

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 $\lambda 4000$ 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.

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

S. MROZOWSKI

*Department of Physics, University of Chicago, Chicago, Illinois**

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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 $\lambda 3760$ and $\lambda 3915$ 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 $\lambda 3245$ and $\lambda 3370$ 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	${}^2\Pi_g\text{CO}_2^+$	${}^2\Pi_u\text{CO}_2^+$
ν_1	1361	1280	1131
ν_2	673	~ 632	$< 560?$
ν_3	2379	$\sim 2305?$	$\sim 1895?$

The rotational constants in the first approximation for the ground state of the ion are thus: $B_{v_1 v_2 v_3}'' = B_{000}'' - 0.0014v_1'' - 0.0042(v_2'' + v_3'')$; $B_e'' = 0.3849$ and 0.3867 for the sub-states ${}^2\Pi_{3/2g}$ and ${}^2\Pi_{1g}$, respectively. In Table IX the rotational analysis is presented for 8 sub-bands from the region $\lambda 3500 - \lambda 3850$. 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

* Now at Research and Development Division, Great Lakes Carbon Corporation, Morton Grove, Illinois.

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

$J - \frac{1}{2}$	(B_0, A_0) $\nu_0 = 25593.5$		(B_1, A_0) $\nu_0 = 26720.9$		(B_2, A_1) $\nu_0 = 26607.7$	
	R	P	R	P	R	P
6			26715.46		26601.35	
7			14.44		00.24	
8		25585.34	13.30		26599.08	
9		84.27	12.18		97.87	
10		83.09	10.93		96.59	
11		81.86	09.72	26611.82	11.82	95.27
12	25598.67	h	80.54	26726.49	h	08.37
13	98.67	e	79.31	26.49	e	11.82
14	98.67	a	77.90	26.49	a	07.04
15		d	76.50	26.49	d	05.62
16			75.09			04.17
17	98.55		73.55	26.29		02.69
18	98.40		72.02	26.07	26699.56	11.29
19	98.17		70.41	25.82	97.88	11.02
20	97.90		68.81	25.51	96.21	10.68
21	97.63		67.11	25.13	94.49	10.19
22	97.30		65.37	24.74	92.70	09.82
23	96.89		63.63	24.28	90.83	09.27
24	96.48		61.76	23.77	89.00	08.74
25	96.00		59.93	23.26	87.04	08.16
26	95.35		58.04	22.67	85.06	07.43
27	94.90		56.04	21.98	83.05	06.45
28	94.30		54.07	21.28	80.97	05.59
29	93.61		51.98	20.55	78.80	04.71
30	92.92		49.85	19.80	76.67	03.73
31	92.15		47.75	18.94	74.42	02.77
32	91.41		45.61	18.07	72.17	
33	90.47		43.37	17.13	69.85	
34	89.62		41.08	16.16	67.50	
35	88.64		38.73	15.13	65.06	
36	87.60			14.07	62.60	
37	86.49			12.90	60.10	
38				11.74		
39				10.48		
40				09.29		
41				07.89		
42				06.60		
43				05.06		
44				03.64		

$$B_0' = 0.3470(0.3485)$$

$$B_0'' = 0.3700(0.3717)$$

$$B_1' = 0.3477$$

$$B_1'' = 0.3720$$

$$B_2' = 0.3465$$

$$B_2'' = 0.3740$$

classified. All the most prominent bands of CO_2^+ in the region $\lambda 2900 - \lambda 5000$ were shown to belong to this array. However, there are many weaker bands in the same region, which show a similar rotational structure and undoubtedly correspond to the same electronic transition ${}^2\Pi_u \rightarrow {}^2\Pi_g$ but definitely cannot be included into the array of the pure symmetrical vibrations. A rotational analysis of quite a number of them (26 in all) was performed, and positions of many weak band edges were determined. In view of the smaller intensity of the bands the results are of a relatively lower accuracy. For this and also other reasons no final correlation to vibrational quantum numbers ν_1 , ν_2 , and ν_3 could be established. Since with the observational material at present available no better results can be obtained, and since the solution of difficulties can only be expected from a reinvestigation of this band spectrum with an improved technique, it seems appropriate to present in this paper all results obtained in this work in spite of their incompleteness, with the hope that these data will facilitate

the solution of the problem in the future. For the same reason tentative classifications for some groups of bands will be given.

RESULTS

Groups of Bands Around $\lambda 3760$ and $\lambda 3915$

Two groups of bands are always observed by investigators of the CO_2^+ spectrum at the same time with the main system of bands (array of symmetrical vibrations). The intensity of the bands in these groups around $\lambda 3760$ and $\lambda 3915$ is relatively quite high; it is comparable to the weaker bands in the symmetrical sequence around $\lambda 3850$. The two groups of bands seem to form two double sequences of sub-bands of the same structure as the main bands. The wave numbers of the lines of these bands are given in Tables I and II. The rotational quantum number assignments can be in error not more than by one unit for the R branches; of the correctness of the numbering in the P branches the author feels reasonably confident. For the sub-band $\lambda 3775$ in which only the R branch was recorded, the numbering can be in error as much as by ± 2 . The B' and B'' values determined by the usual procedure are given in the lower part of the tables. Slightly higher values are obtained by increasing the numbering in the R branches by one unit, but the B -values do not seem to be in such good general agreement, and therefore they are not included. However the possibility of such a correction should be kept in mind.

By comparing the B' and B'' values and the general structure of the two band groups, the vibrational schemes for the two arrays of sub-bands ${}^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$ and ${}^2\Pi_{1/2u} \rightarrow {}^2\Pi_{1/2g}$ given in Tables III and IV were obtained. These tables are arranged similarly to and all designations are the same as in Tables VI and VII of the preceding paper. First of all it should be noted that the B' values for all sub-bands of the $\lambda 3760$ group are almost exactly equal to the B' values obtained for vibrational levels of the excited state from the main system of bands (symmetrical array, see Part III, Tables IV and V). Secondly, the vibrational frequency differences for the upper B differ very little from the differences reported previously for the upper substates ${}^2\Pi_{3/2u}$ and ${}^2\Pi_{1/2u}$. They differ not more than 0.7

cm^{-1} . If the assumption is made that these differences are due to a slightly erroneous dispersion curve for the region $\lambda 3915$ and that for the same reason the B' values for sub-bands of the $\lambda 3915$ group are deviating from the values found in Part III, Tables IV and V, a perfect agreement can be obtained between the vibrational schemes Tables III and IV and the B' and B'' values given in Tables I and II. If the B'' values are increased by amounts corresponding to the necessary corrections of the B' values (all corrected values are given in parentheses), the new B'' values become almost exactly equal to the values obtained for the same vibrational levels from the sub-bands of the $\lambda 3760$ group. The limits of error and the D' and D'' values are not given in Tables I and II, since in general all constants are of a relatively low accuracy. The

accuracy is the lowest for sub-bands with short P branches. An approximate idea of the accuracy can be obtained by inspection of Table III in Part III. Unfortunately, because of unforeseen circumstances no new photographs of the CO_2^+ spectrum could be obtained with the big grating spectrograph, and the supposition of an erroneous dispersion curve in the region $\lambda 3915$ could not be tested. However this view is strongly supported by the consistency of the results presented above and also by the fact that the region around $\lambda 3915$ is the only region for which a correction curve strongly deviating from a parabolic shape was obtained.

It follows from the probable identification of the vibrational levels $B_0 \cdots B_4$ with the levels reported in Part III that $\gamma=0$ in Tables III and IV and $v_2'=v_3'=0$. The vibrational levels

TABLE II. Sub-bands ${}^2\Pi_u \rightarrow {}^2\Pi_g$.

$J - \frac{1}{2}$	(B_0, A_0) $\nu_0 = 25531.7$		(B_1, A_0) $\nu_0 = 26658.4$		(B_1, A_1) $\nu_0 = 25447.8$		(B_2, A_1) $\nu_0 = 26569.2$		(B_3, A_2) $\nu_0 = \sim 26476$	
	R	P	R	P	R	P	R	P	R	P
2										26478.30*
3										78.83
4		25527.98						26565.40		79.53*
5		26.96						64.48		80.05
6		26.02						63.44		80.53*
7		24.99		26651.55				62.38		81.02
8		23.84		50.62				61.28		81.37*
9		22.76		49.53		25438.95		60.16		81.74
10		21.59		48.27		37.69		58.95		81.99*
11		20.42		47.04		36.45		57.73		
12		19.07		45.75		35.24		56.39		
13	25537.45 ^h	17.86	25663.98 ^h	44.46		33.99	26574.64 ^h	55.10	82.65 ^h	
14	37.45 ^e	16.48	63.98 ^e	43.05	25453.48 ^h	32.58	74.64 ^e	53.71	82.65 ^e	
15	37.45 ^a	15.11	63.98 ^a	41.63	53.48 ^e	31.20	74.64 ^a	52.30	82.65 ^a	
16		13.67		40.16	53.48 ^d	29.77		50.80		
17		12.20	63.85	38.64		28.28	74.53	49.32	82.43	
18	37.24	10.67	63.63	37.06	53.30	26.74	74.24	47.72	82.19	
19	37.09	08.94	63.47	35.45	53.07	25.22	74.07	46.13	81.99*	
20	36.90	07.49	63.16	33.77	52.86	23.64	73.73	44.44	81.60	
21	36.67	05.87	62.89	32.11	52.67	21.94	73.48	42.76	81.37*	
22	36.37	04.13	62.51	30.33	52.26	20.23	73.02	40.96	80.85	
23	36.13	02.43	62.16	28.53	51.95	18.49	72.68	39.22	80.53*	
24	35.70	00.63	61.72	26.66	51.51	16.85	72.16	37.30	79.82	
25	35.18	25498.83	61.23	24.79	51.10	14.87	71.68	35.47	79.53*	
26	34.70	96.95	60.60	22.81	50.59	12.97	71.08	33.47	78.56	
27	34.23	95.01	60.09	20.88	50.12	11.09	70.55	31.55	78.30*	
28	33.58	93.07	59.36	18.81	49.50	09.09	69.86	29.45		
29	33.02	91.06	58.75	16.75	48.90	07.07	69.20	27.39		
30	32.35	88.99	58.04	14.62	48.14	05.00	68.44	25.22		
31	31.64	86.95	57.30	12.45	47.59	02.92	67.68	23.11		
32	30.90	84.63	56.38		46.74	00.67	66.76	20.80		
33	30.15	82.60	55.61		45.96	25398.54	65.94	18.59		
34	29.26	80.38	54.75		45.06	95.99	64.94	16.23		
35	28.34	78.11	53.77		44.16	93.80	64.00	13.92		
36	27.48	75.72	52.79		43.19		62.92	11.42		
37	26.50	73.40			42.25		61.92	09.03		
38	25.49	70.95			41.20		60.74	06.46		
39	24.49	68.59			40.19		59.62	03.98		
40	23.35	65.95					58.33	01.29		
41	22.27	63.55								
42	20.95	60.98								
43	19.86	58.40								
44	18.49	55.86								
45	17.33									
46	15.85									
47	14.44									
48	12.98									
49	11.43									
50	09.81									
	$B_0' = 0.3506?(0.3509)$		$B_1' = 0.3500$		$B_1' = 0.3485?(0.3498)$		$B_2' = 0.3486$			
	$B_0'' = 0.3725?(0.3729)$		$B'' = 0.3732$		$B_1'' = 0.3702?(0.3717)$		$B_1'' = 0.3722$			

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

$v_1' \setminus v_1''$	A_0 x	1235	A_1 $x+1$	1245?	A_2 $x+2$
B_0 y	$\lambda 3905$ 25593.5 1.5				
1127.4	$p_2?$				
B_1 $y+1$	$\lambda 3741$ 26720.9 1		$\lambda 3922$ (25491) 0		
1122					
B_2 $y+2$			$\lambda 3757$ 26607.7 <1	$\lambda 3942$ $(25363)?$ <0	(m_2)
1120?					
B_3 $y+3$				$\lambda 3774$ (26487.4) 0	

$A_0, A_1 \dots$ present a set of new vibrational levels situated slightly above the vibrational levels $v_1''=2, 3 \dots; v_2''=v_3''=0$ discussed in Part III. It seems probable there is no corresponding level above $v_1''=1, v_2''=v_3''=0$, since no bands of comparable intensity are observed in the region below $\lambda 3740$. Hence the vibrational level A_0 is probably the lowest level of this type. The vibrational frequency for A_0 measured from the level $v_1''=v_2''=v_3''=0$ is around 2937 cm^{-1} , the level A_0 can only be interpreted, therefore, as a level $v_1''=0(x=0), v_2''=v_3''=1$. Since for the ground state the bending vibration frequency is around 632 cm^{-1} (see Part II, resonance of $v_2''=2$ with ${}^2\Pi_{3/2g}v_1'=1$), the proposed classification leads to a frequency of the antisymmetric vibration $v_3''=2305 \text{ cm}^{-1}$. This value seems quite reasonable, maybe a little too high (see the comparison of vibrational frequencies for CO_2 and CO_2^+ below). The simple rotational structure of a type ${}^2\Pi \rightarrow {}^2\Pi$ does not seem to be in agreement with the fact of the presence of one quantum of bending vibration. However, the rotational structure of the level with a double bending vibration which is in resonance with the level $v_1''=1, v_2''=v_3''=0$ does not have a very different structure (see Part II), and maybe there is little interaction between the electronic state and the molecular vibration for the CO_2^+ molecule. It seems also hard to see why a transition $v_1'', v_2''=v_3''=0 \rightarrow v_1'', v_2''=v_3''=1$ should appear in the spectrum with such a relatively high intensity. It should be finally noted that the interaction with the new levels $A_0, A_1 \dots$ cannot be the cause of the perturbation for the symmetrical levels around $v_1''=5, v_2''=v_3''=0$ discussed in Part III, since the per-

turbing levels should lie below and not above the corresponding symmetrical levels (for $v_1'' \leq 5$).

By shifting the rotational quantum numbering in Tables I and II for R branches by one unit lower and in P branches by one unit higher the bands could be interpreted as a system of bands corresponding to a new higher excited state ${}^2\Pi_g^*$ combining with the excited state ${}^2\Pi_u$. The B' values for the new state ${}^2\Pi_g^*$ would be then considerably smaller than for ${}^2\Pi_u$, which seem reasonable, but the frequency of the symmetrical vibration would be much too high for such large interatomic distances in the molecule. This alternative classification should be discarded also in view of the similarity in the excitation conditions of these bands and of the main system.

Groups of Bands Around $\lambda 3245$ and $\lambda 3370$

Two groups of very weak bands are observed around $\lambda 3245$ and $\lambda 3370$. Their rotational structure and the relative positions of band heads are very much like those of the main progressions of bands around $\lambda 3265$ and $\lambda 3385$; their intensity, however, is of a different order of magnitude. The groups are shifted toward shorter wavelengths relative to the main progressions. Their rotational analysis and the B' and B'' constants are collected in Tables V and VI. The vibrational schemes are given in Tables VII and VIII. Some time ago it was believed* that these bands could be classified as transitions $v_1', v_2'=0, v_3'=1 \rightarrow v_1'', v_2''=0, v_3''=1$. This classification would require that $n=1$ and $m=0$ in Tables

TABLE IV. Sub-bands ${}^2\Pi_{1u} \rightarrow {}^2\Pi_{3g}$.

$v_1' \setminus v_1''$	A_0 x	1210.6	A_1 $x+1$	1210?	A_2 $x+2$	1212?	A_3 $x+3$
B_0 y	$\lambda 3915$ 25531.7 1.5						
1126.7	h_3						
B_1 $y+1$	$\lambda 3749$ 26658.4 1		$\lambda 3928$ 25447.8 h_4	1	f_4		
1121.4							
B_2 $y+2$			$\lambda 3762$ 26569.2 1.5	f_3	$\lambda 3942$ $(\sim 25363)?$ <0	(m_2)	
1116?							
B_3 $y+3$					$\lambda 3775$ (26492.6) <1	(m_4)	
1112?							
B_4 $y+4$							$\lambda 3790$ (26381.3) <1

* S. Mrozowski, Rev. Mod. Phys. 14, 216 (1942), and Part I.

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

$J - \frac{1}{2}$	(D_0, C_0) $\nu_0 = 29793.8$		(D_1, C_0) $\nu_0 = 30904.0$		(D_1, C_1) $\nu_0 = 29638.7$		(D_2, C_1) $\nu_0 = 30749.5$		(D_2, C_2) $\nu_0 = 29553.2$								
	R	P	R	P	R	P	R	P	R	P							
8																	
9																	
10	29797.88	h	29784.38	30907.84	h	30894.10	29643.11	h	29630.42	h	30753.41	h	30740.87	29557.21	h	29543.28	
11		e	83.35		e	92.67		e	29.10		e	53.41		e	57.21	e	42.05
12	97.88	a	81.36		a	91.32		a	27.81		a	53.41		a	38.17	a	40.80
13		d	79.92		d	89.92		d	26.38		d	36.81		d	36.81	d	39.13
14			78.41	07.60		88.37	42.78		24.91			52.88			56.97		37.40
15			76.89	07.39		86.76	42.43		23.31			52.88			56.77		35.73
16	97.45		75.30	07.15		85.16	42.03		21.80			52.47			56.48		34.12
17	97.10		73.58	06.85		83.44	41.64		20.00			52.07			56.22		32.24
18	96.70		71.86	06.37		81.68	41.15		18.45			51.58			55.90		30.52
19	96.42		70.06	06.01		79.84	40.66		16.43			51.05			55.37		28.68
20	95.88		68.19	05.51		77.97	39.92		14.76			50.47			54.77		26.72
21	95.40		66.29	04.91		76.03	39.09					49.80			54.18		24.67
22	94.74		64.39	04.30		73.98	38.16					48.99			53.50		22.63
23	94.13		62.28	03.58		71.92	37.61					48.31			52.80		20.51
24	93.46		60.20	02.73		69.78	36.83					47.49			52.01		18.35
25	92.68		58.10	01.97		67.58	36.03					46.64			51.12		16.06
26	91.83		55.87	01.05		65.35	34.96					45.54			49.24		13.68
27	90.91		53.58	00.13		62.98	33.92					44.34			48.19		11.37
28	89.94		51.24	30899.10		60.60	33.01					43.38			47.06		08.91
29	88.96		48.80	98.03		58.06	31.80					41.99			46.01		06.46
30	87.85		46.31	96.81		55.55									44.88		03.84
31	86.61		43.74	95.42		52.87											01.22
32	85.25		40.95	94.10		49.89											29498.51
33	84.00		38.66	92.67		47.18											
			$B_0' = 0.3462$		$B_0' = 0.3444$		$B_0' \approx 0.3440$		$B_0' = 0.3415$		$B_0' = 0.3425$		$B_0' = 0.3760$		$B_0' = 0.3760$		
			$B_0'' = 0.3760$		$B_0'' = 0.3760$		$B_0'' \approx 0.3745$		$B_0'' = 0.3748$		$B_0'' = 0.3748$						

VII and VIII and further that the frequency of the antisymmetric vibration for the excited state ${}^2\Pi_u$ should be higher than for the ground state. Since $\nu_3'' = 2305 \text{ cm}^{-1}$ (see preceding section) for ν_3' a value of about 2435 cm^{-1} is obtained. An increase in antisymmetric frequency

with increase of interatomic distances is contrary to expectations. If we accept the explanation of the origin of the bands discussed in the preceding section as correct, a similar general structure of bands with and without bending vibration has to be assumed. A satisfactory explanation of the

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

$J - \frac{1}{2}$	(\pm_0, C_0) $\nu_0 = 29731.8$		(D_1, C_0) $\nu_0 = 30841.3$		(D_1, C_1) $\nu_0 = 29616.6$		(D_2, C_1) $\nu_0 = 30682.4$		(D_2, C_2) $\nu_0 = 29518.6$								
	R	P	R	P	R	P	R	P	R	P							
6		29725.72				29610.28		30676.08									
7		24.88				09.21		74.93									
8		23.73				07.98		73.69									
9		22.39		30832.97		06.67	30686.47	h	72.20	29522.85	h	29510.01					
10	29736.36	h	21.14	30845.63	e	20.53	86.47	a	70.93	22.85	e	08.91					
11	36.36	e	19.71	45.63	a	29.07	86.35	d	69.50		a	07.66					
12	36.36	a	18.37		d	27.55	86.23		67.87		d	06.13					
13		d	16.76	45.53		20.34	02.32	86.01	67.87			04.87					
14			15.28	45.33		26.07	00.80	85.76	66.40	22.63		03.18					
15	35.92		13.64	45.09		19.80	29599.03	85.38	64.80	22.36		01.39					
16	35.72		12.04	44.84		19.41	97.53	85.05	63.06	21.84		29499.79					
17	35.33		10.36	44.40		18.45	95.57	84.50	61.21	21.47							
18	35.04		08.67	44.05		17.59	93.86	84.06	59.48	21.08							
19	34.55		06.68	43.49		15.71	91.98	83.49	57.43	20.51							
20	34.15		04.78	43.01		13.84		82.88	55.53	20.09							
21	33.51		02.95	42.31		11.83		82.23	53.50	19.60							
22	32.99		00.98	41.75		09.80		81.41	51.40	18.90							
23	32.23	29698.84	40.92	09.80		15.12		80.63	49.15	18.35							
24	31.63	96.82	40.27	07.68		14.20		79.65	46.90	17.36							
25	30.76	94.58	39.34	05.51		13.25		78.72	44.72	16.69							
26	30.01	92.22	38.49	03.25		12.19		77.70	42.38	15.62							
27	28.99	90.05	37.47	01.06		11.13		76.54	39.91	14.57							
28	28.18	87.59	36.43	30798.57		10.02		75.44	37.40	13.68							
29	27.01	85.30	35.33	96.27		08.76		74.09	34.84	12.52							
30	26.02	82.97	34.28	93.71		07.37		72.94	32.08	11.37							
31		80.32		91.32		06.15		71.44	29.54	10.01							
32		77.46				04.67		70.06	26.73								
33		75.03				03.34		68.56	23.92								
34		70.90				01.88		66.99	21.05								
35						00.26		65.37									
36						29598.30		63.63									
37								61.92									
38								59.94									
39								58.14									
			$B_0' = 0.3485$		$B_0' = 0.3475$		$B_0' \approx 0.3450?$		$B_0' = 0.3440$		$B_0' \approx 0.3440?$						
			$B_0'' = 0.3772$		$B_0'' = 0.3773$		$B_0'' \approx 0.3755?$		$B_0'' = 0.3760$		$B_0'' \approx 0.3765?$						

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

$v_1' \setminus v_1''$	C_0 m	1265.3	C_1 $m+1$	1196.3	C_2 $m+2$
D_0 n	$\lambda 3355$ 29793.8 0				
1110.2					
D_1 $n+1$	$\lambda 3234$ 30904.0 0		$\lambda 3372$ 29638.7 0		
1110.8					
D_2 $n+2$			$\lambda 3251$ 30749.5 0	$\lambda 3382$ 29553.2 0	

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

$v_1' \setminus v_1''$	C_0 m	1224.7	C_1 $m+1$	1163.8	C_2 $m+2$
D_0 n	$\lambda 3362$ 29731.8 0				
1109.5					
D_1 $n+1$	$\lambda 3241$ 30841.3 0		$\lambda 3375$ 29616.6 0		
1065.8					
D_2 $n+2$			$\lambda 3258$ 30682.4 0	$\lambda 3386$ 29518.6 0	

weak bands $\lambda 3245$ and $\lambda 3370$ can be obtained by assuming $m=n=0$ and classifying 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 important feature of this classification is the assumption that $n=0$, which would furnish a good explanation why no corresponding bands are observed on the short wave-length side of the progression of main bands around $\lambda 3500$. As in the former case, the new levels C and D cannot be the cause of the perturbations observed in the main system.

For the suggested classification the frequency of the antisymmetric vibration in the excited state is obtained as $\nu_3'=1895 \text{ cm}^{-1}$, a value which seems a little low in comparison to the ground state ${}^2\Pi_g$ of CO_2^+ , but which compares more favorably with the data for the CO_2 molecule. A comparison of the frequencies of vibrations following from the proposed classifications with the corresponding values for CO_2 is given below.

	CO_2 ground state	$\text{CO}_2^+ - {}^2\Pi_g$	$\text{CO}_2^+ - {}^2\Pi_u$
$\nu_1 =$	1361	1280	1131
$\nu_2 =$	673	~ 632	$< 560?$
$\nu_3 =$	2379	$\sim 2305?$	$\sim 1895?$

The value of ν_2 for ${}^2\Pi_u$ is obtained by observing that there is no resonance splitting of the level $v_1'=1, v_2'=v_3'=0$ by interaction with the double bending vibration and assuming for this reason

$2\nu_2 < \nu_1$. It must be emphasized again that the values of ν_3 for CO_2^+ are hypothetical and based on classifications which are only tentative. It might be of interest to note that the suggested classifications for both groups of bands correspond to a change in the sum of the quantum numbers v_2 and v_3 equal to an even number.

From the suggested classifications and the B'' values for levels of the type A and C an approximate formula for B'' can be deduced: $B_{v_1 v_2 v_3}'' = B_{000}'' - 0.0014v_1'' - 0.0042(v_2'' + v_3'')$. From this formula the rotational constant B_e'' for the non-vibrating CO_2^+ molecule is found to be 0.3849 and 0.3867 for the substates ${}^2\Pi_{3/2g}$ and ${}^2\Pi_{1/2g}$, respectively. It should be again pointed out however that the whole suggested classification of the levels A, B, C , and D is a very hypothetical one, and a classification involving totally symmetrical vibration states of the non-totally symmetrical vibrations (for instance combinations involving $2\nu_3$, or $2\nu_2$ with $l=0$) would be preferred for theoretical reasons.

Unclassified Bands

In Table IX are given the wave-lengths of the lines of weak bands observed in the region $\lambda 3500\text{--}\lambda 3850$. No reasonable classification could be found for these bands. In the lower part of the table two sets of B values are given, namely, for

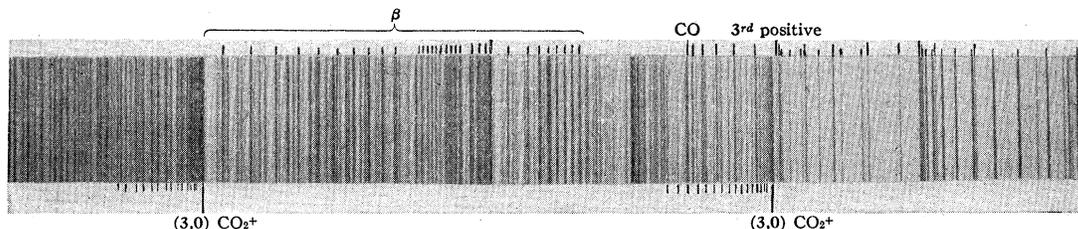


FIG. 1. Unclassified band β of CO_2^+ in the region around $\lambda 3137$. Main branches marked on top. Bands of the main system of CO_2^+ are marked below, and of CO (third positive) above the picture.

TABLE IX. Unclassified sub-bands.

$J-\frac{1}{2}$	$\lambda 3507$		$\lambda 3510$		$\lambda 3540$		$\lambda 3544$		$\lambda 3553$		$\lambda 3572$		$\lambda 3651$		$\lambda 3832$	
	$\nu_0=28502.6$	$\nu_0=28481$	$\nu_0=28237.5$	$\nu_0=28202$	$\nu_0=28125.2$	$\nu_0=27979.4$	$\nu_0=27376.2$	$\nu_0=26085.8$	R	P	R	P	R	P	R	P
1			28479.41?													
2			78.477													
3			77.62													
4			76.57													
5			75.60													
6			74.48													
7			73.47													
8	28506.62		28484.76									27380.57				
9	06.62		84.76		28241.68	28227.71		28129.28		27983.57		80.57	27366.30	26090.66		
10		28491.59	84.76		41.68	26.40	28206.30	29.28		83.57		80.57	65.18	90.56		
11		90.18				24.94	06.30	23.28	28112.55	83.57			63.62	90.56		
12	06.37	88.60				23.56	06.30		11.08			80.33	62.07			
13	06.28	86.72	84.38		41.37	22.00		29.05	09.50	83.41	27963.73	80.11	60.63		26070.77	
14	06.03	85.18	84.05		41.16	20.43	06.06	28.83	07.87	83.17	62.20	79.80	58.77	90.35	69.27	
15	05.67	83.27	83.78		40.84	18.62	05.70	28.64	06.19	82.85	60.54	79.40	56.94	90.21	67.71	
16	05.27	81.60	83.39		40.43	17.11	05.41	28.27	04.47	82.47	58.75	79.03	55.13	89.88	66.03	
17	04.98		82.98		39.97	15.95	05.02	27.86	02.67	82.05	56.89	78.49	53.22	89.59	64.44	
18	04.27		82.43		39.61	13.87	04.57	27.34	00.74	81.54	55.06	77.99	51.36	89.18	62.55	
19	03.71		81.78		39.00	11.68	03.96	26.84	28098.81	80.98	53.13	77.35	49.26	88.91	60.81	
20	02.98		81.16		38.37	09.72	03.27	26.22	96.51	80.37	51.13	76.76	47.29	88.22	58.77	
21	02.29		80.38		37.90	07.74	02.65	25.68	94.50	79.70	49.09	75.94	45.04	87.85	56.98	
22	01.35		79.72		37.06	05.70	01.99?	24.81	92.64	78.96	46.94	75.24	42.83	87.11	54.76	
23	00.57		78.96		36.22	03.46	01.36?	24.06	90.49	78.16	44.72	74.28	40.55	86.62	52.86	
24	28499.70	77.99			35.45	01.02	00.32?	23.14	88.23	77.30	42.44	73.50	38.42	85.68	50.57	
25	98.75	77.04			34.47	28198.32	28199.76?	22.28	85.97	76.33	40.09	72.40	35.84	85.21	48.59	
26	97.69	76.26			33.56			21.37	83.50	75.35	37.72	71.50	33.62	84.07	46.10	
27	96.62	74.98			32.46			20.26		74.20	35.26	70.29	30.96	83.41	44.08	
28	95.36	73.72			31.35			19.02		73.18	32.72	69.26	28.56	82.19		
29	94.23				30.21			18.02		71.98	30.15	67.96	25.83	81.53		
30	92.80				28.90			16.63		70.70		66.79	23.33	80.00		
31								15.44				65.37	20.43	79.41		
32								14.05				64.17	17.68	77.71		
33								12.86				62.15	14.83	77.00		
34								11.31				61.22				
35								09.80								
36								08.20								
37								06.65								
38								05.09								
39								03.42								
	$B' = 0.3500$		$B' = 0.3440$		$B' = 0.3500$		$B' = 0.3485$		$B' = 0.3510$		$B' = 0.3510$		$B' = 0.3510$		$B' = 0.3510$	
	$B'' = 0.3820$		$B'' = 0.3760$		$B'' = 0.3820$		$B'' = 0.3810$		$B'' = 0.3840$		$B'' = 0.3840$		$B'' = 0.3800$		$B'' = 0.3800$	
	$B' = 0.3440$		$B' = 0.3360$		$B' = 0.3440$		$B' = 0.3410$		$B' = 0.3410$		$B' = 0.3410$		$B' = 0.3465$		$B' = 0.3465$	
	$B'' = 0.3760$		$B'' = 0.3705$		$B'' = 0.3740$		$B'' = 0.3730$		$B'' = 0.3770$		$B'' = 0.3770$		$B'' = 0.3720$		$B'' = 0.3720$	

the given numbering of lines in branches and for an alternative numbering, for which J numbers in the R branches are decreased by one unit. In Table X are collected the wave numbers of weak band edges, grouping of lines which in some earlier papers were reported as band edges, and finally of bands of a more complicated structure.

Especially interesting are the six band regions denoted with Greek letters α , β , γ , δ , ϵ , and η , since they are wide groups containing a great number of lines which probably constitute bands of a more complicated character. Group α is composed of two bands shaded in opposite directions with a space free from lines between the two band heads; between α and the band head (4, 0) of the main system ($\nu_0 = 33022 \text{ cm}^{-1}$) a complicated structure of several band heads is observed. Group β is a band composed of several branches; it is reproduced in Fig. 1. In the upper part of Fig. 1 some branches of this band are indicated. Group γ is a very complicated and weak group on the short wave-length side of the

main sequence around $\lambda 3370$. Very little can be said about the group δ since it is strongly overlapped by bands of CO. It seems to be a rather strong band with numerous branches. The band ϵ around $\lambda 3961$ has a very strong main central

TABLE X. Band heads and groupings of lines.

	34087.5			27951.04	
	33778.4	gr.		27821.43	
$S_{m_{10}}?$	~33125	α	S_{m_8}	~27600	δ
S	32990	gr.		~27270	gr.
	32954.46			27238.20	
S	32860.99			27141.52	gr.
	32678.46			27000.40	gr.
S_{r_7}	32587	gr.		26915.00	
S	~31890	β		26659.0	
	31568.48			26576.5	
	31559.86			25701.0	
S	~31490	gr.		25519.1	
S	~31402	gr.		25380.6	
S	~30831	gr.	S	~25240	
	30653.82			24810.9	
	30640.53			24690.5	gr.
	30496.77			24155.0	
F	30446.30		S	~24152	η
	30436.40		F	23201.3	
S	~29700	γ		23158.1	

S —observed by Smyth (Phys. Rev. 38, 2000, 1931), and his designations (m_{10} , r_7 , m_8).
 F —not observed by Smyth, but observed earlier by Fox, Duffendack, and Barker (Proc. Nat. Acad. 13, 302, 1927).
 gr.—grouping of lines, α , β , γ , δ , ϵ , and η see text; all others—probably weak band edges.

part and several side branches. Group η is mixed with the bands of the main sequence around $\lambda 4140$; it seems to have a quite complicated structure. All the bands given in Table X are either too weak or insufficiently resolved or hopelessly overlapped by other bands and require reinvestigation with a much more powerful and purer spectral light source and at least equally high dispersion. It can be expected that a successful analysis of all the weaker band systems described in Part IV, and of the more complicated bands, will lead to a deeper understanding of the electronic spectrum of a triatomic molecule.

In conclusion I should like to express my

sincere thanks to Professor R. S. Mulliken for his continued interest in this work and to Professor H. D. Smyth for putting kindly at my disposal unpublished data and photographs of the spectrum of CO_2^+ obtained by him some time ago with a 21-foot grating spectrograph. The careful study of these photographs revealed very good agreement with my results; the higher purity of the spectrum obtained by Professor H. D. Smyth was an important factor in strengthening my confidence in the correctness of the results reported in this and the preceding paper. I am also very much indebted to Mr. T. J. Kinyon for assistance in computations.

The Conservation of Momentum in the Disintegration of Li^8

R. F. CHRISTY, E. R. COHEN, W. A. FOWLER, C. C. LAURITSEN, and T. LAURITSEN
Kellogg Radiation Laboratory, California Institute of Technology, Pasadena, California
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Apparatus for the introduction of radioactive materials into a cloud chamber has been employed to investigate the conservation of momentum in the β -decay of Li^8 to Be^8 , which subsequently breaks up into two α -particles. The projection on the plane of measurement of the angle between the two α -particles is a measure of one component of the recoil momentum of the Be^8 . Additional information is obtainable from the momentum of the electron but relatively few cases occur where both α -particles and the electron are in the plane of the cloud chamber. The Li^8 is produced by bombarding with deuterons a thin deposit of LiOH on beryllium or gold foils. The mean squares of the observed momenta relative to the maximum possible momenta were 0.247 (Be foil) and 0.349 (Au foil). Corrected for scattering and other errors these become 0.197 ± 0.025 and 0.207 ± 0.034 , respectively, the probable errors quoted being statistical in origin. The weighted mean, rounded off to two figures, is 0.20 ± 0.02 . This value is roughly twice that obtained taking into account only the emitted electrons, and approximately equal to that calculated for an electron and neutrino emitted with no preferred angle of ejection between them.

1. INTRODUCTION

THE conservation of momentum in the disintegration of radioactive nuclei by electron and positron emission and by the capture of electrons from extra-nuclear levels has been the subject of numerous experimental investigations.¹⁻⁵ These investigations have generally

consisted in measuring the energy of the recoiling daughter nucleus either by counting the number of ions formed as the nucleus is brought to rest in a gas or by determining the retarding potential necessary to bring the nucleus to rest in vacuum. As the atomic weight of the daughter nucleus is usually known, its momentum can be calculated and compared with that to be expected theoretically. These experiments have shown that the maximum momentum of the recoiling nucleus is equal to that to be expected from the maximum observed energy of the emitted electron or positron but that the momentum of recoil is

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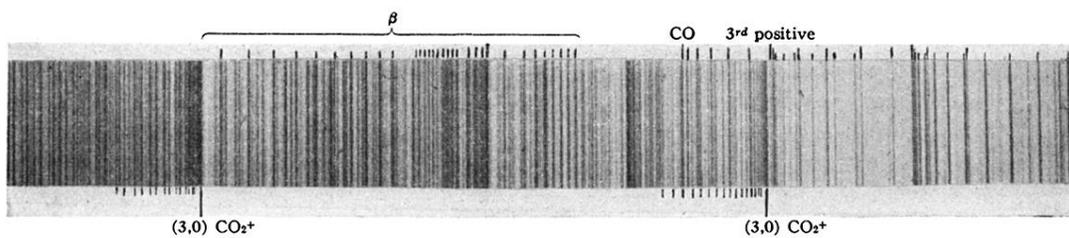


FIG. 1. Unclassified band β of CO_2^+ in the region around $\lambda 3137$. Main branches marked on top. Bands of the main system of CO_2^+ are marked below, and of CO (third positive) above the picture.