distribution curves are zero. These values of r are 3.24A for 1, 3.10A for 2, 3.03A for 4, 3.0A for 5, 2.7A for 6, and 2.6A for 7. This is presumably due to the fact that the more energetic atoms at high temperature approach each other to slightly smaller distances than at the lower temperatures.

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On the $^2\Pi_u \rightarrow {}^2\Pi_g$ Bands of CO_2^+. Part II*

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In continuation of the first part of the work containing the rotational analysis of 10 sub-bands belonging to the progression $v''_1=0$ of the $^2\Pi_u \rightarrow {}^2\Pi_g$ band system of CO_2^+, 24 new sub-bands were analyzed. These bands belong to the progressions $v''_1=1$ and $v''_1=2$. It was found that the substate $^2\Pi_{3/2g}$, $v''_1=1$ is split into two levels, the splitting being probably caused by an interaction (resonance) with some other unidentified substate (very probably one of the vibronic substates corresponding to two quanta of bending vibration). A similar splitting was found in the substate $^2\Pi_{3/2u}$, $v'_1=4$. Weaker perturbations, manifested by anomalous B values, Λ-doubling increasing proportionally to about $J^{2.5}$, and shifts of vibrational levels were detected in several other vibrational levels. A selection rule forbidding transitions between vibrational levels showing opposite perturbation shifts in the vibrational energy has been found. The new constants obtained are: $\Delta G''^a{}_1=1241.77$, $\Delta G''^b{}_1=1287.32$, $\Delta G''^b{}_2=1209.55$ (all $^2\Pi_{3/2g}$): $\Delta G''_1=1265.75$, $\Delta G''_2=1256.89$ ($^2\Pi_{\frac{1}{2}g}$); $\Delta G'^a{}_4=1062.50$, $\Delta G'^b{}_5=1055.25$, $\Delta G'_6=1103.97$ ($^2\Pi_{3/2u}$); $\Delta G'_5=1108.50$, $\Delta G'_6=1106.99$ ($^2\Pi_{\frac{1}{2}u}$). Further, for $^2\Pi_{3/2g}$, $B''^a{}_1=0.3754$, $B''^b{}_1=0.3814$, $B''_2=0.3769$; for $^2\Pi_{\frac{1}{2}g}$, $B''_1=0.3803$, $B''_2=0.3793$; for $^2\Pi_{3/2u}$, $B'^a{}_4=0.3421$, $B'_5=0.3427$, $B'_6=0.3417$; for $^2\Pi_{\frac{1}{2}u}$, $B'_5=0.3460$, $B'_6=0.3458$. The values of the constants reported in Part I are corrected and the Λ-doubling for all levels is evaluated. Formulas for unperturbed values of B (both substates $^2\Pi_{3/2}$ and $^2\Pi_{\frac{1}{2}}$) are: $^2\Pi_g B''_v=B''_0-0.0012v''_1$, $^2\Pi_u B'_v=B'_0-0.0011v'_1$; for unperturbed zero band lines $\nu_{v'v''}=\nu_{00}+1131v'_1-3v'_1(v'_1+1)-1280v''_1+7.25v''_1(v''_1+1)$.

INTRODUCTION

IN the first part of this work published several months ago[1] the rotational analysis of five double bands of the $^2\Pi_u-{}^2\Pi_g$ band system of CO_2^+, belonging to the $v''_1=v''_2=v''_3=0$ progression of the symmetrical vibration (v'_1 varying, $v'_2=v'_3=0$), was reported. It was shown there that the lower state of these bands is the ground state of the CO_2^+ molecule and that the molecule is linear in both $^2\Pi$ states. Both states $^2\Pi$ are inverted. The method of excitation used and the procedure followed in determining wave numbers from the photographs, obtained in the second order of the 30-foot grating spectrograph, were described in Part I. In continuation of this work, the rotational analysis of bands belonging to the $v''_1=1$ and $v''_1=2$ progressions of the symmetrical vibration (v'_1 varying) has now been carried out and is reported below. In contradistinction to the case of the progression $v''_1=0$, this part of the analysis encountered some difficulties caused by specific perturbations occurring in these bands. All bands of the progression $v''_1=0$ show a structure exactly like that of case $a^2\Pi \rightarrow {}^2\Pi$ bands of diatomic molecules, with no measurable Λ-doubling in the $^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$ sub-bands and a linear doubling in the $^2\Pi_{\frac{1}{2}u} \rightarrow {}^2\Pi_{\frac{1}{2}g}$ sub-bands. Only a slight deviation in the $\Delta G'$ values was observed, which pointed to a vibrational perturbation of the levels $v'_1=3$ and (still more) of $v'_1=4$ of $^2\Pi_{3/2u}$. But for the vibrational state $v''_1=1$ the sublevel $^2\Pi_{3/2g}$ is very strongly perturbed: in fact it must be in almost exact resonance with some other unknown level

* Assistance in the preparation of materials was furnished by the personnel of Works Progress Administration Official Project No. 30538.

[1] S. Mrozowski, Phys. Rev. 60, 730 (1941).

(probably one of the vibronic levels corresponding to two quanta of the bending vibration of the same state $^2\Pi_g$), and is split into two levels denoted in this work by 1^a and 1^b. A very strong Λ-doubling increasing faster than proportionally to J^2, and a positive value of the rotational constant D''_1 in both levels 1^a and 1^b accompany this interaction. A similar splitting of a sublevel $^2\Pi_{3/2}$ is found in the excited state $^2\Pi_u$ for $v'_1=4$; and anomalous Λ-doublings appear in the levels $v''_1=2$ of $^2\Pi_{3/2g}$ and $^2\Pi_{\frac{1}{2}g}$, and in $v'_1=4^a$, 5, 6, and 7 of $^2\Pi_{3/2u}$. Although all bands show the same simple rotational structure as for case a $^2\Pi\rightarrow{}^2\Pi$ bands of diatomic molecules, the vibrational analysis has been made difficult by a peculiar selection rule for the a and b perturbed levels (see below). The proper classification of bands could be obtained only by way of the rotational analyses, and since the B values for different vibrational states differ very little, a high accuracy in the determination of wave numbers was indispensable.

Results

The $v''_1=0$ progression of bands. Corrections to Part I

A critical reconsideration of the data reported in Part I, especially of the values of weighted averages of $\Delta_2F''_0$ for the lower values of the rotational quantum number J, and the application of more exact graphical methods, resulted in a slight change of the constants reported in Part I. The new values are the following:

$$\begin{aligned} ^2\Pi_{3/2g}:\ & B''_0=0.3797\pm0.0001 \\ & D''_0=-(1.5\pm0.2)10^{-7}. \\ ^2\Pi_{\frac{1}{2}g}:\ & B''_0=0.3815\pm0.0001 \\ & D''_0=-(1.6\pm0.2)10^{-7} \\ & p''_0=+0.0047\pm0.0010. \end{aligned}$$

For the new B''_0 values, the difference between the $^2\Pi_{\frac{1}{2}}$ and $^2\Pi_{3/2}$ values is in excellent agreement with the results of Bueso-Sanllehi[2] and is exactly equal to the value predicted by the theory of Hill and Van Vleck.[3] On the other hand, both D''_0 values are this time a little greater than the value -1.3×10^{-7} expected on the basis of the formula[4] $D=-4B^3/\nu_1^2$. The new value of the

[2] F. Bueso-Sanllehi, Phys. Rev. **60**, 556 (1941).
[3] Cf. R. S. Mulliken, Rev. Mod. Phys. **2**, 113 (1930).
[4] W. H. Schaffer, unpublished work, showed the applicability of this formula to triatomic linear molecules.

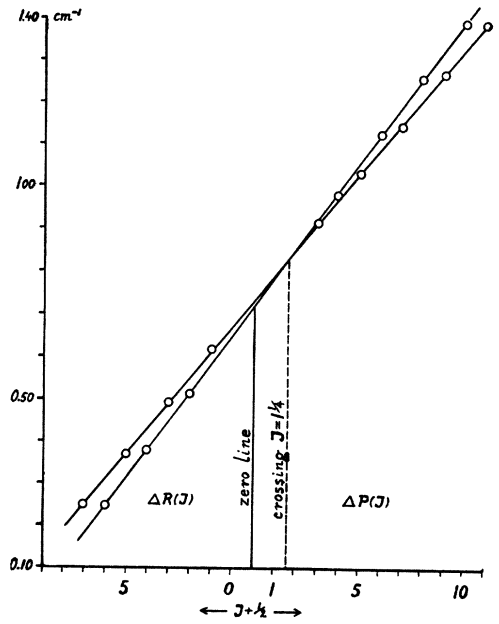

FIG. 1. Illustrating for the case of the sub-band $(1,0)^2\Pi_{\frac{1}{2}u} \rightarrow {}^2\Pi_{\frac{1}{2}g}$ the determination of p''_0 from the crossing point of two straight lines corresponding to the alternate first differences in P and R branches.

Λ-doubling constant [the Λ-doubling of a term $T(J)$ is $\pm\frac{1}{2}p(J+\frac{1}{2})$ and not $\pm p(J+\frac{1}{2})$ as erroneously given in Part I] has been obtained as an average of values determined in many different ways. Since all the differences $p'-p''$ are obtained with high accuracy from the graphs of the first differences in P and R branches (from the angle under which two straight lines cross, see Fig. 1) a fairly exact knowledge of at least one p is very important. All other p's are then found by the use of the differences $p'-p''$ and their absolute values are obtained with almost the same accuracy as that of the original p. The methods applied for determination of p''_0 were: (1) a value a little higher than before is obtained for p''_0 from the corrected averages of $\Delta_2F''_0$; (2) a value for p''_1 has been determined from the average Δ_2F_1's (state $v''_1=1$, $^2\Pi_{\frac{1}{2}g}$ see Table III) and then the value of p''_0 was found by using various differences $p'_{v'}-p''_1$ and $p'_{v'}-p''_0$; (3) the first differences in the P and R branches are linear functions of J, and the two straight lines obtained for alternate distances $\Delta P(J)=P(J+1)-P(J)$ cross at $J_{cr}=p''/(p'-p'')$ (see Fig. 1). With the values $p'-p''$ and J_{cr} obtained from the graph, an approximate value

TABLE I. Sub-bands $^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$.

$J-\frac{1}{2}$	(0,1[a]) $\nu_0=27290.80$ Unres. Q branch $\nu=27290.65$ R	P	(1,1[a]) $\nu_0=28417.6$ R	P	(4[a],1[a]) $\nu_0=31722.9$ R	P	(5,1[a]) $\nu_0=32835.65$ R	P	$^2\Pi_{3/2g}(v_1''=1^a)$ $\Delta_2F_1''a$ Aver.	1st diff.
1	27292.28	missing								
2	92.98	27288.82							4.50	
3	93.56	87.88							5.97	1.47
4	94.01	87.04							7.51	1.54
5	94.45	86.05							9.00	1.49
6	94.80	85.01							10.48	1.48
7	95.14	83.98			31726.67 h			32828.90	11.98	1.50
8	95.37	82.82			31726.67 e		32839.85 h	27.70	13.50	1.52
9		81.65			31726.67 a	31713.14	32839.85 e	26.30	14.98	1.48
10	h	80.38	28422.59 h		31726.67 d	11.81	32839.85 a	24.95	16.42	1.44
11	95.79 e	79.15	28422.59 e		31726.67	10.25	32839.85 d	23.40	18.00	1.58
12	95.79 a	77.74	28422.59 a		26.47	08.68		21.87	19.50	1.50
13	95.79 d	76.36	28422.59 d	28403.00	26.09	07.00	39.42	20.27	21.05	1.55
14	95.63	74.83	22.30	01.43	25.76	05.32	39.12	18.60	22.50	1.45
15	95.63	73.42	22.30	28399.95	25.44	03.64	38.85	16.90	24.05	1.55
16	95.37	71.70	22.05	98.30	25.05	01.80	38.39	15.04	25.55	1.50
17	95.37	70.22	21.88	96.75	24.44	31699.90	37.95	13.27	26.10	1.55
18	94.80	68.37	21.35	94.90	23.91	97.89	37.34	11.27	28.57	1.47
19	94.65	66.79	21.12	93.26	23.31	95.98	36.81	09.37	30.09	1.52
20	94.01	64.80	20.52	91.27	22.55	93.82	35.97	07.20	31.54	1.45
21	93.78	63.11	20.19	89.58	21.76	91.67	35.37	05.20	33.10	1.56
22	92.98	60.93	19.32	87.32	20.99	89.48	34.35	02.87	34.58	1.48
23	92.66	59.25	18.90	85.53	20.17	87.22	33.50	00.74	36.13	1.55
24	91.66	56.84	17.94	83.12	19.06	84.93	32.44	32798.15	37.60	1.47
25	91.30	55.09	17.44	81.30	17.96	82.46	31.58	95.94	39.16	1.56
26	90.12	52.52	16.21	78.60	16.94	79.99	30.28	93.28	40.62	1.46
27	89.70	50.70	15.69	76.70	15.83	77.41	29.23	90.91	42.19	1.57
28	88.30	47.93	14.24		14.53	74.80	27.78	88.02	43.63	1.44
29	87.88	46.08	13.75		13.14		26.70	85.59	45.20	1.57
30	86.26	43.12	12.00				24.95	82.56	46.68	1.48
31	85.78	41.21	11.46				23.75	79.97	48.24	1.56
32	83.98	38.01					21.87	76.72	49.70	1.46
33	83.44	36.02					20.67	74.12	51.27	1.57
34	81.40	32.70					18.57	70.61	52.73	1.46
35	80.84	30.70					17.28	67.95	54.32	1.59
36	78.60	27.04						64.35	55.79	1.47
37	78.02	25.05							57.39	1.60
38	75.55	21.21							58.81	1.42
39	74.90	19.20							60.42	1.61
40	72.21	15.13							61.82	1.40
41	71.50	13.08							63.46	1.64
42	68.63	08.76							64.84	1.38
43	68.00	06.70							66.52	1.68
44	64.80	02.11							67.88	1.36
45	64.17	00.10							69.58	1.70
46	60.73	27195.29							70.88	1.30
47	60.06	93.33							72.68	1.80
48	56.38	88.05							73.95	1.27
49	55.74	86.11							75.78	1.83
50	51.82	80.60								
51	51.14									

of p'' is calculated. This procedure has been applied to all bands of the progression $v''_1=0$ to get p''_0 directly, and to all bands of the progression $v''_1=1$ to get p''_1 and then to determine p''_0 by using the differences $p'-p''$. The bands ending on level $v''_1=2$ were not used since the level $v''_1=2$ shows an anomalous nonlinear Λ-doubling. All values obtained for p''_0 by these different methods lie within the range $0.004-0.006$ and the final value given above has been adopted after critical examination of all these data.

The $v''_1=1$ progression of bands

As already mentioned in the introduction, the sublevel $^2\Pi_{3/2g}$ is split into two levels, here denoted 1^a and 1^b, and therefore instead of two we have three progressions of sub-bands. The wave numbers of the lines and the average $\Delta_2F''_1$ values are presented for these in Tables I, II, and III. Asterisks marking blended lines are omitted, since there are many weak lines present on the plates and it is often very difficult to decide if an anomalous intensity of a line is caused by a real blend, a coincidence with a weak but sharp Rowland ghost, or with an unsharp Lyman ghost. The number of cases where blends have been definitely established by the analysis as belonging to lines of different bands or by the strongly anomalous intensity is relatively much smaller, and the marking only of these cases with asterisks would be far from representing the real situation. Naturally in taking averages of Δ_2F's and evaluation of all

TABLE II. Sub-bands $^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$.

$J-\frac{1}{2}$	(0,1^b) $\nu_0=27245.25$ R	P	(2,1^b) $\nu_0=29494.70$ R	P	(3,1^b) $\nu_0=30614.75$ R	P	(4^b,1^b) $\nu_0=31734.90$ R	P	$^2\Pi_{3/2g}(v_1''=1^b)$ $\Delta_2F_1''b$ Aver.	1st diff.
4				29490.80					7.62	
5		27240.20		89.71		30609.69		31729.77	9.15	1.53
6	27248.82	39.10		88.61		08.59		28.65	10.68	1.53
7	49.03	37.89		87.37	30618.40 h	07.32	31738.41 h	27.34	12.21	1.53
8	49.16 h	36.61	29498.51 h	86.08	30618.40 e	06.03	31738.41 e	26.15	13.73	1.52
9	49.16 e	35.27	29498.51 e	84.72	30618.40 a	04.66	31738.41 a	24.70	15.25	1.52
10	49.16 a	33.89	29498.51 a	83.29	30618.40 d	03.28	31738.41 d	23.29	16.76	1.51
11	49.16 d	32.43	d	81.82		01.76	38.21	21.73	18.28	1.52
12	49.03	30.93	98.22	80.20		00.18	38.10	20.17	19.81	1.53
13	48.82	29.33	98.00	78.52	17.81	30598.45	37.79	18.50	21.34	1.53
14	48.55	27.67	97.68	76.86	17.47	96.77	37.45	16.76	22.86	1.52
15	48.21	25.92	97.24	75.08	17.00	94.99	37.01	14.95	24.38	1.52
16	47.93	24.14	96.78	73.24	16.56	93.16	36.53	13.16	25.92	1.54
17	47.38	22.30	96.24	71.27	15.99	91.08	35.94	11.08	27.44	1.52
18	46.94	20.41	95.71	69.33	15.37	89.15	35.37	09.12	29.00	1.56
19	46.24	18.38	94.93	67.20	14.62	86.95	34.61	06.97	30.52	1.52
20	45.65	16.35	94.26	65.14	13.92	84.88	33.88	04.86	32.08	1.56
21	44.84	14.15	93.30	62.83	12.97	82.56	32.95	02.53	33.56	1.48
22	44.15	12.10	92.53	60.67	12.15	80.37	32.10	00.35	35.11	1.55
23	43.12	09.69	91.41	58.15	11.03	77.87	30.99	31697.90	36.61	1.50
24	42.39	07.54	90.50	55.90	10.12	75.54	30.06	95.54	38.18	1.57
25	41.21	04.91	89.22	53.22	08.79	72.85	28.75	92.81	36.69	1.51
26	40.35	02.70	88.25	50.82	07.79	70.42	27.73	90.37	41.25	1.56
27	39.02	27199.92	86.77	47.97	06.24	67.54	26.19	87.55	42.74	1.49
28	38.01	97.66	85.71	45.52	05.16	65.06	25.09	85.00	44.30	1.56
29	36.52	94.65	84.09	42.47	03.43	62.00	23.32	81.94	45.79	1.49
30	35.48	92.25	82.85	39.88	02.27	59.41	22.26	79.38	47.37	1.58
31	33.74	89.12	81.01	36.63	00.33	56.10	20.25	76.08	48.85	1.48
32	32.70	86.60	79.72	34.01	30599.00	53.40	19.06	73.38	50.44	1.59
33	30.70	83.29	77.64	30.57	96.77		16.76		51.89	1.45
34	29.49		76.33	27.83	95.55		15.48			
35	27.30				93.16					
36	26.12				91.77					
37	23.69									
38	22.49									
39	19.81									
40	18.54									

constants the points corresponding to lines of anomalous intensity or unsymmetrical structure have been treated as less reliable.

The molecular constants obtained from $\Delta_2F''_1$ for the ground state of CO_2^+ with one quantum of symmetrical vibration $v''_1=1$ are the following:

$^2\Pi_{3/2g}$ substate a: $B''_1=0.3754\pm0.0002$
$D''_1=+(6.3\pm0.5)10^{-7}$,
$F''_1<0$.

$^2\Pi_{3/2g}$ substate b: $B''_1=0.3814\pm0.0002$
$D''_1=+(2.2\pm0.4)10^{-7}$,
$F''_1\neq0$.

$^2\Pi_{\frac{1}{2}g}$ $B''_1=0.3803\pm0.0001$
$D''_1=-(1.5\pm0.2)10^{-7}$
$p''_1=+0.0050\pm0.0002$.

The last constant has been obtained by assuming p''_0 to have exactly the value $+0.0047$ given in a preceding section and by the comparison of differences $p'_n-p''_1$ with $p'_n-p''_0$ (all these differences are given at the end of this paper). The limits of errors for p'' and p' here and in all subsequent parts of this work refer to uncertainties relative to p''_0; the much greater uncertainty of the absolute value of p''_0 will not be included in these figures. The substate $v'_1=1$ of $^2\Pi_{\frac{1}{2}g}$ shows no evidence of any perturbation. Both substates a and b of $^2\Pi_{3/2g}$ are very anomalous: both have positive and relatively large D values, while the Λ-doublings have opposite signs in the a and b states and increase faster than proportionally to J^2. Since the exponent varies slightly with J it was decided not to try to represent the Λ-doubling by a simple formula but to give the dependence of Λ-doubling on J in the form of a graph. The curves 1^a and 1^b in Fig. 4 are directly obtained from the second differences in the P and R branches, since the levels $v'_1=0$, 1, 2, 3, and 4^b of $^2\Pi_{3/2u}$ show no observable Λ-doubling. Having obtained the Λ-doubling in the 1^a, $^2\Pi_{3/2g}$ substate, we determine the Λ-doublings in $v'_1=4^a$ and 5 of $^2\Pi_{3/2u}$ from the bands (4^a, 1^a) and (5, 1^a). The Λ-doubling of $^2\Pi_{3/2u}$, 4^a is almost equal to that of the $^2\Pi_{3/2g}$, 1^a substate and that of $^2\Pi_{3/2u}$, 5 amounts to a little more than a half of this.

The splitting of the state $^2\Pi_{3/2g}$, 1 into two substates must be caused by a very strong interaction with some other vibrational state of the $^2\Pi_{3/2g}$ or of the $^2\Pi_{\frac{1}{2}g}$ electronic state, since it is practically certain that no other electronic

TABLE III. Sub-bands $^2\Pi_{\frac{1}{2}u} \rightarrow {}^2\Pi_{\frac{1}{2}g}$.

$J-\frac{1}{2}$	(0,1) $\nu_0=27202.65$ R	P	(1,1) $\nu_0=28328.65$ R	P	(2,1) $\nu_0=29449.55$ R	P	(3,1) $\nu_0=30565.55$ R	P	(4,1) $\nu_0=31677.35$ R	P	(5,1) $\nu_0=32785.82$ R	P	$^2\Pi_{1/2g}(v_1''=1)$ Δ_2F_1'' Aver.	1st diff.
1		27201.49						30563.48						
2		00.64						62.64						
3		27199.76						61.60		31673.28				
4		98.78						60.55		72.33		32780.86		
5		97.77					30569.35	59.41	31680.92	71.17	32789.32	79.62		
6		96.68					30569.35	58.26	31680.92	70.00	32789.32	78.44	12.20	
7		95.53			29453.60		69.55 h	56.97	81.21 h	68.71	89.69 h	77.16	13.70	1.50
8		94.29			29453.60 h		69.55 e	55.72	81.21 e	67.42	89.69 e	75.93	15.20	1.50
9	27207.18	93.11	28333.01 h		53.68 e		69.55 a	54.23	81.21 a	66.00	89.69 a	74.47	16.70	1.50
10	27207.18 h	91.77	28333.01 e		53.68 a	29438.50	69.55 d	52.90	81.21 d	64.56	89.69 d	73.10	18.22	1.52
11	27207.18 e	90.40	28333.01 a		53.68 d	37.07	69.35	51.31	80.92	62.98	89.32	71.42	19.74	1.52
12	27207.18 a	88.98	28333.01 d	28314.79	53.60	35.52	69.35	49.84	80.92	61.45	89.32	69.92	21.28	1.54
13	27207.18 d	87.48		13.33	53.60	34.01	68.93	48.11	80.51	59.70	88.79	68.14	22.82	1.54
14	06.97	85.92	32.75	11.70	53.22	32.35	68.75	46.47	80.31	58.06	88.60	66.50	24.33	1.51
15	06.82	84.36	32.50	10.14	53.00	30.57	68.24	44.65	79.78	56.16	88.02	64.51	25.85	1.52
16	06.49	82.66	32.15	08.40	52.64	28.92	67.92	42.88	79.38	54.38	87.72	62.77	27.37	1.52
17	06.27	80.97	31.82	06.69	52.31	27.21	67.33	40.88	78.70	52.38	86.90	60.65	28.90	1.53
18	05.82	79.17	31.42	04.77	51.79	25.28	66.86	39.02	78.22	50.50	86.49	58.82	30.42	1.52
19	05.46	77.36	30.90	02.97	51.30	23.42	66.10	36.87	77.41	48.31	85.55	56.56	31.92	1.50
20	04.91	75.42	30.33	00.96	50.66	21.39	65.52	—Cu—	76.81	46.30	85.05	54.59	33.46	1.54
21	04.42	73.52	29.75	28299.04	50.13	19.38	64.59	32.63	75.85	43.95	83.90	52.17	34.97	1.51
22	03.75	71.46	29.02	96.90	49.28	17.20	63.90	30.52	75.12	41.84	83.27	50.06	36.47	1.50
23	03.14	69.45	28.40	94.86	48.59	15.13	62.89	28.12	73.98	39.33	81.98	47.50	38.01	1.54
24	02.37	67.28	27.57	92.58	47.64	12.80	62.00	25.87	73.17	37.10	81.28	45.27	39.54	1.53
25	01.64	65.14	26.81	90.41	46.84	10.53	60.85	23.32	71.88	34.47	79.78	42.50	41.05	1.51
26	00.74	62.83	25.83		45.73	08.08	59.93	20.98	70.93	32.11	78.94	40.18	42.56	1.51
27	27199.92	60.59	24.99		44.85	05.80	58.62	18.24	69.48	29.33	77.34	37.29	44.09	1.53
28	98.87	58.19			43.52	03.10	57.54	15.80	68.44	26.84	76.39	34.83	45.59	1.50
29	97.86	55.83			42.60	00.79	56.07	12.98	66.84	23.90	74.59	31.76	47.13	1.54
30	96.79	53.29			41.24	29398.04	54.91	10.38	65.69	21.33	73.54	29.26	48.62	1.49
31	95.76	50.83			40.05	95.47	53.34	07.38	63.94	18.27	71.69	25.97	50.17	1.55
32	94.47	48.18			38.64	92.63	52.00	04.70	62.64	15.51	70.52	23.35	51.66	1.49
33	93.33	45.60			37.30	89.93	50.22	01.58	60.77	12.28	68.37	19.95	53.20	1.54
34	91.91	42.83			35.65	87.00	48.81	30498.76	59.36	09.47	67.05	17.27	54.70	1.50
35	90.65	40.11			34.31		46.88	95.48	57.32	06.10	64.71	13.65	56.20	1.50
36	89.13	37.23			32.55		45.39	92.54	55.78	03.17	63.35	10.81	57.72	1.52
37	87.78	34.46					43.38	89.14	53.60	31599.59	60.93	07.06	59.26	1.54
38		31.40					41.74	86.07	51.95	96.53	59.47	04.12	60.76	1.50
39		28.51					39.53	82.55	49.58	92.85	56.83	00.19	62.30	1.54
40		25.36					37.77	79.33	47.87	89.68	55.27	32697.20	63.78	1.48
41		22.33					—Cu—	75.69	45.30	85.83	52.49	93.08	65.33	1.55
42		19.08					33.50	72.39	43.47	82.57	50.73	89.96	66.80	1.47
43		15.92					31.12	68.56	40.80	78.55		85.79	68.34	1.54
44		12.58					29.10	65.11	38.86	75.20		82.49	69.84	1.50
45		09.35					26.40	61.10	36.05	71.00		78.01	71.37	1.53
46		05.79					24.28	57.62	33.93	67.52		74.61	72.88	1.51
47		02.49					21.56	53.52	30.96	63.16		70.09	74.40	1.52
48		27098.86					19.31	49.92	28.77	59.53		66.61	75.92	1.52
49		95.36					16.47		25.66	55.04		61.88	77.41	1.49
50		91.66							23.37	51.36		58.31	78.92	1.51
51		88.02								47.64			80.50	1.58
52		84.23								42.87				
53		80.47								38.13				
54		76.43												

state is very close to the ground state. The smaller values of the constants D''_1 and F''_1 and of the Λ-doubling for the substate 1^b indicate that this substate is the less anomalous one and probably contains more of the character of the $v''_1=1$, $^2\Pi_{3/2g}$ substate than the other one (1^a). Nevertheless both interacting substates are certainly in a very close resonance; in fact, for the unperturbed $^2\Pi_{\frac{1}{2}g}$ substates $v''_1=0$ and 1, we obtain $\Delta G''_1=1265.75$ cm^{-1} which is only slightly more (1.2 cm^{-1}) than the average of $\Delta G''_1$ for the 1^a and 1^b substates. In Fig. 2 a level scheme is presented which shows the bands observed in the double progression $v''_1=1$, $^2\Pi_{3/2g}$ and the substates involved. The perturbations of the positions of the levels are drawn on a greatly exaggerated scale in order to make the relations more evident; the shifts Δ from the unperturbed positions are given in cm^{-1} on the right-hand side of the drawing. For the states $v''_1=1^a$ and 1^b, $^2\Pi_{3/2g}$ the Δ's were obtained by assuming the $\Delta G''_1$ value to be equal to 1265.75, in other words by assuming the $^2\Pi_g$ doublet separation to be independent of the vibrational quantum number. (This, of course, may not be quite correct. If, for example, actually the $^2\Pi_g$ separation decreases with increase in vibrational number, $\Delta G''_1$ would be greater than 1265.75, and the calculated Δ's would be more asymmetrical than in Fig. 1.) The Δ's for the excited state $^2\Pi_{3/2u}$ were calculated by assuming for the unperturbed positions of the levels the values obtained from the vibrational formula given at the end of this paper. The values of the vibrational constants

were chosen so as to make the Δ for the levels $v'_1=6$ and 7 ($^2\Pi_{3/2u}$) very small, as seems to be required by consideration of the dependence of the B' values on v'_1 (cf. Fig. 5). On the right-hand side of Fig. 2 is also given the magnitude of the Λ-doubling in cm^{-1} for the arbitrarily chosen sample level, $J=37\frac{1}{2}$. Astonishingly enough, positive perturbations of position ($\Delta>0$) are in the case of $^2\Pi_{3/2u}$ not accompanied by a positive Λ-doubling, as they are for $^2\Pi_{3/2g}$. Just the absence of a Λ-doubling was the reason for no anomalous behavior of the bands (3, 0) and (4, 0) [this last band will now be denoted (4^b, 0)] was observed in the case of the $v''_1=0$ progression described in Part I, although the values of the $\Delta G''$s pointed toward the existence of a perturbation.

All the transitions observed are represented in Fig. 2 by arrows, the thickness of the lines giving an idea about their relative intensities. Besides the transitions investigated and included in Tables I and II, two more arrows were inserted, including one corresponding to the band (1, 1^b) which has been observed, but which lines have not been measured, since they are extremely weak and barely visible among other stronger lines. The inclusion of this band would not increase the accuracy of the average values of $\Delta_2F''_1$. The position of the band edge was determined and found to agree very well with the predicted value. The second transition included in Fig. 1 is the band (6, 1^a) which was not observed in this work, but has been identified as the band λ2945 observed by Fox, Duffendack, and Barker[5] and by Smyth (Smyth's b_7 band).[6] The operation of a special selection rule can be inferred from Fig. 2: transitions with observable intensity occur between moderately or strongly perturbed levels only if the positions of both upper and lower level are shifted in the same direction. By denoting the levels with positive Δ's as type b, with negative Δ's as type a, this selection rule can be expressed in the following way: only the transitions $a\rightarrow a$ and $b\rightarrow b$ are strongly allowed. It is very astonishing that transitions from the moderately perturbed levels ($v'_1=2$, 3, and 5) to the other sublevel $v''_1=1$, $^2\Pi_{3/2g}$ do not occur at least weakly. This point, however, was carefully checked and no traces of any weak band edges were detected at the predicted positions. Unperturbed or very weakly perturbed levels are simultaneously of both type a and b. Since only one double level (i.e., a and b) in $^2\Pi_{3/2u}$ and one in $^2\Pi_{3/2g}$ were observed it is impossible to say at present if the direction of the shift solely determines the type of the level. The preliminary analysis shows that the level $v''_1=5$ of $^2\Pi_g$ (both substates) is very strongly perturbed, and it will probably be possible to study further the operation of the selection rule in that case. In general the relations are not completely clear, since a weak band edge corresponding to the transition (4^b, 2), $^2\Pi_{3/2u}\rightarrow{}^2\Pi_{3/2g}$ is observed, and no traces of a corresponding edge for the transition (4^a, 2) could be detected, although according to the rule only the latter should be present (see the next paragraph below: the substate $v''_1=2$, $^2\Pi_{3/2g}$ is perturbed downwards and has a negative Λ-doubling, hence should be of type a). On the other hand Fox, Duffendack, and Barker,[5] and Smyth[6] reported a quite strong band λ3280.5 (g_7)

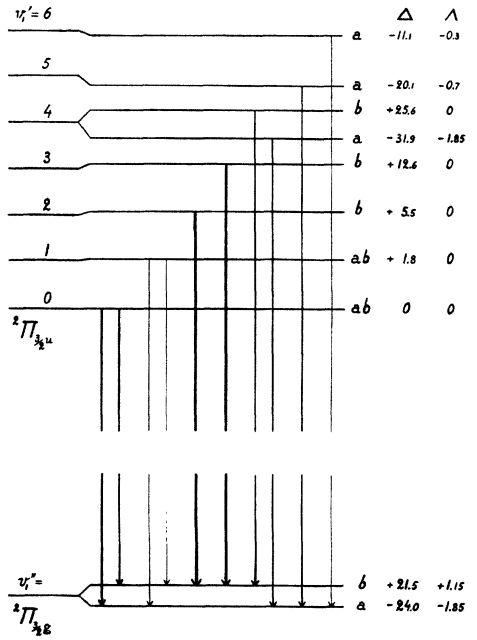

FIG. 2. Graphical presentation of transitions observed in the progression $v''_1=1$ for the sub-bands $^2\Pi_{3/2u}\rightarrow{}^2\Pi_{3/2g}$. Δ represents the shift (in cm^{-1}) from the calculated position of the level, caused by perturbation. Λ is the Λ-doubling for the level $J=37\frac{1}{2}$.

[5] G. W. Fox, O. J. Duffendack, and E. F. Barker, Proc. Nat. Acad. **13**, 320 (1927).
[6] H. D. Smyth, Phys. Rev. **38**, 2000 (1931).

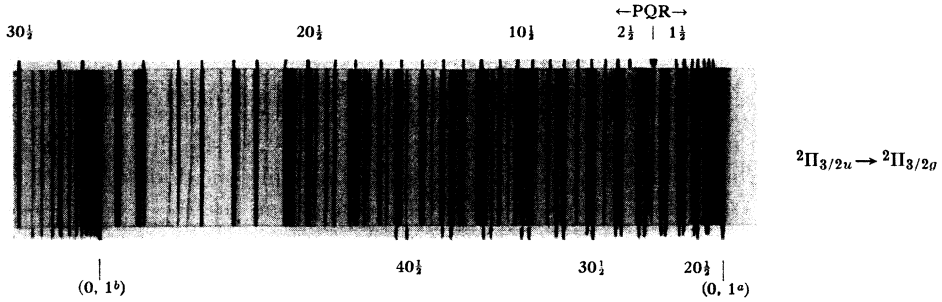

FIG. 3. Enlargement of a photograph of the sub-band λ3662 with the quantum numbers of lines given.

which exactly fits into the scheme as the missing ⟨4^a, 2) band. Further, the identification of the level 4^a, $^2\Pi_{3/2u}$ could be considered as doubtful, since the rotational analysis of only one band originating from this state was obtained. But a band edge at λ3032 has been detected that is exactly at the position where the sub-band (4^a, 0) is expected. Since the lines of this band are very weak, approximately as weak as the lines of the sub-band (4^b, 0), but are overlapped by the stronger sub-band (4, 0) $^2\Pi_{\frac{1}{2}u} \rightarrow {}^2\Pi_{\frac{1}{2}g}$, no rotational analysis has been tried in this case.

The two sub-bands (0, 1^a) λ3662.5 and (0, 1^b) λ3668.8 form the greater part of the so-called double band λ3660, which was studied in detail with high resolution by Schmid.[7] The

[7] R. Schmid, Zeits. f. Physik **84**, 732 (1933).

TABLE IV. Sub-bands $^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$.

$J-\frac{1}{2}$	(0,2) ν_0=26035.67 R	P	(1,2) ν_0=27162.45 R	P	(2,2) ν_0=28285.20 R	P	(5,2) ν_0=31580.50 R	P	(6,2) ν_0=32684.55 R	P	$^2\Pi_{3/2g}(v_1''=2)$ Δ_2F_2'' Aver.	1st diff.
2		26033.66										
3		32.76								32681.66		
4		31.80								80.68		
5		30.80				28280.28				79.62		
6		29.71				79.09		31574.39		78.43		
7		28.62				78.09	h	73.31	h	77.23		
8		27.43		27154.38		76.76	31584.26 e	71.94	32688.06 e	75.91		
9		26.23	h	53.00	28289.44 h	75.61	31584.26 a	70.66	32688.06 a	74.61	15.06	
10	26040.25 h	24.91	27166.90 e	51.79	28289.44 e	74.14	31584.26 d	69.26	32688.06 d	73.20	16.55	1.49
11	26040.25 e	23.60	27166.90 a	50.32	28289.44 a	72.88		67.74		71.68	18.07	1.52
12	26040.25 a	22.17	27166.90 d	48.91	28289.44 d	71.43		66.20		70.09	19.58	1.51
13	26040.25 d	20.75		47.30		69.92	83.79	64.55	87.52	68.48	21.10	1.52
14	40.12	19.21	66.70	45.83		68.29	83.46	62.89	87.26	66.73	22.60	1.50
15	40.00	17.67	66.49	44.27	88.91	66.73	83.03	61.09	86.83	65.02	24.12	1.52
16	39.72	16.01	66.24	42.58	88.58	65.00	82.57	59.28	86.39	63.19	25.64	1.52
17	39.45	14.36	65.89	40.88	88.23	63.27	82.11	57.35	85.79	61.24	27.14	1.50
18	39.08	12.59	65.46	39.07	87.78	61.44	81.48	55.44	85.21	59.25	28.63	1.49
19	38.69	10.83	65.07	37.23	87.30	59.58	80.75	53.37	84.52	57.20	30.13	1.50
20	38.20	08.93	64.49	35.34	86.71	57.58	80.08	51.36	83.75	55.10	31.64	1.51
21	37.73	07.08	64.02	33.40	86.14	55.66	79.21	49.12	82.85	52.91	33.14	1.50
22	37.11	05.08	63.33	31.39	85.41	53.56	78.42	46.90	82.05	50.61	34.65	1.51
23	36.53	03.10	62.79	29.35	84.74	51.49	77.42	44.54	81.04	48.28	36.16	1.51
24	35.78	00.97		27.14	83.89	49.25	76.50	42.27	80.04	45.89	37.67	1.51
25	35.11	25998.88		25.03	83.10	47.08	75.30	39.70	78.88	43.38	39.16	1.49
26	34.23	96.64		22.70	82.13	44.71	74.39	37.40	77.72	40.90	40.67	1.51
27	33.45	94.47		20.45	81.23	42.43	72.97	34.59	76.44	38.19	42.19	1.52
28	32.44	92.08		18.00	80.06	39.91	71.94	32.10	75.21	35.57	43.69	1.50
29	31.58	89.81			79.09	37.53	70.38	29.22	73.80	32.83	45.21	1.52
30	30.46	87.28			77.82	34.81	69.16	26.65	72.38	29.90	46.71	1.50
31	29.51	84.93			76.76	32.36	67.52		70.84	27.08	48.22	1.51
32	28.24	82.24			75.29	29.62	66.16		69.25	24.18	49.72	1.50
33	27.19	79.82			74.14	27.02	64.14		67.55	21.07	51.22	1.50
34	25.79	77.01			72.54	24.10			65.77	18.01	52.72	1.50
35	24.64	74.48			71.28	21.38			63.98	14.88	54.23	1.51
36	23.09	71.55			69.54	18.33			62.12	11.57	55.73	1.50
37	21.86	68.91			68.14	15.54			60.17	08.25	57.23	1.50
38	20.16	65.84			66.28	12.33			58.17	04.90	58.72	1.49
39	18.85	63.12			64.77	09.47			56.08	01.43	60.22	1.50
40	17.03	59.91			62.79	06.06				32598.06	61.70	1.48
41	15.62	57.11			61.20	03.12					63.24	1.54
42	13.65	53.78			59.04	28199.56					64.72	1.48
43	12.17	50.85			57.42						66.22	1.50
44	10.04	47.43			55.08							
45	08.53				—							
46	06.22				50.84							
47	04.57				—							
48	02.14				46.33							
49	00.43											

TABLE V. Sub-bands $^2\Pi_{\frac{1}{2}u} \rightarrow {}^2\Pi_{\frac{1}{2}g}$.

$J-\frac{1}{2}$	(0,2) $\nu_0=25945.78$ R	P	(1,2) $\nu_0=27071.75$ R	P	(2,2) $\nu_0=28192.65$ R	P	(5,2) $\nu_0=31528.95$ R	P	(6,2) $\nu_0=32635.95$ R	P	$^2\Pi_{1/2g}(v_1''=2)$ Δ_2F_2'' Aver.	1st diff.
3								31526.05		32633.06		
4	25948.77	25942.00						25.08		32.02		
5		40.96		27066.92				24.10		31.02		
6	49.55	39.92		65.80			31532.66	22.88	32639.62	29.90		
7		38.75		64.66			31532.66	21.73	32639.62	28.71	12.15	
8		37.58		63.47		28184.31	32.90 h	20.42	39.84 h	27.37	13.65	1.50
9		36.36	27076.32 h	62.21	28196.97 h	83.06	32.90 e	19.17	39.84 e	26.15	15.15	1.50
10	50.51 h	35.10	27076.32 e	60.92	28196.97 e	81.69	32.90 a	17.73	39.84 a	24.60	16.65	1.50
11	50.51 e	33.72	27076.32 a	59.56	28196.97 a	80.33	32.90 d	16.37	39.84 d	23.30	18.17	1.52
12	50.51 a	32.28	27076.32 d	58.12	28196.97 d	78.83	32.66	14.75	39.62	21.62	19.70	1.53
13	50.51 d	30.84	27076.32	56.62		77.36	32.66	13.24	39.62	20.18	21.22	1.52
14	50.34	29.33	76.08	55.08	96.67	75.74	32.27	11.50	38.97	18.38	22.75	1.53
15	50.22	27.79	75.90	53.52	96.49	74.12	32.09	09.90	38.97	16.81	24.25	1.50
16	49.99	26.15	75.63	51.77	96.12	72.40	31.50	07.97	38.19	14.88	25.78	1.53
17	49.74	24.50	75.34	50.12	95.80	70.68	31.16	06.29	38.19	13.22	27.29	1.51
18	49.36	22.70	74.90	48.30	95.34	68.81	30.51	04.19	37.31	11.07	28.82	1.53
19	49.00	20.98	74.52	46.52	94.90	66.97	30.05	02.34	36.96	09.30	30.34	1.52
20	48.54	19.06	73.97	44.56	94.29	64.97	29.22	00.16	36.02	06.96	31.86	1.52
21	48.07	17.18	73.47	42.67	93.74	63.06	28.65	31498.21	35.57	05.06	33.37	1.51
22	47.49	15.16	72.79	40.61	92.98	60.94	27.60	95.86	34.37	02.62	34.88	1.51
23	46.92	13.22	72.18	38.65	92.34	58.89	26.99	93.79	33.96	00.70	36.37	1.49
24	46.20	11.10	71.39	36.42	91.48	56.62	25.82	91.31	32.62	32598.06	37.90	1.53
25	45.52	09.00	70.68	34.27	90.71	54.44	25.08	89.05	32.02	96.01	39.40	1.50
26	44.68	06.79	69.76	31.98	89.71	52.07	23.73	86.48	30.52	93.19	40.94	1.54
27	43.89	04.60	68.89	29.73	88.81	49.77	22.88	84.18	29.90	90.98	42.43	1.49
28	42.96	02.28	67.90	27.32	87.74	47.28	21.43	81.32	28.16	88.04	43.97	1.54
29	42.00	25899.92	66.92	24.99	86.68	44.87	20.42	78.88	27.37	85.80	45.46	1.49
30	40.96	97.52	65.80	22.45	85.50	42.26	18.81	75.96	25.56	82.69	46.98	1.52
31	39.90	95.08	64.66	19.95	84.31	39.71	17.73	73.44	24.60	80.32	48.48	1.50
32	38.75	92.55	63.47	17.27	82.98	36.96	15.94	70.32	22.63	77.02	50.00	1.52
33	37.58	89.94	62.21	14.66	81.69	34.34	14.75	67.76	21.62	74.52	51.50	1.50
34	36.36	87.35	60.92	11.99	80.26	31.42	12.81	64.48	19.41	71.09	53.04	1.54
35	35.03	84.63	59.56	09.16	78.83	28.64	11.58	61.73	18.38	68.55	54.54	1.50
36	33.78	81.95	58.12	06.33	77.29	25.68	09.38	58.25	15.98	64.90	56.08	1.54
37	32.28	79.06	56.62	03.44	75.74	22.76	07.97	55.44	14.88	62.30	57.55	1.47
38					74.12	19.68	05.70	51.84	12.37		59.11	1.56
39					72.40	16.62	04.19	48.93	11.07		60.57	1.46
40					70.68	13.45	01.80	45.14	08.25		62.14	1.57
41						10.27	00.16	42.12	06.96		63.60	1.46
42						06.92	31497.60	38.14	04.23		65.17	1.57
43						03.61	95.86	35.12	02.65		66.64	1.47
44						00.22	93.20	30.96			68.15	1.51
45							91.31	27.83				
46							88.49					
47							86.48					
48							83.66					
49							81.32					

new photographs show that Schmid's sub-band λ3661.5 is non-existent, and that the sub-band λ3670.2 is formed by an irregular grouping of lines which definitely do not belong to our system. The real structure of the two sub-bands λ3662.5 and λ3668.8 was not recognized by Schmid, because of the lower resolution available to him. The extremely great Λ-doubling in the level 1^a is the cause of the misleading apparent doublet structure in the lines of the sub-band λ3662.5 (see Fig. 3). Schmid investigated the Zeeman effect in the CO_2^+ bands and found that, in the entire region 3000–4000A, only the double band λ3660 shows noticeable effects. This is in excellent agreement with the classification given above, since for all bands ending on one of the two levels 1^a and 1^b strong Zeeman shifts are expected. The absence of an influence of the magnetic field on all the unperturbed $^2\Pi_u \rightarrow {}^2\Pi_g$ bands is to be explained by an approximate equality of the Zeeman shifts of energy levels in the upper and lower states, together with the selection rules for the magnetic quantum numbers.[8] If, however, one of the states is perturbed by another possessing a very different magnetic behavior, considerable shifts of lines should be produced. According to this explanation all bands corresponding to transitions involving perturbed levels in Fig. 2 should show relatively strong Zeeman effects. Unfortunately, among these transitions, only the double band λ3660 was observed by Schmid, since all the others are situated on the long wave-length sides of bands belonging to the progression $v''_1=0$ and are strongly overlapped by the P branch lines of these bands; this was especially unfavorable in the case of Schmid's investigations because the temperature of the discharge was in his case quite considerable.

[8] F. H. Crawford, Rev. Mod. Phys. 6, 90 (1934).

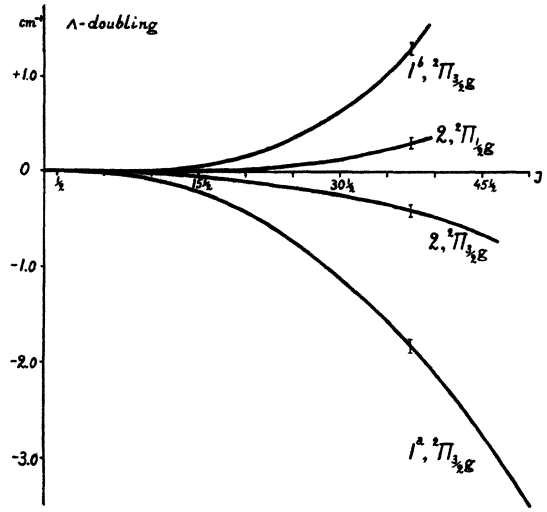

FIG. 4. Λ-doubling of rotational states in the ground state $^2\Pi_g$ of the CO_2^+ molecule for $v''_1=1$ and 2. In each case the uncertainty limits of the doubling are marked by a bar.

The $v_1''=2$ progression of bands

The wave numbers of the lines and the average $\Delta_2F''_2$ values for the levels $v''_1=2$, $^2\Pi_g$ are given in Tables IV and V. The molecular constants obtained from $\Delta_2F''_2$ for the ground state of CO_2^+ with two quanta of the symmetrical vibration ($v''_1=2$) are the following:

$$^2\Pi_{3/2g}\quad B''_2=0.3769\pm0.0001$$
$$D''_2=-(1.5\pm0.2)\times10^{-7}$$
$$^2\Pi_{½g}\quad B''_2=0.3793\pm0.0001$$
$$D''_2=-(1.6\pm0.2)\times10^{-7}.$$

The Λ-doubling is in both substates anomalous. For the substate $^2\Pi_{3/2g}$ it is negative showing that this level is probably shifted downwards by a perturbation. The same conclusion can be reached by considering the B''_2 value, which appears to be lower than the value 0.3773 calculated on basis of the formula given at the end of this paper. In case of the substate $^2\Pi_{½g}$ the sign of the anomalous Λ-doubling and the anomaly in the B''_2 are opposite to those in $^2\Pi_{3/2g}$. The total Λ-doubling for the $^2\Pi_{3/2g}$ substate and the increase of the Λ-doubling relative to the level $v''_1=1$ for the $^2\Pi_{½g}$ substate are given in Fig. 4. It is very probable that in the last case the increase is composed of two parts: one linearly dependent on J and corresponding to the increase of the coefficient p'' in passing from $v''_1=0$ to $v''_1=1$ and $v''_1=2$ (probable increase of p'' around 0.0003) and another greater part caused by the perturbation mentioned and increasing approximately proportionally to $J^{2.5}$.

From the data obtained in the analysis of all three progressions $v''_1=0$, $v''_1=1$, and $v''_1=2$ the constants for all excited $^2\Pi_u$ levels so far identified can be calculated. The values obtained for $p'-p''$ in the levels $^2\Pi_{½u}$ are:

$p'_0-p''_0=0.0030$	$p'_0-p''_1=0.0027$	$p'_0-p''_2=0.0025$
$p'_1-p''_0=0.0037$	$p'_1-p''_1=0.0033$	$p'_1-p''_2=0.0033$
$p'_2-p''_0=0.0049$	$p'_2-p''_1=0.0046$	$p'_2-p''_2=0.0044$
$p'_3-p''_0=0.0065$	$p'_3-p''_1=0.0061$	
$p'_4-p''_0=0.0087$	$p'_4-p''_1=0.0082$	
	$p'_5-p''_1=0.0110$	$p'_5-p''_2=0.0106$
		$p'_6-p''_2=0.0148.$

The differences $p'_n-p''_2$ were obtained from the staggering for low rotational lines where the influence of the anomalous Λ-doubling cannot be felt. From these values and the value of p''_0 the following Λ-doubling constants are obtained:

$$p'_0=0.0077\pm0.0002\qquad p'_3=0.0112\pm0.0002$$
$$p'_1=0.0084\pm0.0002\qquad p'_4=0.0133\pm0.0003$$
$$p'_2=0.0096\pm0.0002\qquad p'_5=0.0161\pm0.0004$$
$$p'_6=0.0201\pm0.0006.$$

The B' constants could now be determined with higher accuracy than the values reported in Part I. Since still better values will be available after the analysis of higher progressions is

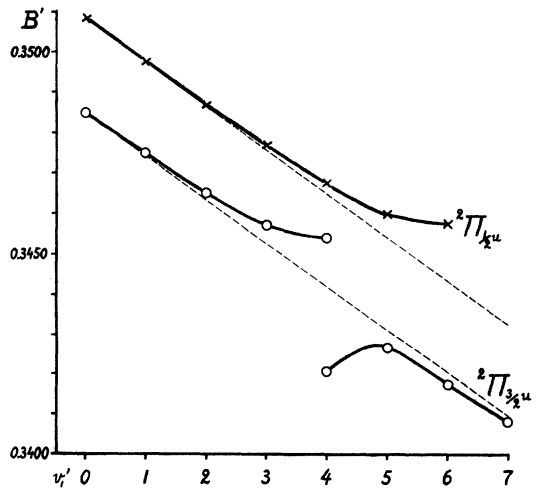

FIG. 5. Graphical presentation of the change of the B' value with vibrational quantum number v'_1 for the excited state $^2\Pi_u$.

completed, the results obtained are presented here only in the form of a graph in Fig. 5, where for $^2\Pi_{3/2u}$ a point found from the analysis of the sub-band (7, 3) has been added. The increasing perturbation of the $^2\Pi_{\frac{1}{2}u}$ substates with increasing v'_1 is clearly indicated; up to now, however, the expected double level $v'_1=7$ has not been identified. For the double substate $^2\Pi_{3/2u}$, 4 as in the case of the double level $^2\Pi_{3/2g}$, 1, we find that the average value of the B's obtained is smaller than the value calculated assuming a linear decrease of the B's in both substates. This can be explained if the perturbing state possesses a smaller value of B than the substates given. On the contrary, for the substates possessing two quanta of bending vibration, a B value greater than that for the lowest level is expected. In fact, this relation has been confirmed in the cases of CS_2 and CO_2.[9] On the other hand, the perturbation by the double bending vibration seems to offer the only possibility of explanation of the existence of the described perturbation in the ground state $^2\Pi_g$, $v''_1=1$. Since the ground state of the CO_2^+ molecule is different from the molecules of CS_2 and CO_2 and represents a more complicated case a thorough theoretical examination of this case seems to be necessary. The general discussion of Λ-doublings, perturbations, and their probable causes is postponed until all data concerning the $^2\Pi_u \rightarrow {}^2\Pi_g$ system of bands are available.

In view of the perturbations present in higher vibrational levels of both states $^2\Pi_g$ and $^2\Pi_u$ formulas for unperturbed values of B's and the unperturbed energy levels as functions of the quantum number of the symmetrical vibration can be calculated on the basis of data already obtained. These values will not be improved by the subsequent extension of the analysis of the $^2\Pi_u \rightarrow {}^2\Pi_g$ system of bands. The formulas are found by assuming the spin doubling to be independent of the vibrational energy of the molecule, which for the lowest levels should represent at least a fair approximation.

$$^2\Pi_g: \quad B''_v = B''_0 - 0.0012v''_1;$$
$$T''(v_1) = T''_0(0) + 1280v''_1 - 7.25v''_1(v''_1+1)$$
$$^2\Pi_u: \quad B'_v = B'_0 - 0.0011v'_1;$$
$$T'(v_1) = T'_0(0) + 1131v'_1 - 3.0v'_1(v'_1+1).$$

The equilibrium constants and the origins of both subsystems cannot be found since the dependence on the two other vibrational quantum numbers v_2 and v_3 is not known. The spin-orbit coupling constant A for $^2\Pi_u$ is -95.4 cm^{-1}.

The author is very much indebted to Professor R. S. Mulliken for many discussions and suggestions and to Messrs. J. B. Coon and T. J. Kinyon for assistance in computations.

[9] L. S. Liebermann, Phys. Rev. 60, 496 (1941).

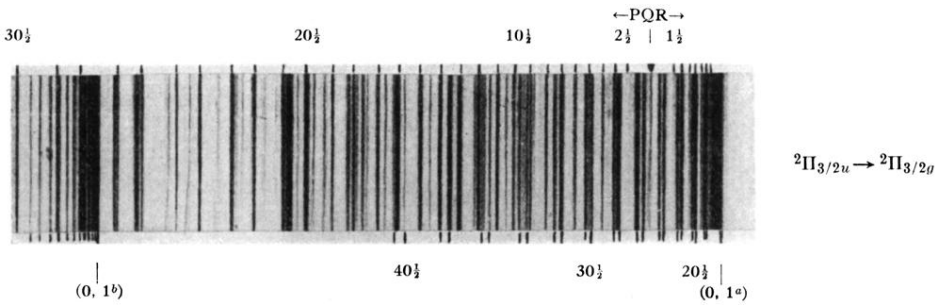

FIG. 3. Enlargement of a photograph of the sub-band λ3662 with the quantum numbers of lines given.