

FURTHER INVESTIGATIONS ON COLUMBIUM OXIDE BANDS

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INTRODUCTION

After the analysis of the three bands (1, 0), (0, 0) and (0, 1) of columbium oxide described in a previous paper has been obtained, it is found that besides the lines forming the *R* and *P* branches there are a number of fainter rotational lines which occur at the end nearer the head. A further study of these lines has indicated that they might form members of a satellite branch. In this paper the results of this study and a discussion of the electronic transition giving rise to this system of bands of CbO are given.

SATELLITE BRANCH

The higher resolution, sharply focussed photographs of the three bands reproduced in Plate IX revealed that the unassigned rotational lines mentioned above

TABLE I
Satellite branch in (1, 0) Band

Wave number	First difference	Wave number	First difference
22148.70		22121.78	
147.29	1.41
145.79	1.50	116.89	..
144.17	1.62
142.44	1.73	111.49	..
140.62	1.82	108.88	2.61
138.94	1.68
137.07	1.87	103.14	..
135.09	1.98
132.79	2.30	096.85	..
130.95	1.84	094.16	2.69
128.92	2.03	091.04	3.12
126.54	2.38	087.84	3.20
124.30	2.24	084.61	3.23
	2.52		

TABLE II
Satellite branch in (0, 0) Band

Wave number	First difference	Wave number	First difference
21312.97		21262.61	
	1.05		2.93
311.92	1.34	259.68	2.96
310.58	1.25	256.72	2.61
309.33	1.13	254.11	3.13
308.20	1.48	250.98	2.90
306.72	1.86	248.08	3.25
304.86	1.35	244.83	3.32
303.51	1.49	241.51	3.00
302.02	1.55	238.51At	3.33
300.47	1.61	235.18	3.52
298.86	1.71	231.66	3.30
297.15	..	228.36	3.58
..	..	224.78	3.55
..	..	221.23	3.58
..	..	217.65	3.88
..	..	213.77	..
287.44	2.21
285.23	2.10	206.28	4.06
283.13	2.31	202.22	3.92
280.82At	2.17	198.30	4.02
278.65	2.22	194.28	4.10
275.43	2.83	190.18	3.88
272.60At	2.14	186.30	4.36
270.46	2.58	181.94	4.31
267.88	2.73	177.63	4.35
265.15	2.54	173.28	4.51
		168.77	

TABLE III
Satellite branch in (0, 1) Band

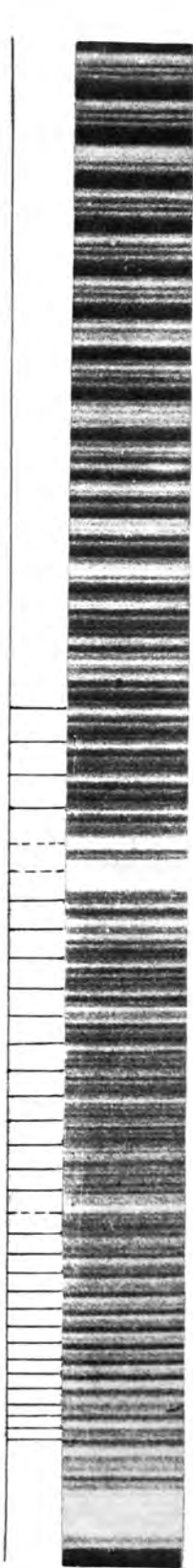
Wave number	First difference	Wave number	First difference
20323.53	1.39	20295.34	2.39
322.14	1.42	292.95	..
320.72	1.51
319.21	1.34	288.76	3.15
317.87	1.41	285.61	2.69
316.46At	1.67	282.92	2.51
314.79	..	280.41	2.71
..	..	277.70	2.93
310.18	..	274.77	2.75
..	..	272.02	2.48
..	..	269.54At	..
..
301.95	2.09	263.05	3.19
299.86	2.24	259.86	3.09
297.62	2.28	256.77	

show a gradual rise and fall in intensity. They occur in proximity to the members of the *P* and *R* branches. The interval from the respective *P* or *R* lines is found to be increasing as one proceeds away from the head. These could be grouped into a branch as shown in the Tables I, II and III, which give the wave numbers together with the first differences in the satellite branch in the three bands (1, 0), (0, 0) and (0, 1) respectively. These lines are shown marked for each band in Plate IX. The interpretation of the satellite branch is given in the discussion on the electronic transition.

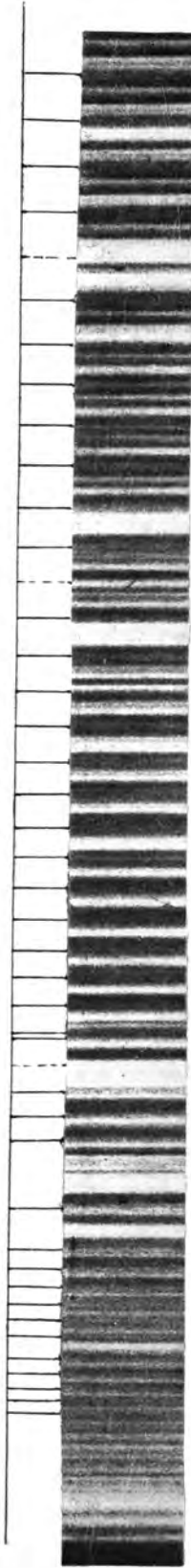
ELECTRONIC TRANSITION

From the analysis given in the previous paper it is difficult to determine conclusively the electronic transition involved in the emission of this system. But a few inferences are drawn from the structure as far as it is identified and a general discussion is presented of various considerations bearing on the nature of this electronic transition. These considerations indicate that the transition is $\Sigma-\Sigma$ with a multiplicity of either two or a higher even value (probably four) for the two states.

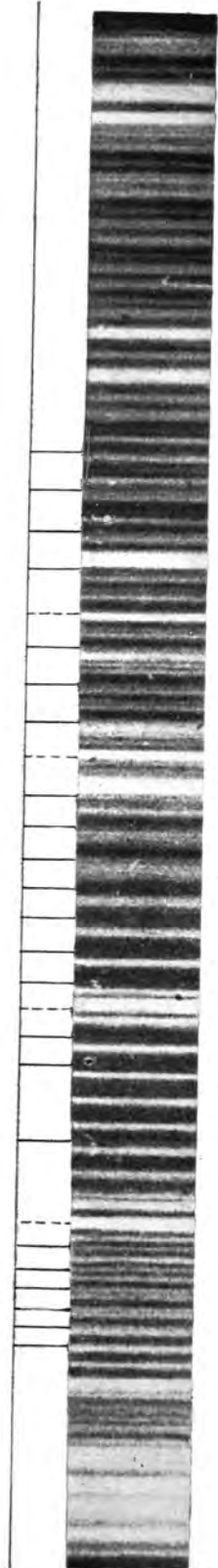
As a first step, one may predict from theoretical considerations the possible electronic states of the molecule from the usual standpoints: either from the states of the separated atoms or from the probable electronic configurations of the molecule.



(1,0) Band



(0,0) Band



(0,1) Band

Satellite branch in CbO Bands

(1) The low-lying states of the columbium atom established by Meggers and Humphreys (1945) correspond to the configuration $4d^45s$ (ground configuration), giving the deepest term 6D and $4d^35s^2$, giving the term 4F ; oxygen has the normal configuration $2s^22p^4$ leading to the ground term 3P . In the formation of the molecule CbO from these two atoms, the following molecular states are obtained, taking $4d^45s$ as the normal configuration of columbium atom as definitely established by Meggers and Humphreys.

With the usual notation

$$\begin{aligned}
 S_1 &= 5/2 \text{ and } S_2 = 1 \text{ so that } S = 7/2, 5/2, 3/2 \\
 \Lambda &= 0, 1; \quad {}^8\Sigma, {}^8\pi; \quad {}^6\Sigma, {}^6\pi; \quad {}^4\Sigma, {}^4\pi \\
 &= 0, 1, 2; \quad {}^8\Sigma, {}^8\pi, {}^8\Delta; \quad {}^6\Sigma, {}^6\pi, {}^6\Delta; \quad {}^4\Sigma, {}^4\pi, {}^4\Delta \\
 &= 0, 1, 2, 3; \quad {}^8\Sigma, {}^8\pi, {}^8\Delta, {}^8\phi; \quad {}^6\Sigma, {}^6\pi, {}^6\Delta, {}^6\phi; \quad {}^4\Sigma, {}^4\pi, {}^4\Delta, {}^4\phi
 \end{aligned}$$

No doublet electronic states occur among the molecular states predicted above.

(2) Considering the electronic configuration of the molecule as a whole, the diatomic molecule CbO may give rise to the following states:—

$$\begin{array}{lll}
 \sigma^2\sigma^2\sigma^2\pi^4\pi & 2\pi & (1) \\
 \sigma^2\sigma^2\sigma\pi^4\pi^2 & 4\Sigma & (2) \\
 \sigma^2\sigma^2\sigma^2\pi^3\pi^2 & 4\pi \text{ or } 2\pi & (3) \\
 \sigma^2\sigma^2\sigma\pi^4\pi\pi & 4\Sigma & (4)
 \end{array}$$

and so on. Regarding the multiplicity of the expected electronic states it is evident that it must be even. The multiplicity may be two or four since higher multiplicity terms are not expected even from a general survey of the structure of the spectrum. But regarding the nature of the terms in the upper and lower states there are obviously several possibilities as noted from the above two methods.

On the basis of a resemblance between the electronic configurations of the CbO molecule and the yttrium atom (similar to what has been shown by Lowater (1929) to exist between TiO molecule and the calcium atom), Ramakrishna Rao (1950) tentatively assigned this system in CbO to the transition $4\pi-4\pi$. While in TiO, Christy (1929) suggested the transition $3\pi-3\pi$ from the rotational analysis, Ramakrishna Rao's conclusion about the system A of CbO as a $4\pi-4\pi$ transition was not based on rotational structure data.

Titanium and zirconium occur in the fourth left sub-group, vanadium and columbium in the fifth left sub-group and oxygen in the sixth right sub-group of the periodic table. A similarity may therefore be expected from the electronic transitions of titanium oxide and zirconium oxide and among vanadium oxide and columbium oxide. The latter may resemble the ionized molecule O_2^+ .

The rotational structure of the first and second negative bands of O_2^+ establishes the electronic transitions ${}^2\pi_u-{}^2\pi_g$ and ${}^4\Sigma_g^- - {}^4\pi_u$ as characteristic of O_2^+ . If an analogy can be drawn between the three molecules which have the same number of outer electrons (11) one should expect the above transitions in vanadium oxide and columbium oxide also. The structure, relative intensities and energy terms in the case of band systems for a ${}^4\Sigma-{}^4\pi$ transition were calculated by Budo (1937) and also by Nevin (1938). As many as 48 branches may be expected from such a transition or at least 40, on account of the blending of the levels $F'_1(K)$ and $F'_4(K)$ and $F'_2(K)$ and $F'_3(K)$ of the ${}^4\Sigma$ level. The existence of four components corresponding to the splitting in the ${}^4\pi$ level should be a distinct feature of this system. Four such components were actually observed by Nevin at intervals of about 50 cm.^{-1} in the first negative bands of O_2^+ and each of these branches indicated also a separation of 0.45 cm.^{-1} associated with the spin fine structure of the ${}^4\Sigma$ state.

Dealing with this band system of CbO, its analogy with O_2^+ led the writer in the early stages to detect, if possible, the existence of the structure described. Four components could not at all be identified. No doubt three closely situated heads right at the beginning of the band are observed in the earlier photographs but in the later higher resolution pictures, only one of these three heads appears to be a genuine one, the other two having a distinctly different, diffuse appearance, as described in the previous paper. Further, even three independent groups of branches could not be associated with these heads nor could an extensive Q branch be identified. The structure of the CbO bands on the whole was found relatively simpler than what might be expected of a $4\Sigma-4\pi$ transition.

A $2\pi-2\pi$ transition also does not seem to be consistent with the observed structure, as the expected structure for this transition for both case (a) and case (b) states can be predicted from the well-known structure of the β system of NO and the ultraviolet bands of O_2^+ . The appearance of double, double-headed system, characteristic of $2\pi-2\pi$ is not found in CbO. Further, a π state of any multiplicity whatsoever cannot perhaps be postulated at all since no evidence is found of Λ -type doubling even for high values of K , which normally varies quadratically with K .

For vanadium oxide Mahanti suggested $2\Delta-2\Delta$ as a probable transition concerned in the emission of the band system. This transition might be expected in the spectrum of CbO also since both occur in the same sub-group. But no positive evidence was given by Mahanti in support of his suggestion, such as the number of missing lines, the intensities or the variation of the R and P intervals with K . The last criterion has been studied by the author (unpublished) in VO and in CbO and the variation of the R and P intervals with K has been found to be distinctly linear in VO and nearly so in CbO (which can be seen to be the case theoretically for a $\Sigma-\Sigma$ transition), whereas for a $2\Delta-2\Delta$ transition one should expect, theoretically, a non-linear variation, as is observed in NiH bands (Pearse, 1935).

The possibility of ascribing this system (system A of CbO) to a $\Sigma-\Sigma$ transition in which both the Σ states are either doublets or quartets is next examined. It is well known that in a 2Σ state there is a case (b) spin doubling of each rotational level but no Λ -type doubling. Six branches are to be expected from the selection rules— $P_1(J)$, $P_2(J)$, ${}^P Q_{12}(J)$, ${}^R Q_{21}(J)$, $R_1(J)$, $R_2(J)$. The first three branches lie close together and the last three form another close group. There will be a gap due to the absence of one line $K' = 0 \rightarrow K'' = 0$. The P and R branches are of relatively high and equal intensities, while the two satellite branches are feeble and rapidly fall off in intensity as K increases.

Comparing this structure with the one observed in CbO there is no doubt a good agreement as far as the number of the main branches is concerned. But the observed satellite branch or branches are relatively rather too strong for $2\Sigma-2\Sigma$ transition. Further, it can also be predicted that in a $2\Sigma-2\Sigma$ transition the relative disposition of the satellites with respect to the main branches will be as shown on page 248 (Herzberg, 1951). The ${}^P Q_{12}$ occurs to the violet side of the P lines while the ${}^R Q_{21}$ occurs on the red side of the R lines.

In the present case whether the electronic transition is $2\Sigma-2\Sigma$ cannot be definitely decided since (a) the two predicted satellite branches are not identified (only one satellite branch is observed and the other that is expected if the transition is $2\Sigma-2\Sigma$ may have been missed on account of superposition) and (b) the position of the observed satellite branch with respect to the main branch lines, that is, whether it occurs on the short wavelength or the long wavelength side of it, could not be ascertained because the numbering could not be definitely arrived at.

For examining the possibility of 4Σ states a detailed study is made of this transition since in the existing literature there does not seem to be any band system so far observed that is ascribed to a $4\Sigma-4\Sigma$ transition. The energy level diagram and the expected branches are given in a previous paper (1954), which is drawn up on

the basis of the theoretical calculations of the energy expressions derived by Budo for the 4Σ state. For this state F_1 and F_4 levels lie close together and similarly F_2 and F_3 are close so that the electronic state can be regarded in effect as consisting of only two levels. According to the J, K and $+ \rightleftharpoons -$ selection rules 18 branches will be obtained. They form into two groups, namely, an R -form group consisting of $R_1, R_4; R_2, R_3, {}^R Q_{32}; {}^R Q_{43}, {}^R P_{42}; {}^R Q_{21}, {}^R P_{31}$ and a P -form group made up of $P_1, P_4; P_2, P_3, {}^P Q_{23}; {}^P R_{24}, {}^P Q_{34}; {}^P Q_{12}, {}^P R_{13}$. No main Q branches will be obtained according to the $+ \rightleftharpoons -$ selection rule. On account of the blending of the levels in a 4Σ state referred to above, the nine R form components and the nine P form ones may give rise to actually four branches in each group as shown below.

R form Group	P form Group
R_1, R_4	P_1, P_4
$R_2, R_3, {}^R Q_{32}$	$P_2, P_3, {}^P Q_{23}$
${}^R Q_{43}, {}^R P_{42}$	${}^P Q_{34}, {}^P R_{24}$
${}^R Q_{21}, {}^R P_{31}$	${}^P Q_{12}, {}^P R_{13}$

To indicate this on the diagram the branches which form a blend are marked close together. Effectively eight branches can be expected in a $4\Sigma-4\Sigma$ transition. Even this eight branch structure can perhaps be observed only for high K values. For the lowest K values all the R form lines may merge into one line and the P form lines into another line thus giving rise to just two series of strong lines near the head—an appearance that closely corresponds to the observed feature in all the three bands of CbO .

For high values of K , the R form and the P form blends may be separated from the respective main components and one or more satellite branches may be resolved depending on the resolution. Actual observation and identification has shown only one satellite branch and the numbering is not definite. Hence it is not possible to draw any definite conclusion as to whether the system belongs to the transition $4\Sigma-4\Sigma$ or not, from this standpoint. Regarding the nature of the observed satellite branch the following remarks may be made.

(a) Considering this in the first instance as an R -form satellite branch (either as ${}^R P_{31}$ (${}^R Q_{21}$) or as ${}^R P_{42}$ (${}^R Q_{43}$) by reference to the transition diagram of $4\Sigma-4\Sigma$ given in a previous paper) all possible sets of frequency differences with the four main branch lines are formed and compared with the combination differences already arrived at from the main branches for the upper and the lower states for checking up the combination relations which are as follows:

$$\begin{aligned}
 & {}^R P_{31}(K) ({}^R Q_{21}) - {}^P R_{24}(K) ({}^P Q_{34}) = R_2(K) - P_2(K) = \Delta_2 F'_2(K) \text{ or} \\
 & {}^R P_{42}(K) ({}^R Q_{43}) - {}^P R_{13}(K) ({}^P Q_{12}) = R_1(K) - P_1(K) = \Delta_2 F'_1(K) \text{ and} \\
 & {}^R P_{31}(K-1) ({}^R Q_{21}) - {}^P R_{24}(K+1) ({}^P Q_{34}) = R_1(K-1) - P_1(K+1) = \Delta_2 F''_1(K) \text{ or} \\
 & {}^R P_{42}(K-1) ({}^R Q_{43}) - {}^P R_{13}(K+1) ({}^P Q_{12}) = R_2(K-1) - P_2(K+1) = \Delta_2 F''_2(K)
 \end{aligned}$$

It is found that in all the three bands for a particular numbering of the satellite branch, the above relations are satisfied under the assumption that one of the four main branches has to be also regarded as a satellite branch (either as ${}^P R_{24}$ (${}^P Q_{43}$) or as ${}^P R_{13}$ (${}^P Q_{12}$) as the case may be). The K -numbering of the satellite branch determined from the above combination relations is given below for the three bands:

(1, 0) Band: Satellite branch $\nu 22147.29$ ($K = 32$) Main branch $\nu 22102.72$ ($K = 32$) (on which a satellite branch is supposed to be superposed).

- (0, 0) Band: Satellite branch $\nu 21256.72$ ($K = 32$) Main branch $\nu 21302.79$ ($K = 32$) (on which a satellite branch is supposed to be superposed).
- (0, 1) Band: Satellite branch $\nu 20323.53$ ($K = 33$) Main branch $\nu 20276.58$ ($K = 33$) (on which a satellite branch is supposed to be superposed).

Thus, if the transition is a $^4\Sigma - ^4\Sigma$, the satellite branches identified in the three bands may be either (1) $^R P_{31}$ ($^R Q_{21}$) in which case the satellite branch $^P R_{24}$ ($^P Q_{34}$) should be assumed to be superposed on a main branch, or (2) $^R P_{42}$ ($^R Q_{43}$) in which case the satellite branch $^P R_{13}$ ($^P Q_{12}$) should be assumed to be superposed on a main branch, with the numbering given above. But it has not been possible to decide between the two alternatives. Further it should be mentioned that, if this numbering is correct, these branches could be traced in all the three bands up to K values as high as nearly 60.

(b) The observed satellite branch may also be regarded as either $^P R_{24}$ ($^P Q_{34}$) or $^P R_{13}$ ($^P Q_{12}$) and attempts to check up the combination relations have not been possible with this interpretation because it is not possible to obtain the values of the combination differences for members corresponding to small K values. It may, however, be stated that on the assumption that this is a P -form R branch, the maximum observed value of K would be much less than 60.

The transition cannot be a $^6\Sigma - ^6\Sigma$ or a $^8\Sigma - ^8\Sigma$ since the number of main branches, besides the satellite branches, will be greater than the number of observed branches in CbO , in spite of the blending of levels with the same $|J - K|$ (six in the former and eight in the latter transition), whereas the number of observed branches is five out of which four are main branches. Even under a higher resolution than has been used in these investigations it is not likely that the number of branches may be greater than six at best.

These considerations indicate that the transition is $\Sigma - \Sigma$ with a multiplicity of either two or more probably four for the two states.

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ABSTRACT (SUMMARY)

A further study of sharply focussed photographs of the (1, 0), (0, 0) and (0, 1) bands of system A of columbium oxide led to the detection of a satellite branch in each band, in addition to the main P and R branches reported previously. A discussion is given of the electronic transition of the band system. This is indicated to be probably a $^4\Sigma - ^4\Sigma$, corresponding to which there is no band system as yet known.

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