phys. Rev. **32**, 213 (1928).

Eqs. (1)–(2) and (9)–(10) can be simultaneously satisfied, and the objections which apply to Eqs. (3)–(6) can be avoided, by assuming that the following Eqs. (11)–(14) hold instead of (3)–(6). It should be noted that Eqs. (11) and (13) are formally identical with Eqs. (3) and (5); only (12) and (14) involve essential changes. The formal relations expressed by Eqs. (11), (12), and (13) have also been assumed by Ossenbrüggen.

$$R(j) = F'(j+1) - F_2''(j) \tag{11}$$

$$^{R}Q(j) = F'(j) - F_1''(j) \tag{12}$$

$$P(j) = F'(j-1) - F_2''(j) \tag{13}$$

$$^{P}Q(j) = F'(j) - F_3''(j) \tag{14}$$

Eqs. (11)–(14) correspond to a ^1S upper electron level, and a ^3S lower level with the respective designations F_1, F_2 and F_3 for the rotational levels according as $j = j_k + 1$, j_k, or $j_k - 1$; these designations correspond to the system of notation recently proposed by the writer.[6] Levels $F_1(j+1)$, $F_2(j)$, and
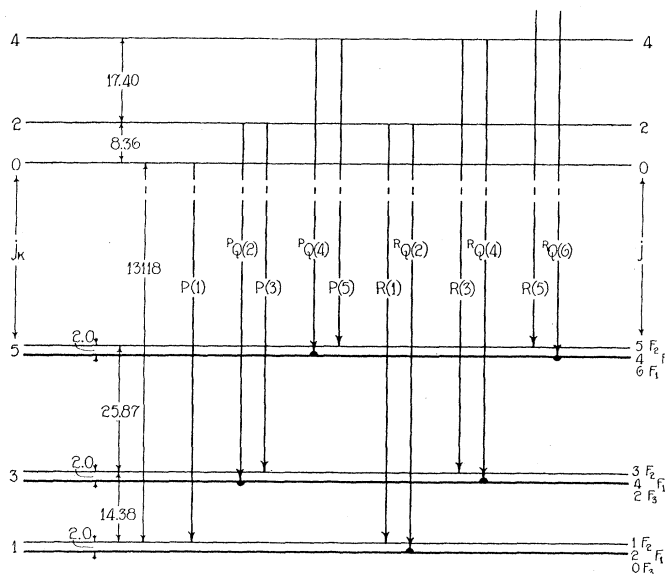

Fig. 2. *Lowest rotational levels of electronic states involved in atmospheric oxygen bands, and transitions corresponding to lines shown in Fig. 1.* The spacings of the levels (in wavenumbers) are given in the figure, except for the small intervals $F_3 - F_1$ in the ^3S levels. The latter are not large enough to show with the scale used (cf. Table I for data). Note that the *sign* of $F_3 - F_1$ reverses at $j_k = 5$.

$F_3(j-1)$, for a given value of j, should form a close triplet, since the rotational energy is mainly given by $Bj_k(j_k+1)$; hence $R(j)$ and $^{R}Q(j+1)$, $P(j)$ and $^{P}Q(j-1)$, form the observed doublets.

The four observed branches are completely accounted for by Eqs. (11)–(14), if the rotational levels corresponding to $j = 0$, 2, 4, $\cdots$ are present in

[6] R. S. Mulliken, Phys Rev. **30**, 144, 788 (1927).

the upper state, and, as in the Schumann bands, those corresponding to $j_k = 1, 3, 5, \cdots$ in the lower state. The way in which Eqs. (11)–(14) account for the observed relations can best be seen from Fig. 2. As can be seen from this figure, the four observed branches are the only branches which are possible, with the selection rule $\Delta j = 0, \pm 1$, for a ${}^1S \rightarrow {}^3S$ combination in a homopolar molecule composed of atoms with no nuclear spin.[7,7a]

Intensity relations. A characteristic feature of the atmospheric bands is the absence of one component in the first doublet of the P branch. This is now accounted for by the fact that the missing line in question, which would be ${}^PQ(0)$, is ruled out by the special prohibition of the transition $0 \rightarrow 0$ for j.[8]

The approximately equal intensity of the P and R branches is as expected for an $S \rightarrow S$ transition. No detailed explanation of other intensity relations can be given, however, since the intensity theory has not been developed for inter-system transitions, and since the intensity relations may be greatly distorted by the strong absorption. A few remarks based on the observed relations can, however, be made. In each doublet, one component has $\Delta j = \pm 1 = \Delta j_k$, the other has $\Delta j = 0 \neq \Delta j_k$.[7a] In a ${}^3S \rightarrow {}^3S$ transition, lines with $\Delta j \neq \Delta j_k$ would be very weak, but here this rule evidently does not apply, since the components with $\Delta j = 0$ are of about the same strength as the other components.[10] At the beginning of each branch there is, however, a decided inequality of intensity of the components of each doublet, in such a way that the component for which the mean value of j, i.e., $(j' + j'')/2$, is larger, is the more intense. In agreement with this formulation, the inequalities gradually disappear as j increases. This situation is at least superficially similar to that which exists in the doublets of ${}^2S \rightarrow {}^2S$ transitions.[9]

Isolation of rotational terms. From Eqs. (11)–(14) we have:

$$R(j-1) - P(j+1) = F_2''(j+1) - F_2''(j-1) = \Delta_2 F_2''(j) \quad (15)$$

$$D_R(j) = {}^RQ(j+1) - R(j) = F_2''(j) - F_1''(j+1) \quad (16)$$

$$D_P(j) = {}^PQ(j-1) - P(j) = F_2''(j) - F_3''(j-1) \quad (17)$$

$$R(j) - P(j) = F'(j+1) - F'(j-1) = \Delta_2 F'(j) \quad (18)$$

[7] If alternate rotational levels were not missing (characteristic of a homopolar molecule whose atoms have no nuclear spin—cf. W. Heisenberg, Zeits. f. Physik **41**, 239 (1927) and F. Hund, Zeits. f. Physik **42**, 106 (1927)), additional branches should be present.

[7a] The observed branches conform to the selection rule $\Delta j_k = \pm 1$, but it is possible that this is not significant, since it is an automatic consequence of the alternate missing levels and of the selection rule $\Delta j = 0, \pm 1$.

[8] The quantum numbers j_k, s and j in a case b molecular state like ${}^3S$ are completely analogous in the determination of intensity relations to l, s, and j in an atom.[9] The transitions from a ${}^1S$ molecular level with $j = 0$ to a ${}^3S$ molecular level with $j_k = 1$ are then entirely analogous to those from a ${}^1S$ to a ${}^3P$ atomic level, in which ${}^1S \rightarrow {}^3P_0$ is ruled out by the $0 \rightarrow 0$ prohibition, and only ${}^1S \rightarrow {}^3P_1$ occurs (e.g. Hg $\lambda 2537$).

[9] Cf. e.g. the discussion of $S \rightarrow S$ transitions by the writer, Phys. Rev. **30**, 139 (1927).

[10] This result is rather unexpected, and conflicts with a probably not well-founded statement made earlier by the writer[6] to the effect that lines for which $\Delta j \neq \Delta j_k$ should be weak in ${}^3S \rightarrow {}^1S$ transitions as in other cases. Intersystem transitions apparently show exceptional behavior.

Except for notation, Eqs. (15) and (18) are just as consistent with Eqs. (3, 5) as with Eqs. (11, 13). Hence for $\Delta_2 F'(j)$ and $\Delta_2 F_2''(j)$ the results of Dieke and Babcock and Ossenbrüggen still hold.[11] Their formulas for $F'(j)$ and $F_2''(j)$, which can be determined in the usual manner from the $\Delta_2 F$'s, also remain valid. These results are, $F'(j) = B'[j(j+1)] + \cdots, j = 0, 2, 4, \cdots,$ with $B' = 1.392$ for $n' = 0$; and $F_2''(j) = B''[j_k(j_k+1)] + \cdots, \; j_k(=j) = 1, 3, 5, \cdots,$ with $B'' = 1.438$. The effective rotational quantum numbers are almost accurately integral in both cases, i.e., only a very small linear term in j is needed in representing $F(j)$. If desired, the exact term values (except for an additive constant) can be built up by summation of $\Delta_2 F$'s (cf. Fig. 2).

For the F_1'' and F_3'' levels, the $\Delta_2 F''$ expressions can be obtained by suitable combination of the quantities in Eqs. (15) and (16) or (17). Using the data of Dieke and Babcock, it is found that the expressions $\Delta_2 F_1''(j_k)$, $\Delta_2 F_2''(j_k)$, and $\Delta_2 F_3''(j_k)$ are almost identical, i.e. B'' is practically the same for all three, and the effective rotational quantum numbers differ only very slightly for the three levels.[12] As shown by the application of Eqs. (16) and

TABLE I. *Spacings of triplets in rotational levels of ^3S state.*

$j(=j_k)$	$D_P(j) = F_2(j) - F_3(j-1)$	$D_R(j) = F_2(j) - F_1(j+1)$	Average	$j(=j_k)$	$F_2 - F_3$	$F_2 - F_1$	Average
1		1.88		15	1.86	2.31*	*
3	2.09	1.94	2.015	17	1.87	2.29*	*
5	1.99	2.01	2.000	19	1.86	2.13*	*
7	1.94	2.01	1.975	21	1.82*	2.13*	*
9	1.92	2.07	1.995	23	1.81	2.19	2.00
11	1.90	2.09	1.995	25	1.80	2.19*	*
13	1.88	2.15	2.015	27	1.77	2.21*	*

Notes. The above values of $D_P(j)$ and $D_R(j)$ are the doublet separations in the P and R branches, respectively, according to the data of Dieke and Babcock, for the A band. (Better values could be obtained by using average values obtained from the whole series of bands, but the above data are sufficient to show the trend of affairs.) The meaning of the numerical values of j and j_k will be clear from Eqs. (16) and (17) together with the fact that $j_k = j$ for F_2 levels, $j_k = j+1$ for F_3 levels, and $j_k = j-1$ for F_1 levels. From the data given, it will be seen that $F_3 - F_1$ is negative for the smallest values of j_k, but soon becomes positive and then increases slowly with j_k, remaining, however, in the observed range, always much smaller than the constant interval of 2.0 between F_2 and the average of F_1 and F_3.

(17), there is, however, an approximately constant difference of about 2 wave numbers between $F_2(j_k)$ and $[F_1(j_k) + F_3(j_k)]/2$. F_1 and F_3 themselves form a very narrow doublet whose size changes slowly with j_k; also, $F_3(j_k) - F_1(j_k)$ changes sign at about $j_k = 5$. The relationships of the F_1'', F_2'', and F_3'' levels are best appreciated by a study of the doublet separations $D_R(j)$ and $D_P(j)$ of Eqs. (16) and (17) as shown in Table I and Fig. 2.

[11] Thus $\Delta_2 F'(j)$ of Eq. (18) is the same as Dieke and Babcock's F_1' $(j+1) - F_1'(j-1)$, and $\Delta_2 F_2''(j)$ of Eq. (15) is the same as Dieke and Babcock's $F_1''(j+1) - F_1''(j-1)$.

[12] These conclusions differ greatly from those of Mecke and Dieke and Babcock, according to whom[3] one set (their F_1) of F' and of F'' levels had effective quantum numbers almost exactly integral, another (their F_2) had effective quantum numbers departing considerably from integers (cf. ref. 4).

Difficulties. In the writer's opinion, the above interpretation of the atmospheric bands is the only one yet given which accounts for all the observed features of the strong band lines without obvious conflict with existing theory. It has, however, some weaknesses. First of all (in common with all earlier interpretations) it lacks the support of combination relations for the initial electronic states. These can be obtained only by new experimental work on the absorption of hot oxygen, so as to get detectable absorption from molecules with $n'' > 0$; this will be very difficult, because of the extremely low coefficients of absorption, requiring high pressure and long gas columns.

Another feature of the present interpretation which might give rise to doubts as to its validity is the peculiar spacing of the triplets in the ^3S levels (cf. Fig. 2 and Table I). This, however, does not appear to the writer to be a serious objection, for the following reasons. A consideration of the dissociation of a ^3S O_2 molecule into two atoms indicates that the molecules in F_2 states should give atomic states slightly different from those given by molecules in F_1 and F_3 states; e.g. perhaps the F_1 and F_3 levels both go over into $O(^3P_2)+O(^3P_2)$, while the F_2 levels go over into $O(^3P_2)+O(^3P_1)$. If an energy separation corresponding to $^3P_1-^3P_2$ (about 150 wave-numbers) exists in the dissociated molecule, one may reasonably expect a corresponding separation to persist to some extent in the united molecule. These considerations indicate that the interval of 2 wave-numbers, independent of j_k, which separates the F_2 from the average of the F_1 and F_3 levels, is not in contradiction with a ^3S classification. The much smaller interval F_3-F_1, increasing with j_k, may reasonably be attributed in the usual manner to the interaction of the spin with the magnetic field developed by the molecular rotation.

Perhaps the most serious objection to the present interpretation is that the energy levels of Fig. 2 cannot be made to account for the various faint absorption lines which are present in the atmospheric bands in addition to the strong lines. Thus in the (0, 0) band (A band) there is a very faint series of doublets (A' band) comprising the lines of a P' and an R' branch whose members alternate with the strong P and R doublets. If these alternate weak doublets were spaced symmetrically between the strong doublets, they could be interpreted as being the alternate missing lines of the strong series. These might perhaps after all be expected in very low intensity, corresponding to some small interaction neglected in the ordinary theory, even in a homopolar molecule without nuclear spin. But they are not symmetrically spaced, so that the suggested explanation seems improbable, since there is no evident reason why the alternate energy levels should be systematically perturbed.

It might be argued that the A' band is entirely independent of the A band, but if so, it is very difficult to understand why its lines have so nearly the same arrangement and spacing as the lines of the A band (cf. especially Ossenbrüggen's discussion).[1] It therefore seems probable that the present interpretation will need to be modified to account for the A' lines simultaneously with the A lines. Nevertheless, especially in view of the fact that

the A' lines are exceedingly weak as compared with the A lines,[13] it seems reasonable to regard the present interpretation as at least a probable first approximation to the complete explanation. It should also be remarked that the present is no worse than earlier interpretations in its inability to explain the A' lines.

BEARING OF RESULTS ON ELECTRONIC LEVELS OF THE OXYGEN MOLECULE

The writer has suggested elsewhere[5] that the normal, ^3S, state of O_2 is the lowest of the three states, ^3S, ^1D, and ^1S which are to be expected from an electron configuration $(1s^s)^2 (2s^p)^2 (2s^s)^2 (3s^p)^2 (2p^p)^4 (3s^s)^2 (3p^p)^2$. According to this suggestion, the ^1D and ^1S states should be metastable excited states lying within a few volts of the normal state. The reason for predicting metastability for the ^1D and ^1S states is similar to that for the expected ^1D and ^1S states of the O atom which have the same configuration as the normal, ^3P, state of the latter.

The ^1S upper level of the atmospheric bands seems to meet the specifications just given. It lies 1.62 volts above the ^3S level, with which it combines exceedingly weakly: the entire thickness of the earth's atmosphere gives only a moderate absorption for the transition $^3S \rightarrow {}^1S$, while for ordinary laboratory thicknesses, air is practically completely transparent. The fact that $^3S \rightarrow {}^1S$ corresponds to an inter-system combination tends of course to make the absorption coefficient low, but this fact alone is altogether inadequate to account for the actual *very* low coefficient.[14] Hence it appears that the ^1S state may rightly be classed as metastable. The interval of 1.62 volts between ^3S and ^1S is a reasonable one on the hypothesis that these states have the same electron configuration. It may for example be compared with the interval of 1.63 volts between $3^3 P$ and $3^1 P$ of the Mg atom, or with that of 0.8 volts between 2^3S and 2^1S of the He atom.

If this interpretation of the low ^3S and ^1S levels of O_2 is correct, one may predict the existence of a metastable ^1D level probably lying between them. Correspondingly, there should probably be infra-red atmospheric absorption bands associated with a weak transition $^3S \rightarrow {}^1D$.

According to the interpretation given above, there would be a considerable analogy between the emission transition $^1S \rightarrow {}^3S$ in O_2 (observed, absorption $^3S \rightarrow {}^1S$) and the emission of the green aurora line, which corresponds according to Sommer[15] to the transition $^1S \rightarrow {}^3P$ in the neutral oxygen atom.

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[13] Although many of the A lines appear as very broad absorption lines in the solar spectrum, the corresponding A' lines are so narrow as to be difficult to detect (cf. e.g. Dieke and Babcock[1]). This indicates an *enormously* greater absorption probability for frequencies corresponding to the centers of A lines than for A' lines.

[14] Thus in the case of CO, the combination $^1S \rightarrow {}^3P$ occurs in absorption with sufficient intensity to be readily studied in moderate thicknesses of gas at atmospheric pressure or less, and the same bands (Cameron bands) are also observed in emission; cf. Birge, Phys. Rev. **28**, 1157 (1926) for references.

[15] L. A. Sommer, Naturwiss, **16**, 219 (1928). Cf. also the nebulium lines: cf. W. Grotrian, Naturwiss. **16**, 177 and 193 (1928) for review.