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

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The rotational analysis of additional 14 sub-bands of the band system ${}^2\Pi_u \rightarrow {}^2\Pi_g$ of the molecule of CO_2^+ leads to the identification of vibrational levels $v_1''=3$, 4, 5, 6, and 7 for the ground state of the molecule (Tables I–III). All 48 sub-bands analyzed and reported in Parts I, II, and III are arranged in a vibrational scheme into which many weaker, not analyzed bands (not less than 46) can be fitted. (Tables VI and VII). The distribution of the intensities of the bands corresponds to a Franck-Condon parabola with an extra intensity maximum on the diagonal. All vibrational and rotational constants for this band system (corresponding to different quanta of the symmetric vibration) are given in this and the previous paper, Part II. B'', D'', and p'' values for the levels $v_1''=0$, 1, and 2 and p' values for levels $v_1'=0$ to 6 were given in Part II. B'' and D'' for $v_1''=3$ and 4 are given on pages 682–683 of this paper; B'', D'', and p'' for $v_1''=5$, 6, and 7 are given in Table III. Tables IV and V contain the rotational constants for the excited state ${}^2\Pi_u$. The dependence of the Λ-doubling on the rotational quantum number J is represented in Fig. 4, Part II and Fig. 1, Part III. The values of B'' (Fig. 2), of B' (Fig. 5, Part II), of the Λ-doubling for $J=30\frac{1}{2}$ (Figs. 3 and 4), and finally of the deviation of the vibrational energy from the calculated values (Figs. 5 and 6) are represented as functions of the vibrational quantum number. From these curves the character of the perturbations occurring for the substate ${}^2\Pi_{3/2g}$ at $v_1''=1$, for ${}^2\Pi_{3/2u}$ at $v_1'=4$, for ${}^2\Pi_{\frac{1}{2}u}$ at $v_1'=7$, and finally for both substates in the ground level at $v_1''=5$ can be conveniently studied. A discussion of these perturbations is included; however, no explanation is given, since this would require a special theoretical investigation.

INTRODUCTION

In the first two parts of this work[1,2] the results of a rotational analysis of 34 sub-bands of the system of bands ${}^2\Pi_u \rightarrow {}^2\Pi_g$ of the molecule CO_2^+ were reported. These bands were frequently observed in the past; some progress already had been made in the vibrational analysis by Smyth[3] and in the rotational analysis by Schmid.[4] However, no definite results could be obtained in view of the insufficient resolution. In this work the analysis was made possible thanks to the high resolving power of the Chicago 30-foot grating spectrograph. In Part I a discussion of previous work on the spectrum of CO_2^+, a description of the experimental procedure and the results of the analysis of 10 sub-bands belonging to the progression $v_1''=v_2''=v_3''=0$ of the symmetrical vibration (v_1' varying, $v_2'=v_3'=0$) were presented. In Part II the analysis of bands belonging to the progressions $v_1''=1$ and 2 of the symmetrical vibration was reported. The molecule CO_2^+ appears to be linear for both the excited ${}^2\Pi_u$ and the ground ${}^2\Pi_g$ states. For the substate ${}^2\Pi_{3/2}$ very interesting perturbations were found in the ground state for $v_1''=1$ and in the excited state for $v_1'=4$, the perturbation consisting in a doubling of the energy level accompanied by the operation of a special selection rule forbidding transitions between vibrational levels showing opposite perturbational shifts in the vibrational energy. In this paper the results of the rotational analysis of the remaining progressions of the symmetrical vibration (in all 14 sub-bands) and of the vibrational analysis for the whole system of symmetrical vibrations are reported. Also molecular constants for the whole band system and a discussion of perturbations are included.

RESULTS

The $v_1''=3$ and 4 Progressions of Bands

The wave numbers of the lines of sub-bands and the Δ_2F'' values for the levels $v_1''=3$ and 4 are given in Tables I and II. The molecular constants obtained from Δ_2F_3'' for the ground state of CO_2^+ with three quanta of the symmetrical vibration ($v_1''=3$) are the following:

$$
\begin{aligned}
{}^2\Pi_{3/2g}:\ & B_3''=0.3755\pm0.00015\\
& D_3''=-(1.1\pm0.2)\times10^{-7}\\[1ex]
{}^2\Pi_{\frac{1}{2}g}:\ & B_3''=0.3788\pm0.0002\\
& D_3''=-(1.6\pm0.3)\times10^{-7}.
\end{aligned}
$$

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

[2] S. Mrozowski, Phys. Rev. 62, 270 (1942). Part II.

[3] H. D. Smyth, Phys. Rev. 38, 2000 (1931).

[4] See the references in Part I.

The Λ-doubling is in both substates anomalous. For $^2\Pi_{3/2g}$ with $v_1''=3$ it is negative as for the level $v_1''=2$, but the absolute values are a little smaller. For $^2\Pi_{\frac{1}{2}g}$ with $v_1''=3$ the Λ-doubling is positive and bigger than for $v_1''=2$.

The molecular constants obtained from Δ_2F_4'' for the ground state with four quanta of symmetrical vibration ($v_1''=4$) are the following:

$$^2\Pi_{3/2g}\!: \quad B_4''=0.3790\pm0.0002$$
$$D_4''=-(1.4\pm0.3)\times10^{-7}$$

$$^2\Pi_{\frac{1}{2}g}\!: \quad B_4''=0.3791\pm0.0003$$
$$D_4''=-(1.5\pm0.5)\times10^{-7}.$$

Again the Λ-doubling is in both substates anomalous; however, here it is positive for both substates. The total Λ-doubling for the substate $^2\Pi_{3/2g}$ and the relative increase of the Λ-doubling for the substate $^2\Pi_{\frac{1}{2}g}$ over the values for $v_1''=1$ as function of the rotational quantum number J are given in Fig. 1.

The relatively lower accuracy of the results for $v_1''=4$ is caused by the weakness of the corresponding bands analyzed. Although only one band per substate was analyzed, the rotational analysis definitely points toward the accepted assignment and the latter appears to be well substantiated by the vibrational analysis (see below, Tables VI and VII).

The $v_1''=5$, 6 and 7 Progressions of Bands

The wave numbers of the lines of the bands corresponding to the levels $v_1''=5$, 6 and 7 are given in Table III. The identification of the bands met considerable difficulties. The bands are overlapped by strong bands of CO and the measurements are for this and other reasons less accurate. Some unexplainable irregularities in the

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

	(1,3) $\nu_0=25920.95$		(3,3) $\nu_0=28163.8$		(6,3) $\nu_0=31443.0$		(7,3) $\nu_0=32540.75$		$^2\Pi_{3/2g}(v_1''=3)$		(4^b,4) $\nu_0=28034.0$		$^2\Pi_{3/2g}(v_1''=4)$	
$J-\frac{1}{2}$	R	P	R	P	R	P	R	P	Δ_2F_3'' av.	1st diff.	R	P	Δ_2F_4''	1st diff.
3		25918.13												
4		17.18						32536.89						
5		16.18						35.80						
6		15.11						34.68						
7		13.98						33.44						
8		12.80			31446.76 h		32544.33 h	32.16			28037.77 h			
9		11.57	28168.05 h		46.76 e		44.33 e	30.80	14.89		37.77 e			
10	25925.57 h	10.28	68.05 e	28152.96	46.76 a		44.33 a	29.44	16.43	1.54	37.77 a			
11	25.57 e	08.97	68.05 a	51.59	d	31430.24	d	27.93	17.98	1.55	37.77 d		18.08	
12	25.57 a	07.55	68.05 d	50.10	46.57	28.78	44.10	26.47	19.46	1.48	37.65	28019.69	19.74	1.66
13	25.57 d	06.11	67.85	48.60	46.29	27.16	43.81	24.80	21.00	1.54	37.41	18.03	21.23	1.49
14	25.41	04.57	67.74	47.07	45.93	25.45	43.55	23.03	22.52	1.52	37.16	16.42	22.74	1.51
15	25.29	03.01	67.53	45.42	45.55	23.69	43.10	21.26	24.03	1.51	36.84	14.57	24.23	1.49
16	25.05	01.38	67.23	43.73	45.14	21.95	42.71	19.46	25.54	1.51	36.42	12.93	25.82	1.59
17	24.73	25899.70	66.85	42.02	44.57	20.10	42.07	17.53	27.05	1.51	35.92	11.02	27.26	1.44
18	24.41	97.96	66.49	40.22	44.10	18.13	41.51	15.57	28.54	1.49	35.39	09.16	28.79	1.53
19	23.95	96.17	66.01	38.35	43.41	16.09	40.85	13.53	30.04	1.50	34.73	07.13	30.27	1.48
20	23.51	94.32	65.47	36.45	42.67	14.04	40.26	11.48	31.53	1.49	34.13	05.12	31.83	1.56
21	22.98	92.40	64.95	34.49	41.87	11.86	39.20	09.24	33.02	1.49	33.29	02.90	33.35	1.52
22	22.41	90.45	64.26	32.47	41.04	09.69	38.35	07.03	34.53	1.51	32.57	00.78	34.84	1.49
23	21.78	88.45	63.53	30.38	40.14	07.37	37.40	04.67	36.03	1.50	31.58	27998.44	36.38	1.54
24	21.06	86.35	62.80	28.27	39.19	05.02	36.34	02.38	37.53	1.50	30.73	96.19	37.87	1.49
25	20.37	84.24	61.96	26.01	38.14	02.65	35.30	32499.81	39.04	1.51	29.63	93.71	39.41	1.54
26	19.53	82.01	61.02	23.72	37.00	00.23	34.12	97.34	40.55	1.51	28.65	91.32	40.97	1.56
27	18.70	79.81	60.11	21.40	35.77	31397.63	32.83	94.74	42.03	1.48	27.38	88.66	42.48	1.51
28	17.77	77.49	59.05	19.02	34.58	94.97	31.55	92.08	43.52	1.49	26.26	86.18	43.97	1.49
29	16.78	75.16	58.00	16.63	33.15	92.24	30.19	89.31	45.03	1.51	24.83	83.41	45.50	1.53
30	15.78	72.74	56.86	14.05	31.72	89.50	28.71	86.51	46.51	1.48	23.59	80.76	46.99	1.49
31	14.73	70.34	55.74	11.51	30.24		27.25	83.65	48.02	1.51	22.03	77.84	48.54	1.55
32	13.52	67.73	54.44	08.86	28.78		25.71	80.74	49.53	1.51	20.64	75.05	50.05	1.51
33	12.41	65.20	53.18	06.20	27.16		24.10	77.67	51.03	1.50	18.93	71.98	51.54	1.49
34	11.10	62.51	51.77	03.46			22.38	74.58	52.52	1.49	17.45	69.10	53.04	1.50
35	09.87	59.87	50.44	00.74			20.60	71.47	54.02	1.50	15.60	65.89	54.57	1.53
36	08.41	57.07	48.90	28097.76			18.68	68.30	55.52	1.50	14.00	62.88	56.06	1.49
37	07.04	54.33	47.47	94.92			16.70	64.91	57.01	1.49	12.06	59.54	57.53	1.47
38	05.51	51.40	45.78				14.84	61.67	58.51	1.50	10.31	56.47		
39	04.05	48.53	44.29				12.75		60.03	1.52	08.19			
40	02.30	45.47							61.55	1.52				
41	00.82	42.50							62.93	1.38				
42	25899.03	39.37							64.52	1.59				
43	97.49	36.30							66.02	1.50				
44	95.42	33.02												
45	93.67													
46	91.63													
47	89.81													
48	87.61													
49	85.74													
50	83.31													
51	81.33													
52	78.81													

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

	(1,3) $\nu_0=25821.55$		(3,3) $\nu_0=28058.45$		(6,3) $\nu_0=31385.70$		$^2\Pi_{1/2g}(v_1''=3)$		(4,4) $\nu_0=27919.4$		$^2\Pi_{1/2g}(v_1''=4)$	
$J-\frac{1}{2}$	R	P	R	P	R	P	Δ_2F_3'' av.	1st diff.	R	P	Δ_2F_4''	1st diff.
1	25823.18	25820.41	28060.11									
2	23.75	19.57	60.58	28056.42			4.54					
3	24.26	18.64	61.11	55.56			6.03	1.49				
4	24.68	17.68		54.60			7.58	1.55				
5	25.08	16.67		53.53			9.09	1.51				
6	25.39	15.59		52.47	31389.34		10.63	1.54				
7		14.45	62.49	51.31	89.34		12.15	1.52				
8		13.24	62.49	50.07	89.57 h	31377.13	13.65	1.50				
9		12.01	62.65 h	48.80	89.57 e	75.78	15.10	1.45	27923.26 h			
10	26.10 h	10.71	62.65 e	47.40	89.57 a	74.42	16.65	1.55	23.26 e			
11	26.10 e	09.40	62.65 a d	46.06	89.57 d	72.87	18.16	1.51	23.26 a d			
12	26.10 a d	07.93	62.49	44.56	89.34	71.24	19.65	1.49			19.41	
13		06.48	62.49	43.06	89.34	69.83	21.15	1.50		27903.85		
14	25.88	04.94	62.25	41.43	88.98	68.20	22.69	1.54	22.95	02.16		
15	25.74	03.34	62.09	39.80	88.78	66.58	24.20	1.51	22.80	00.64	24.09	
16	25.48	01.72	61.66	38.04	88.24	64.74	25.77	1.57	22.48	27898.87	25.64	1.55
17	25.19	00.00	61.34	36.33	87.89	63.99	27.22	1.45	22.12	97.15	27.21	1.57
18	24.85	25798.24	60.84	34.45	87.20	61.02	28.77	1.55	21.65	95.27	28.68	1.47
19	24.41	96.38	60.38	32.57	86.75	59.13	30.27	1.50	21.19	93.44	30.19	1.51
20	23.92	94.54	59.76	30.61	85.88	56.94	31.80	1.53	20.59	91.46	31.79	1.60
21	23.37	92.58	59.17	28.58	85.44	55.00	33.26	1.46	19.94	89.40	33.32	1.53
22	22.80	90.64	58.42	26.48	84.44	52.69	34.84	1.58	19.21	87.27	34.88	1.56
23	22.15	88.52	57.69	24.33	83.90	50.50	36.33	1.49	18.39	85.05	36.33	1.45
24	21.48	86.45	56.83	22.10	82.70	48.12	37.86	1.53	17.54	82.87	37.94	1.61
25	20.66	84.24	55.96	19.83	82.20	46.10	39.36	1.50	16.55	80.45	39.34	1.40
26	19.89	82.09	55.01	17.52	80.77	43.35	40.96	1.60	15.65	78.20	40.92	1.58
27	18.95	79.74	54.00	15.11	79.90	41.00	42.42	1.46	14.46	75.63	42.44	1.52
28	18.07	77.48	52.95	12.67	78.36	38.25	43.99	1.57	13.42	73.21	44.00	1.56
29	17.00	74.96	51.80	10.11	77.43	35.82	45.53	1.44	12.03	70.47	45.46	1.46
30	16.04	72.64	50.59	07.56	75.78	32.91	47.00	1.57	10.97	67.96	46.96	1.50
31	14.80	69.96	49.32	04.86	74.70	30.41	48.42	1.42	09.35	65.07		
32	13.77	67.54	48.06	02.25	72.87	27.36	50.01	1.59	08.15			
33	12.38	64.73	46.60	27999.38	71.72	24.69	51.43	1.42				
34	11.26	62.27	45.23	96.65		21.48	53.02	1.59				
35	09.68	59.31	43.62	93.65		18.71	54.47	1.45				
36	08.54	56.72	42.16	90.82		15.37	56.04	1.57				
37	06.84	53.56	40.36	87.65		12.45	57.44	1.40				
38	05.58		38.81	84.73		08.99	58.98	1.54				
39	03.67			81.39		05.97	60.41	1.43				
40	02.34			78.40		02.40						
41				74.92								
42				71.78								
43				68.08								
44				64.98								
45				61.84								
46				58.56								
47				54.36								

dispersion curve in the region λ4090–λ4140 were observed which made a definite decision about the assignment impossible in view of the small differences in B' values for the excited state $^2\Pi_u$. However, it was found that by slightly correcting the correction curves for the dispersion the Δ_2F' values can be brought into agreement with the Δ_2F' values for the corresponding vibrational levels of the excited state. At first this assignment was considered only as tentative, since it gives a very strong vibrational perturbation for the level $v_1''=5$ for both substates and, what seemed more peculiar, no other bands for this progression could be detected. Further it was expected that for such a strong perturbation a doubling of the level should occur, but no bands belonging to the other component level could be identified in spite of a very careful search. However the vibrational analysis for the higher levels $v_1''=6$, 7, 8, and 9 gives such a good agreement with the observations that the author feels reasonably certain the assignment after all is correct.

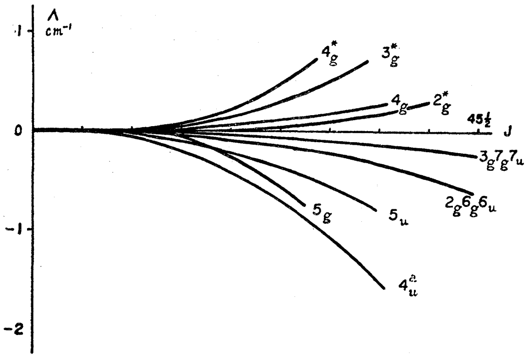

FIG. 1. Λ-doubling of rotational states in the ground substate $^2\Pi_{3/2g}$ of the CO_2^+ molecule for $v_1''=2$ to 7 and in the excited substate $^2\Pi_{3/2u}$ for $v_1'=4^a$, 5, 6, and 7. The three curves for the ground substate $^2\Pi_{1/2g}$ and $v_1''=2$, 3, and 4 are marked by asterisks and represent the excess of the Λ-doubling over the value of the Λ-doubling for the level $v_1''=1$.

The molecular constants obtained from Δ_2F'' for the ground state $^2\Pi_g$ for $v_1''=5$, 6, and 7 of the symmetrical vibration are given in the lower part of Table III. In view of the uncertainties in the dispersion curve the results naturally are still less exact than for $v_1''=3$ and 4. The anomalous negative Λ-doublings for $^2\Pi_{3/2g}$, $v_1''=5$, 6, and 7 are given in Fig. 1. The Λ-doublings for $^2\Pi_{\frac{1}{2}g}$, $v_1''=5$ and 6 are normal, that is are linear with J. The linear coefficients p'' are given in the lower part of the Table III.

The Ground State $^2\Pi_g$

The dependence of the rotational constant B'' on the quantum number of the symmetrical vibration is represented in Fig. 2. The values were taken from Part II and from the preceding sections of this paper. The broken line corresponds to the formula $B_v''=B_0''-0.0014\cdot v_1''$. In order to visualize the type of perturbation occurring for both substates at $v_1''=5$, the Λ-doubling for an arbitrarily chosen rotational

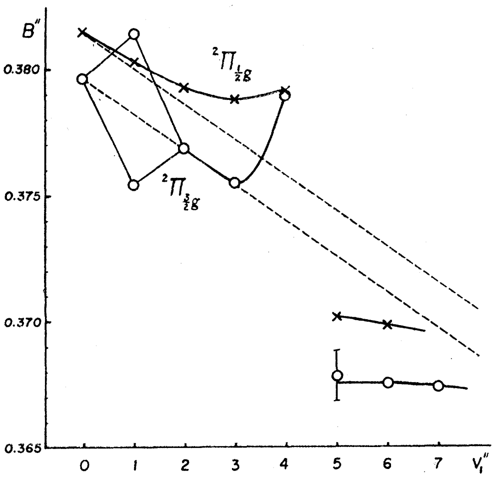

FIG. 2. Graphical presentation of the change of the B''-value with the vibrational quantum number v_1'' for the ground state $^2\Pi_g$.

TABLE III.

	Sub-bands $^2\Pi_{3/2u}\rightarrow{}^2\Pi_{3/2g}$						Sub-bands $^2\Pi_{\frac{1}{2}u}\rightarrow{}^2\Pi_{\frac{1}{2}g}$			
	(2,5)		(3,6)		$(4^b,7)$		(2,5)		(3,6)	
	$\nu_0=24404.0$		$\nu_0=24327.45$		$\nu_0=24250.2$		$\nu_0=24321.25$		$\nu_0=24240.2$	
$J-\frac{1}{2}$	R	P	R	P	R	P	R	P	R	P
2				24325.50						
3			24330.20	24.64	24252.89					
4			30.70	23.75	53.37			24317.55		24236.25
5			31.15	22.94	53.84			16.68		35.20
6			31.57	21.74				15.71		34.21
7		24397.93	31.93	20.89	54.71			14.64		33.18
8		96.85	32.26	19.78	55.13			13.63		32.16
9		95.75		18.67	55.48			12.52		31.00
10		94.59		17.55				11.40		29.86
11		93.40		16.33				10.15		28.69
12		92.08		15.09				08.99		27.43
13		91.00	33.20} h	13.81	55.70} h	24236.38		07.67	24245.62} h	26.16
14	24410.50} h e	89.67	33.20} e	12.52	55.70} e	34.97	24327.40} h	06.46	45.62} e	24.81
15	10.50} a	88.34	33.20} a	11.12	55.70} a	33.66	27.40} e	05.10	45.62} a	23.45
16	10.50} d	86.90	33.20} d	09.70	55.70} d	32.17	27.40} a	03.58	45.62} d	22.00
17		85.51		08.24		30.78	27.40} d	02.20		20.58
18	10.32	84.13	32.95	06.72		29.10		00.71		19.04
19	10.20	82.30	32.78	05.10	55.55	27.66	27.15	24299.20		17.55
20	09.95	80.89	32.59	03.57	55.33	26.14	26.94	97.61		15.89
21	09.77	79.30	32.40	01.98	54.92	24.37	26.72	96.05		14.32
22	09.29	77.40	32.07	00.27	54.52	22.83	26.48	94.39	44.58	12.56
23	09.02	75.80	31.78	24298.50	54.14	21.02	26.20	92.75	44.30	10.93
24	08.40	73.65	31.33	96.77	53.66	19.23	25.86	90.95	43.80	09.03
25	08.20	72.40	30.92	95.11	53.19	17.35	25.50	89.24	43.31	07.40
26	07.45	70.20	30.39	93.32	52.68	15.49	25.08	87.35	42.78	05.27
27	07.20	68.24	29.95	91.25	52.09	13.53	24.64	85.41	42.24	03.62
28	06.22	66.20	29.35	89.25	51.49	11.56	24.16	83.65	41.51	01.23
29			28.78	87.35	50.84	09.52	23.57	81.69	40.76	
30			28.06	85.40	50.15	07.39	23.06		40.13	
31			27.40	82.21	49.36	05.27	22.33		39.39	
32			26.72	81.03	48.64	03.18	21.59		38.62	
33			25.86	78.91	47.74	00.98	20.89		37.71	
34			25.08	76.68	46.91	24198.71	20.19		36.72	
35			24.16	74.47			19.39		35.71	
36			23.28	72.14			18.52		34.75	
37			22.33	69.75			17.55		33.66	
38			21.19	67.39					32.57	
39			20.19	64.72					31.46	
40			19.01						30.32	
41			17.99							
42			16.68							
43			15.44							
44			14.06							
	$B_5''=0.3678\pm0.0010$ $^*D_5''=1.5\cdot10^{-7}$ assumed		$B_6''=0.3675\pm0.0003$ $D_6''=-(1.3\pm0.4)10^{-7}$		$B_7''=0.3674\pm0.0004$ $D_7''=-(1.4\pm0.5)10^{-7}$		$B_5''=0.3702\pm0.0004$ $D_5''=-(1.2\pm0.4)10^{-7}$ $p_5''=0.0090\pm0.0006$		$B_6''=0.3698\pm0.0005$ $D_6''=-(1.2\pm0.7)10^{-7}$ $p_6''=0.0106\pm0.0006$	

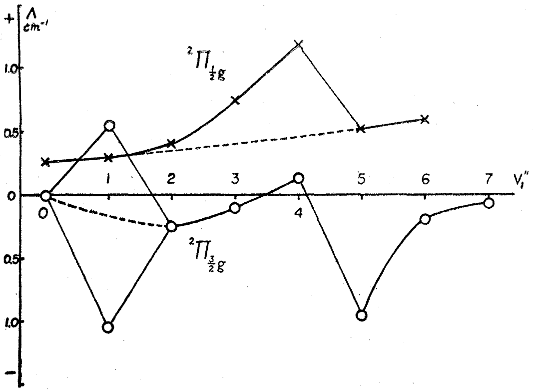

FIG. 3. Λ-doubling for the rotational level $J=30\frac{1}{2}$ in dependence on the vibrational quantum number v_1'' of the ground state $^2\Pi_g$ of the molecule CO_2^+.

quantum number ($J=30\frac{1}{2}$) is given in Fig. 3 as a function of the vibrational quantum number. For all levels of the substate $^2\Pi_{3/2g}$, except $v_1''=0$, an anomalous Λ-doubling is observed. On the contrary, in $^2\Pi_{\frac{1}{2}g}$ the anomalous Λ-doubling is observed only for levels below the perturbation, that is $v_1''=2$, 3, and 4. The value of the contribution of the anomalous Λ-doubling is given for $^2\Pi_{\frac{1}{2}g}$ by the distance from the broken curve, corresponding to the normal Λ-doubling effect. This latter Λ-doubling is linear with J and is probably caused by the interaction with an hypothetical excited state $^2\Sigma_g^+$.[5] For both substates a similar trend in curves Fig. 3 is observed, with the difference that strong anomalous

TABLE IV. Combination differences for $^2\Pi_{3/2u}$.

	$v_1'=0$		$v_1'=1$		$v_1'=2$		$v_1'=3$		$v_1'=4^a$		$v_1'=4^b$		$v_1'=5$		$v_1'=6$		$v_1'=7$	
$J-\frac{1}{2}$	Δ_2F_0' av.	1st diff.	Δ_2F_1' av.	1st diff.	Δ_2F_2' av.	1st diff.	Δ_2F_3' av.	1st diff.	$\Delta_2F_{4}a'$	1st diff.	$\Delta_2F_{4}b'$ av.	1st diff.	Δ_2F_5' av.	1st diff.	Δ_2F_6' av.	1st diff.	Δ_2F_7'	1st diff.
2	4.16		4.23															
3	5.59	1.43	5.60	1.37	5.55													
4	6.96	1.37	6.96	1.36	6.93	1.38												
5	8.39	1.43			8.31	1.38												
6	9.75	1.36			9.70	1.39												
7	11.14	1.39			11.03	1.33	11.08				11.07		10.95					
8	12.55	1.41			12.42	1.39	12.41	1.33			12.26	1.19	12.22	1.27	12.14		12.17	
9	13.89	1.34	13.83		13.80	1.38	13.74	1.33	13.53		13.73	1.47	13.57	1.35	13.45	1.31	13.53	1.36
10	15.28	1.39	15.20	1.37	15.22	1.42	15.13	1.39	14.86	1.33	15.18	1.45	14.94	1.37	14.85	1.40	14.89	1.36
11	16.66	1.38	16.60	1.40	16.55	1.37	16.58	1.45	16.42	1.56	16.48	1.30	16.46	1.52				
12	18.07	1.41	18.02	1.42	18.00	1.45	17.96	1.38	17.79	1.37	17.95	1.47			17.79		17.64	
13	19.48	1.41	19.46	1.44	19.42	1.42	19.32	1.36	19.09	1.30	19.33	1.38	19.20		19.12	1.33	19.01	1.37
14	20.88	1.40	20.88	1.42	20.80	1.38	20.71	1.39	20.44	1.35	20.75	1.42	20.55	1.35	20.50	1.38	20.52	1.51
15	22.30	1.42	22.27	1.39	22.17	1.37	22.08	1.37	21.80	1.36	22.10	1.35	21.96	1.41	21.83	1.33	21.83	1.31
16	23.70	1.40	23.67	1.40	23.57	1.40	23.45	1.37	23.25	1.45	23.47	1.37	23.32	1.36	23.19	1.36	23.25	1.42
17	25.10	1.40	25.05	1.38	24.96	1.39	24.85	1.40	24.54	1.29	24.86	1.39	24.71	1.39	24.55	1.36	24.54	1.29
18	26.48	1.38	26.42	1.37	26.36	1.40	26.25	1.40	26.02	1.48	26.25	1.39	26.05	1.34	25.96	1.41	25.94	1.40
19	27.87	1.39	27.82	1.40	27.73	1.37	27.66	1.41	27.35	1.33	27.63	1.38	27.41	1.36	27.32	1.36	27.24	1.30
20	29.27	1.40	29.20	1.38	29.12	1.39	29.03	1.37	28.73	1.38	29.00	1.37	28.74	1.33	28.65	1.33	28.78	1.54
21	30.67	1.40	30.60	1.40	30.50	1.38	30.41	1.38	30.09	1.36	30.39	1.39	30.13	1.39	30.01	1.36	29.96	1.18
22	32.04	1.37	31.98	1.38	31.89	1.39	31.78	1.37	31.47	1.38	31.76	1.37	31.50	1.37	31.40	1.39	31.32	1.36
23	33.43	1.39	33.37	1.39	33.26	1.37	33.16	1.38	32.95	1.48	33.14	1.38	32.87	1.37	32.76	1.36	32.73	1.41
24	34.83	1.40	34.74	1.37	34.63	1.37	34.54	1.38	34.13	1.18	34.54	1.40	34.26	1.39	34.15	1.39	33.96	1.23
25	36.25	1.42	36.12	1.38	36.01	1.38	35.95	1.41	35.50	1.37	35.91	1.37	35.62	1.36	35.50	1.35	35.49	1.53
26	37.62	1.37	37.53	1.41	37.43	1.42	37.33	1.38	36.95	1.45	37.31	1.40	36.99	1.37	36.82	1.32	36.79	1.30
27	39.03	1.41	38.91	1.38	38.81	1.38	38.71	1.38	38.42	1.47	38.72	1.41	38.35	1.36	38.21	1.39	38.09	1.30
28	40.40	1.37	40.29	1.38	40.18	1.37	40.08	1.37	39.73	1.31	40.09	1.37	39.76	1.41	39.60	1.39	39.47	1.38
29	41.81	1.41	41.66	1.37	41.58	1.40	41.45	1.37			41.44	1.35	41.11	1.35	40.93	1.33	40.88	1.41
30	43.20	1.39	43.04	1.38	42.98	1.40	42.84	1.39			42.85	1.41	42.45	1.34	42.28	1.35	42.20	1.32
31	44.59	1.39	44.42	1.38	44.38	1.40	44.23	1.39			44.21	1.36	43.78	1.33	43.76	1.38	43.60	1.40
32	46.00	1.41	45.81	1.39	45.72	1.34	45.61	1.38			45.61	1.40	45.16	1.38	45.07	1.31	44.97	1.37
33	47.40	1.40	47.21	1.40	47.09	1.37	47.00	1.39			46.97	1.36	46.55	1.39	46.48	1.41	46.43	1.46
34	48.77	1.37	48.59	1.38	48.47	1.38	48.38	1.37			48.32	1.35	47.96	1.41	47.76	1.28	47.80	1.37
35	50.16	1.39	49.99	1.40	49.88	1.41	49.70	1.32			49.71	1.39	49.33	1.37	49.09	1.33	49.13	1.33
36	51.55	1.39	51.37	1.38	51.23	1.35	51.14	1.44			51.12	1.41			50.55	1.46	50.38	1.25
37	52.96	1.41	52.75	1.38	52.62	1.39	52.55	1.41			52.52	1.40			51.92	1.37	51.79	1.41
38	54.34	1.38	54.14	1.39	53.97	1.35					53.84	1.32			53.27	1.35	53.17	1.38
39	55.72	1.38	55.53	1.39	55.33	1.36									54.65	1.38		
40	57.09	1.37	56.90	1.37	56.72	1.39												
41	58.50	1.41	58.29	1.39	58.08	1.36												
42	59.87	1.37	59.68	1.39	59.48	1.40												
43	61.28	1.41	61.11	1.43														
44	62.64	1.36	62.43	1.32														
45	64.07	1.43																
46	65.44	1.37																
47	66.84	1.40																
48	68.28	1.44																
49	69.62	1.34																
50	71.00	1.38																

$B_0'=0.3485_5\pm0.0001$ $B_1'=0.3475_5\pm0.00015$ $B_2'=0.3466\pm0.00015$ $B_3'=0.3457\pm0.0002$ $B_{4}a'=0.3421\pm0.0003$
$D_0'=-(1.0\pm0.2)10^{-7}$ $D_1'=-(1.5\pm0.2)10^{-7}$ $D_2'=-(1.7\pm0.3)10^{-7}$ $D_3'=-(1.3\pm0.4)10^{-7}$ $D_{4}a'=+(0.6\pm0.3)10^{-7}$
$B_{4}b'=0.3454\pm0.0001$ $B_5'=0.3426_5\pm0.0001$ $B_6'=0.3417\pm0.00015$ $B_7'=0.3408\pm0.0002$
$D_{4}b'=-(0.1\pm0.1)10^{-7}$ $D_5'=-(0.4\pm0.15)10^{-7}$ $D_6'=-(1.7\pm0.2)10^{-7}$ $D_7'=-(0.5\pm0.2)10^{-7}$

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[5] S. Mrozowski, Rev. Mod. Phys. **14**, 216 (1942). The discussion of the vibrational perturbations given there on p. 217 requires modifications.

Table V. Combination differences for $^2\Pi_{\frac{1}{2}u}$.

	$v_1'=0$		$v_1'=1$		$v_1'=2$		$v_1'=3$		$v_1'=4$		$v_1'=5$		$v_1'=6$	
$J-\frac{1}{2}$	Δ_2F_0' av.	1st diff.	Δ_2F_1' av.	1st diff.	Δ_2F_2' av.	1st diff.	Δ_2F_3' av.	1st diff.	Δ_2F_4' av.	1st diff.	Δ_2F_5' av.	1st diff.	Δ_2F_6' av.	1st diff.
1			2.77		2.80									
2			4.22	1.45	4.20	1.40	4.17							
3			5.65	1.43	5.67	1.37	5.55	1.38						
4	6.90		7.02	1.37	7.03	1.36								
5			8.43	1.41	8.37	1.34								
6	9.58		9.80	1.37			9.79		9.75		9.70		9.73	
7			11.34	1.54	11.14		11.10	1.31	10.92	1.17	10.92	1.22	10.91	1.18
8	12.71		12.53	1.19	12.51	1.37	12.48	1.38	12.49	1.57	12.48	1.56	12.44	1.51
9	14.07	1.36	13.96	1.43	13.91	1.40	13.85	1.37	13.78	1.29	13.75	1.27	13.79	1.35
10	15.41	1.34	15.36	1.40	15.28	1.37	15.26	1.41	15.26	1.48	15.17	1.42	15.20	1.41
11	16.80	1.39	16.76	1.40	16.70	1.42	16.65	1.39	16.63	1.37	16.54	1.37	16.65	1.45
12	18.22	1.42	18.17	1.41	18.09	1.39	18.04	1.39	17.94	1.31	17.90	1.36	18.02	1.37
13	19.66	1.44	19.73	1.46	19.59	1.50	19.47	1.43	19.44	1.50	19.40	1.50	19.44	1.42
14	21.05	1.39	20.99	1.36	20.89	1.30	20.85	1.38	20.81	1.37	20.70	1.30	20.72	1.28
15	22.45	1.40	22.37	1.38	22.30	1.41	22.28	1.43	22.22	1.41	22.14	1.44	22.17	1.45
16	23.85	1.40	23.77	1.40	23.69	1.39	23.65	1.37	23.60	1.38	23.52	1.38	23.44	1.27
17	25.27	1.42	25.17	1.40	25.11	1.42	25.05	1.40	24.97	1.37	24.91	1.39	24.93	1.49
18	26.66	1.39	26.58	1.41	26.52	1.41	26.42	1.37	26.36	1.39	26.28	1.37	26.21	1.28
19	28.08	1.42	27.98	1.40	27.90	1.38	27.83	1.41	27.74	1.38	27.68	1.40	27.64	1.43
20	29.49	1.40	29.38	1.40	29.29	1.39	29.19	1.36	29.12	1.38	29.03	1.35	28.99	1.35
21	30.89	1.41	30.77	1.39	30.69	1.40	30.61	1.42	30.51	1.39	30.45	1.42	30.47	1.48
22	32.31	1.42	32.16	1.39	32.06	1.37	31.97	1.36	31.91	1.40	31.74	1.29	31.75	1.28
23	33.70	1.39	33.58	1.42	33.46	1.40	33.39	1.42	33.30	1.39	33.20	1.46	33.26	1.51
24	35.10	1.40	34.98	1.40	34.84	1.38	34.75	1.36	34.68	1.38	34.51	1.31	34.57	1.31
25	36.51	1.41	36.40	1.42	36.26	1.42	36.17	1.42	36.06	1.38	36.01	1.50	36.06	1.49
26	37.89	1.38	37.78	1.38	37.63	1.37	37.52	1.35	37.44	1.38	37.28	1.27	37.42	1.36
27	39.31	1.42	39.17	1.39	39.04	1.41	38.93	1.41	38.83	1.39	38.72	1.44	38.91	1.49
28	40.69	1.38	40.57	1.40	40.43	1.39	40.34	1.41	40.20	1.37	40.08	1.36	40.13	1.22
29	42.11	1.42	41.96	1.39	41.81	1.38	41.72	1.38	41.57	1.37	41.54	1.46	41.59	1.46
30	43.49	1.38	43.36	1.40	43.20	1.39	43.08	1.36	42.96	1.39	42.84	1.30	42.87	1.28
31	44.90	1.41	44.76	1.40	44.59	1.39	44.49	1.41	44.36	1.40	44.28	1.44	44.28	1.41
32	46.28	1.38	46.16	1.40	45.98	1.39	45.90	1.41	45.75	1.39	45.67	1.39	45.57	1.29
33	47.70	1.42	47.57	1.41	47.37	1.39	47.26	1.36	47.12	1.37	47.08	1.41	47.02	1.45
34	49.08	1.38	48.95	1.38	48.73	1.36	48.62	1.36	48.49	1.37	48.38	1.30	48.31	1.29
35	50.49	1.41	50.38	1.43	50.15	1.42	50.02	1.40	49.89	1.40	49.81	1.43	49.84	1.53
36	51.87	1.38	51.77	1.39	51.55	1.40	51.42	1.40	51.22	1.33	51.09	1.28	51.08	1.24
37	53.28	1.41	53.20	1.43	52.95	1.40	52.84	1.42	52.62	1.40	52.53	1.44	52.59	1.51
38	54.76	1.38	54.46	1.26	54.36	1.41	54.22	1.38	54.00	1.38	53.87	1.34		
39	56.15	1.39	55.93	1.47	55.75	1.39	55.63	1.41	55.42	1.42	55.32	1.45		
40	57.51	1.36	57.36	1.43	57.12	1.37	56.98	1.35	56.73	1.39	56.65	1.33		
41			58.69	1.33	58.52	1.40	48.40	1.42	58.18	1.45	58.10	1.45		
42			60.09	1.40	59.90	1.38	59.75	1.35	59.46	1.28	59.42	1.32		
43			61.50	1.41	61.31	1.41	61.15	1.40	60.90	1.44	60.77	1.35		
44			62.85	1.35	62.67	1.36	62.55	1.40	62.25	1.35	62.24	1.47		
45			64.22	1.37	64.05	1.38	63.97	1.42	63.66	1.41	63.47	1.23		
46			65.60	1.38	65.42	1.37	65.31	1.34	65.05	1.39				
47					66.80	1.38	66.66	1.35	66.41	1.36				
48					68.20	1.40	68.03	1.37	67.80	1.39				
49					69.58	1.38	69.42	1.39	69.24	1.44				
50					70.93	1.35			70.61	1.37				
51					72.38	1.45			72.01	1.40				
	$B_0'=0.3509\pm0.0001$ $D_0'=-(0.5\pm0.2)10^{-7}$ $p_0'=0.0077\pm0.0002$		$B_1'=0.3498_5\pm0.0001$ $D_1'=-(0.8\pm0.1)10^{-7}$ $p_1'=0.0084\pm0.0002$		$B_2'=0.3488\pm0.0001$ $D_2'=-(1.3\pm0.2)10^{-7}$ $p_2'=0.0096\pm0.0002$		$B_3'=0.3478\pm0.0001$ $D_3'=-(1.1\pm0.2)10^{-7}$ $p_3'=0.0112\pm0.0002$		$B_4'=0.3468\pm0.0001$ $D_4'=-(1.4\pm0.2)10^{-7}$ $p_4'=0.0133\pm0.0003$		$B_5'=0.3460\pm0.0001$ $D_5'=-(1.3\pm0.2)10^{-7}$ $p_5'=0.0161\pm0.0004$		$B_6'=0.3460\pm0.0002$ $D_6'=-(1.3\pm0.3)10^{-7}$ $p_6'=0.0201\pm0.0006$	

Λ-doublings for $^2\Pi_{\frac{1}{2}g}$ are occurring below, and for $^2\Pi_{3/2g}$ above the perturbation. For $^2\Pi_{3/2g}$ there is a general tendency for a negative Λ-doubling, which is only overbalanced by strong positive perturbations at $v_1''=1$ and $v_1''=4$.

The Excited State $^2\Pi_u$

In Tables IV and V the values of Δ_2F' for the excited state are collected. They were calculated as weighted averages of differences of frequencies of the band lines given in Parts I–III. In the lower part of the tables the values of the rotational constants determined from these Δ_2F' values by application of usual methods are collected.

A drawing corresponding to Fig. 2 but for the excited state $^2\Pi_u$ was already given in Part II, Fig. 5, where the broken lines were drawn accord-

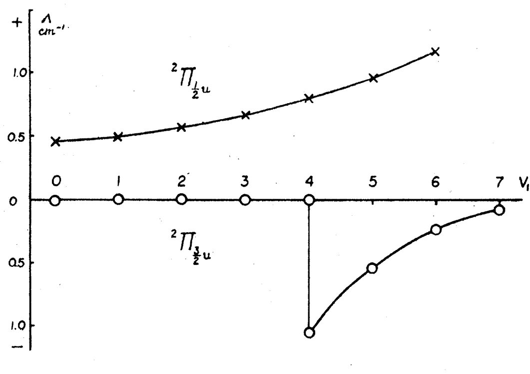

Fig. 4. Λ-doubling for the rotational level $J=30\frac{1}{2}$ in dependence from the vigrational quantum number v_1' of the excited state $^2\Pi_u$ of the molecule CO_2^+.

ing to the equation $B_v' = B_0' - 0.0011 \cdot v_1'$. The dependence of the Λ-doubling (for $J = 30\frac{1}{2}$) on the vibrational quantum number is represented in Fig. 4. It seems very interesting that for $^2\Pi_{3/2u}$ no doubling below the perturbation $v_1' = 4$ is observed at all. Λ-doublings as function of J are given for anomalous levels of the substate $^2\Pi_{3/2u}$ and $v_1' = 4^a$, 5, 6, and 7 in Fig. 1. For $^2\Pi_{\frac{1}{2}u}$ the Λ-doubling up to $v_1' = 6$ is perfectly normal, that is linear with J, although it seems quite certain that some kind of perturbation is occurring for this substate at $v_1' = 7$ (see below). The normal Λ-doubling in $^2\Pi_{\frac{1}{2}u}$ is caused by the interaction with the $^2\Sigma_u{}^+$ state.[5] Since the $^2\Sigma_u{}^+$ state is at a distance of only about 6050 cm^{-1} above the $^2\Pi_{\frac{1}{2}u}$ substate, for $v_1' = 6$ the substate $^2\Pi_{\frac{1}{2}u}$ is already above the state $^2\Sigma_u{}^+$ with $v_1' = 0$. However, no perturbation occurs between $v_1' = 5$ and 6, and no excessive Λ-doublings are observed for the substate $^2\Pi_{\frac{1}{2}u}$. The Λ-doubling is increasing relatively slowly up to $v_1' = 6$. This shows very conclusively that for the occurrence of perturbations (namely, the Λ-doubling) the Franck-Condon condition has to be satisfied in the same manner as for the occurrence of radiational transitions.

The Vibrational Scheme

In Tables VI and VII the vibrational schemes for the systems of sub-bands $^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$ and $^2\Pi_{\frac{1}{2}u} \rightarrow {}^2\Pi_{\frac{1}{2}g}$ are given. For all bands with boldface zero line frequencies the assignment was obtained by the rotational analysis. For many bands which are too weak to be analyzed the position of the head was measured, and the frequencies thus obtained are given in parentheses. For a few bands not observed with the big grating spectrograph, the band head frequencies obtained by Smyth[3] are given (values in parentheses denoted by a letter S). From the known B' and B'' values and the measured positions of heads, the frequencies of the zero lines were calculated and are given in the tables for a considerable number of bands. For all progressions

TABLE VI. Vibrational scheme sub-bands $^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$.

v_1' \ v_1''	0	1241.77	1^a	45.55	1^b	1209.55	2	1241.50	3	1249.80	4	1390.0	5	1196.7	6	1197.25	7	~1224	8
0	λ3503 **28532.60** 4	a_2	λ3663 **27290.80** 4	c_2?	λ3669 **27245.25** 3	b_1	λ3839 **26035.67** 5	n_1	λ4030 24794.0(98.84) 2										
1126.76																			
1	λ3370 **29659.31** 5	a_3	λ3517 **28417.6** <1		λ3523 28372.0(75.7) <1	b_2	λ3680 **27162.45** 3		λ3856 **25920.95** 4	e_2	λ4051 24671.2(76.2) 3	k_1			λ4526 c				
1122.72																			
2	λ3247 **30781.97** 5	a_4			λ3389 **29494.70** 3	b_3	λ3534 **28285.20** 4	n_3	λ3696 27043.8(48.3) 0		λ3875 25794.0(98.9) 1		λ4095 **24404.0** 2	h_2	λ4306 (23217.6) 1	f_2	λ4541 c		λ4809 c
1120.12																			
3	λ3133 **31902.19** 3	a_5			λ3265 **30614.75** 4	b_4	λ3399 29405.4(09.4) 0		λ3549 **28163.8** 2	e_4					λ4108 **24327.45** 3		λ4320 (23140.5) 2		λ4563 c
1062.50																			
4^a	λ3032 32964.0(68.02) 0		λ3151 **31722.9** 3																
57.50																			
4^b	λ3027 **33022.15** 1	a_6			λ3150 **31734.90** 4	b_5	λ3275 30525.4(29.3) 0		λ3413 29283.8(87.93) 1	e_5	λ3565 **28034.0** 2						λ4122 **24250.2** 3		λ4340 (23036.0) 3
1055.25																			
5	λ2933 34077.0(80.5) 1		λ3044 **32835.65** 3	b_6			λ3165 **31580.50** 3	g_8											
1103.97																			
6			λ2945 33939.5(43.0) 2	b_7			λ3058 **32684.55** 2	g_9	λ3179 **31443.0** 1	r_6									
1097.73																			
7							λ2959 33782.5(86.0) 0	g_{10}	λ3072 **32540.75** 1	k_8									

TABLE VII. Vibrational scheme sub-bands $^2\Pi_{\frac{1}{2}u}\rightarrow{}^2\Pi_{\frac{1}{2}g}$.

v_1' \ v_1''	0	1	2	3	4	5	6	7	8	9
		1265.75	1256.89	1250.21	1250.78	1370.25	1197.06	1217	1220	1230
0	λ3511 **28468.46** 4 c_3	λ3674 **27202.65** 5 d_3	λ3852 **25945.78** 5 j_2	λ4047 24695.7(00.4) 2 r_0						
1125.99										
1	λ3378 **29594.41** 5 c_4	λ3528 **28328.65** 1 d_4	λ3692 **27071.75** 4 e_3j_3	λ3871 **25821.55** 4 r_1	λ4068 24570.8(75.3) 2		λ4540.5 c			
1120.87										
2	λ3254 **30715.20** 5 c_5	λ3394 **29449.55** 3 d_5	λ3545 **28192.65** 4 j_4		λ3891 25691.5(95.8) 1	λ4109 **24321.25** 3 f_3	λ4321.5 (23133.9) 2 m_1	λ4561 c	λ4830 c	
1116.01										
3	λ3140 **31831.29** 4 c_6	λ3270 **30565.55** 4 d_6		λ3562 **28058.45** 3 r_3k_4			λ4123 **24240.2** 3 m_2	λ4341.5 (23037.3)	λ4583 c	λ4858 c
1111.79										
4	λ3034 **32943.05** 3 c_7	λ3156 **31677.35** 4 d_7	λ3286 30420.35(24.35) 1 j_6	λ3427 29170.2(74.3) 1 k_5	λ3580 **27919.4** 1			λ4141 (24142.9) 3	λ4361 (22925.0) 1.5	λ4608 c
1108.50										
5	λ2936 34051.5(55.1) 1 c_8	λ3049 **32785.82** 3 d_8	λ3170 **31582.95** 3 e_7j_7	λ3301 (30279 S) 1 k_6?	λ3443 29028.0(31.6) 1 l_5				λ4160 (24030.7) 3	λ4384 c
1106.99										
6		λ2949 33893.0(96.5) 1 d_9	λ3063 **32635.95** 2 e_8j_8	λ3185 **31385.70** 1 k_7						λ4182 (23906.2) 2
?∼1015										
7^a		λ2863 (34916 S) 00 n_9	λ2971 (33649 S) 0 (r_8)							
1∼ 96										
7^b		λ2856 (35008 S) 1 d_{10}	λ2962 (33750 S) 0 j_9	λ3075 (32510 S) 1 k_8						

$v_1''=0$ to 4 an excellent agreement is obtained (differences smaller than 0.1 cm^{-1}).

In Tables VI and VII for many bands in the right-hand lower corner the letter designations of Smyth[3] are inserted. It is interesting to note how successful Smyth was in spite of the low dispersion of his spectrograph in picking out several progressions. In the left-hand lower corners the relative intensities of the bands are given, estimated on a scale of 5. The intense bands form a typical Franck-Condon parabola, with a subsidiary maximum along the diagonal. For the sub-bands $^2\Pi_{\frac{1}{2}u}\rightarrow{}^2\Pi_{\frac{1}{2}g}$ a tentative assignment for 5 bands observed by Smyth is given by ascribing them to a perturbed double level $v_1'=7^{a,b}$.

The vibrational scheme for $v_1''\geqslant 5$ is very incomplete. The CO_2^+ spectrum obtained by the author was in the longer wave-length region strongly overlapped by bands of CO and in general was very weak—no rotational analysis could be performed for bands beyond λ4130. Only band heads for the λ4300 group were measured; this was the last group observable on my spectrograms. Smyth[3] reported the existence of many bands at longer wave-lengths, but he did not measure their positions exactly and did not include the frequencies of those bands in his tables. However, he included in this paper a photograph of the spectrum as far as λ5000, and this photograph constitutes at present the only available source of information about those bands. The wave-lengths of several long wave-length bands were calculated from the vibrational scheme (values denoted by c in Tables VI and VII), and in comparing them with the photograph in Smyth's paper a reasonably good agreement can be observed.

Perturbations

In the band system studied several vibrational perturbations are observed in the lower and in the upper states. In Figs. 5 and 6 the deviations of

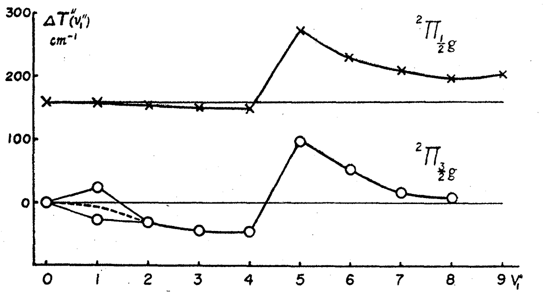

FIG. 5. Deviations of the positions of the vibrational levels from positions calculated according to the formula $T''(v_1'')=T''(0)+1271v_1''-2.5v_1''(v_1''+1)$ as a function of the vibrational quantum number v_1'' for the ground state $^2\Pi_g$.

the vibrational levels from calculated values are presented as functions of the vibrational quantum number. The calculated values were obtained on the basis of the formulas $T''(v_1'')=T''(0)+1271v_1''-2.5v_1''(v_1''+1)$, and $T'(v_1')=T'(0)+1131v_1'-3.0v_1'(v_1'+1)$, where $T'(0)-T''(0)$ are equal to 28532.57 and 28468.42, respectively, for the sub-bands $^2\Pi_{3/2u}\rightarrow{}^2\Pi_{3/2g}$ and $^2\Pi_{\frac{1}{2}u}\rightarrow{}^2\Pi_{\frac{1}{2}g}$. The formulas were chosen so as to give the smallest deviations for levels which show little perturbation in Λ-doubling and in the B values. The distances of the crosses from corresponding circles for a given vibrational quantum number indicate directly the splitting of the state $^2\Pi$ in the given vibrational state. The following perturbations are observed:

(1) Splitting of the substate $^2\Pi_{3/2g}$ into two levels for $v_1''=1$, $v_2''=v_3''=0$ which is undoubtedly caused by the interaction with the level $v_2''=2$, $v_1''=v_3''=0$ (double bending vibration). Sublevel a shows a vibrational perturbation downwards, possesses a lower B'' value and an anomalous negative Λ-doubling. Sublevel b shows exactly opposite perturbations.

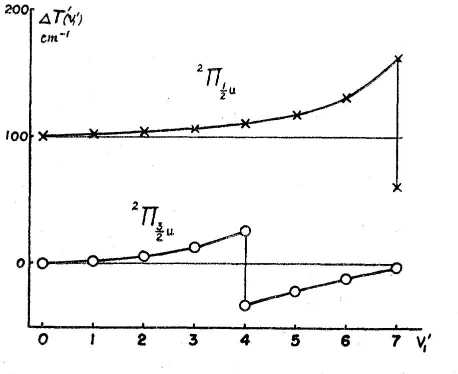

FIG. 6. Deviations of the positions of the vibrational levels from positions calculated according to the formula $T'(v_1')=T'(0)+1131v_1'-3.0v_1'(v_1'+1)$ as a function of the vibrational quantum number of v_1' for the excited state $^2\Pi_u$.

(2) Splitting of the substate $^2\Pi_{3/2u}$ into two levels for $v_1'=4$ is similar in general character to the previous perturbation, with the exception that no anomalous Λ-doubling for sublevels b is observed. The corresponding vibronic levels perturbing the levels $v_1'\leqslant 3$ and $v_1'\geqslant 5$ are in a greater distance and the corresponding perturbations are decreasing in moving away from $v_1'=4$.

(3) The perturbation of the substate $^2\Pi_{\frac{1}{2}u}$ at $v_1'=7$ seems to be similar to the perturbation 2. No anomalous Λ-doubling for levels below the perturbation is observed. The levels become with increasing vibrational quantum number predominantly of the b-type.

(4) The perturbation occurring between $v_1''=4$ and 5 for both substates of the ground state $^2\Pi_g$ shows a reversed correlation between the vibrational shift on the one hand, and the B'' value and the Λ-doubling on the other. Levels showing vibrational perturbation downwards have excessively big B-constants and anomalously high Λ-doubling, and *vice versa*. There is, however, the similarity with cases 2 and 3 in that the levels $^2\Pi_{\frac{1}{2}g}$ with upward vibrational perturbation do not show any anomalous Λ-doubling. From the vibrational analysis of the sub-bands $^2\Pi_{3/2u}\rightarrow{}^2\Pi_{3/2g}$ it can be seen that no bands corresponding to transitions $v_1'=4^a$, 5, $6\rightarrow v_1''=7$, 8 are observed; the levels of $^2\Pi_{3/2g}$ for $v_1''\geqslant 5$ should therefore be classified according to the selection rule formulated in Part II ($a\rightarrow b$ forbidden) as levels of a b-type, in spite of their reversed perturbations in rotational constants. However for $v_1''\leqslant 4$ the levels are also not of the a-type as can be seen from the vibrational scheme, since they are also combining only with the levels of $^2\Pi_{3/2u}$ of a b-type. It seems therefore that maybe the classification into levels of an a- and b-type has a meaning relative only to perturbations of the type described under 1 and 2 (maybe 3) and only because such perturbations lead to the prohibition of mixed $a\rightarrow b$ transitions.

An interesting feature of the perturbation now under discussion is that it leads to a very weak emission of bands of the progression $v_1''=5$. It should be pointed out also, that with the exception of the perturbation 1 very little influence of the perturbations on the values of the D-constants is noticeable.

CONCLUDING REMARKS

In this work a very complete analysis of the band system $^2\Pi_u \rightarrow {}^2\Pi_g$ of the molecule CO_2^+ is given for the system of symmetrical vibrations. A rotational analysis of all strongest and some of the weaker bands in all of 48 sub-bands was reported. In the vibrational scheme 94 (possibly 99) sub-bands are classified. Almost all vibrational and rotational constants for this array of symmetrical vibrations are contained in this paper and should be supplemented only by the following data from Part II: B'', D'', and p'' values for the levels $v_1''=0$, 1, and 2, p'-values for the levels $v_1'=0$ to 6 and by the data contained in Figs. 4 and 5. In several instances strong perturbations are observed, the explanation of which seems to require a thorough theoretical investigation of the rotational structure of the vibronic states of such a molecule and their mutual interaction. In the band system the long wave-length bands were not investigated with sufficient accuracy, and in order to get better data for the higher vibrational levels of the ground state $^2\Pi_g$ a reinvestigation of the bands in the region beyond λ4000 seems necessary. A source emitting a purer spectrum of CO_2^+, perhaps of the kind used by Smyth,[3] should be applied for this purpose.

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

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In this last part of the work on the $^2\Pi_u \rightarrow {}^2\Pi_g$ bands of the CO_2^+ molecule all data are collected on bands for which no classification could be found or for which the classification suggested is for any reason considered as hypothetical. Bands belonging to two groups around λ3760 and λ3915 are classified tentatively as transitions $v_1'=0$, 1, 2, 3, 4; $v_2'=v_3'=0 \rightarrow v_1''=0$, 1, 2, 3; $v_2''=v_3''=1$. The upper states are probably identical with the vibrational levels of the symmetrical array discussed in the first three parts of this work. The rotational analysis of the bands (8 sub-bands) is given in Tables I and II, the vibrational schemes for the two systems of sub-bands (12 in all) are presented in Tables III and IV. Very weak bands around λ3245 and λ3370 are classified as transitions $v_1'=0$, 1, 2; $v_2'=0$; $v_3'=1 \rightarrow v_1''=0$, 1, 2; $v_2''=1$; $v_3''=0$. The rotational analysis of the bands (10 sub-bands) is given in Tables V and VI, the vibrational schemes for the two systems of sub-bands are presented in Tables VII and VIII. The tentative classification of these four groups of bands leads to provisional values for the frequencies of the antisymmetric vibration ν_3. These values are included in the following table presenting a comparison for the ground state of the molecule CO_2 with the corresponding frequencies for the ground state $^2\Pi_g$ and the excited state $^2\Pi_u$ of the molecule CO_2^+.

	CO_2	$^2\Pi_g CO_2^+$	$^2\Pi_u CO_2^+$
ν_1	1361	1280	1131
ν_2	673	~ 632	<560?
ν_3	2379	~2305?	~1895?

The rotational constants in the first approximation for the ground state of the ion are thus: $B_{v_1v_2v_3}''=B_{000}''-0.0014v_1''-0.0042(v_2''+v_3'')$; $B_e''=0.3849$ and 0.3867 for the substates $^2\Pi_{3/2g}$ and $^2\Pi_{\frac{1}{2}g}$, respectively. In Table IX the rotational analysis is presented for 8 sub-bands from the region λ3500−λ3850. No classification for these bands could be found. In Table X the remainder of observed but not classified weak band edges, groupings of lines and bands of a more complicated structure are listed. Several of them present special features of interest for future investigations.

INTRODUCTION

In the first three parts of this work (see the preceding paper) the results of an extensive and quite complete rotational and vibrational analysis of the band system $^2\Pi_u \rightarrow {}^2\Pi_g$ of the molecule CO_2^+ were presented for the array of symmetrical vibrations ($v_1'v_1''$ array, for $v_2'=v_3'=v_2''=v_3''=0$). Not less than 94 bands were

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