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THE EMISSION SPECTRUM OF CARBON DIOXIDE

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Abstract

The emission spectrum of carbon dioxide has been studied by the electron beam excitation method used by Smyth and Arnott. The whole range of the spectrum from 6500 to 1400 has been examined and only the bands reported by Fox, Duffendack and Barker in the region from 2700 to 5000 have been observed. A particular effort was made to get in emission the extreme ultraviolet bands reported by Leifson in absorption but it was unsuccessful. The "second negative bands of carbon" are shown to be probably identical with parts of the Fox, Duffendack and Barker system. This system of some two hundred bands is partially analyzed into fifteen progressions of band heads given by the formula $\nu=26{,}271-\nu_x+1136.85v-1.85v^2$ where ν_x takes on a particular value for each progression and $v=0, 1 \cdots 10$. About one hundred bands fit into this arrangement. This empirical analysis is shown to be consistent with a scheme of energy levels involving two normal modes of vibration (ν_1' and ν_2') in the upper electronic state and two (ν_1'' and ν_3'') in the lower electronic state. The $2\nu_2'$ state is split into two separated by 166 cm^{-1}; this and the values of the frequencies are consistent with Dennison's and Barker and Martin's analysis of the infrared spectrum but since the spectrum here analyzed presumably does not involve the normal state the frequencies are numerically different.

During the past fifteen years the study of band spectra has made enormous contributions to our knowledge of molecular structure and of radiation processes. Most of this work has been concerned with diatomic molecules and naturally so, since even diatomic band spectra offer complications requiring the greatest ingenuity and care for their interpretation. There remain many details of diatomic spectra still to be examined, but there seems little doubt that the main principles of interpretation have been laid down. Perhaps it is time, therefore, to consider the possibility of applying these principles to the study of molecules containing more than two atoms.

Of course a start has already been made by the study of infrared spectra, Raman effect and absorption spectra. But little or no progress has been made in the study of emission spectra. The difficulties are two. In the first place, the excitation of a gas is very likely to disrupt its molecules and, therefore, the spectrum obtained may well come, not from the molecule it is desired to study, but from one of its component parts. In the second place, once a spectrum is obtained it is likely to be so complicated as to defy analysis. Both these difficulties have been overcome in some measure in older work but it seems worth while to attempt a systematic attack on the general problem aided by recent developments in technique and theory.

The present writer was inspired to undertake such an attack by some experiments which Arnott and he[1] had made on the excitation of the band spec-

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[1] Smyth and Arnott, Phys. Rev. **36**, 1023–33 (1930).

tra of nitrogen by electron impact. In these experiments the spectrum was excited by a beam of electrons passing into a water-cooled chamber into which fresh gas flowed continually. Such conditions should be very unfavorable to the excitation of dissociation products. Furthermore, in the nitrogen spectra excited by this method nearly the entire intensity was concentrated in a few bands. It was thought that similar effects might occur in triatomic gases and simplify the spectrum. Such a method of excitation, therefore, might hope to overcome the two main difficulties cited above.

Carbon dioxide was chosen as the first gas to be studied because much is already known about its structure, its ionization potentials and, most important of all, the spectra of its components, carbon monoxide, oxygen and carbon.

PREVIOUS WORK

According to Kayser[2] the first discontinuous spectrum ever observed was that from a candle flame studied by Wollaston in 1802. It is not surprising therefore that there is a vast body of literature on the spectra of carbon and its compounds. The results of the work up until 1910 have been digested and presented by Kayser. Of the groups of bands that he gives only one seems possibly attributable to CO_2. It is the so-called "second negative group of carbon," a group of some twenty bands as reported by Kayser and later by Hof[3] and Bair.[4] Most of the bands in this group can be identified in the much more extensive system studied by Fox, Duffendack and Barker[5] and discussed in detail later in the present paper. They are observed in the negative glow of discharge tubes through which CO_2 is flowing but give way to CO bands as soon as the flow is stopped. This suggests that they should be assigned to carbon dioxide, probably to CO_2^+.

In their study of the carbon dioxide system Fox, Duffendack and Barker[5,6] excited it by impact of low voltage electrons. Duffendack and Smith[7] also excited it by collisions of the second kind in mixtures of CO_2 with the rare gases and finally Duncan[8] studied the fine structure of the two strongest bands by using a low voltage arc and a 21-foot grating. The conclusion of these authors was that the excitation potential of this spectrum was about nineteen volts and that it probably came from CO_2^+ ions.

Further evidence on the probable origin of the two strongest bands of the system ($\lambda 2883$ and $\lambda 2896$) is to be found in their frequent appearance in lists of the first negative bands of CO though authors[9] usually have some difficulty in fitting them in this system. Also, Maxwell[10] studied the effect of electric fields on the emission of these two bands and the comet tail bands of CO. He

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[2] Kayser, Handbuch der Spectroskopie **V**, 198, 190–234 (1910).

[3] Hof, Zeits. f. wiss. Photo. **14**, 83 (1914).

[4] Blair, Astrophys. J. **52**, 301 (1920).

[5] Fox, Duffendack and Barker, Proc. Nat. Acad. **13**, 302 (1927).

[6] Duffendack and Fox, Astrophys. J. **65**, 234 (1927).

[7] Duffendack and Smith, Phys. Rev. **34**, 68 (1929).

[8] Duncan, Phys. Rev. **34**, 1148 (1929).

[9] For example see Jevons, Phil. Mag. **47**, 586 (1924).

[10] Maxwell, Jour. Frank. Inst. **210**, 427 (1930).

found the former unaffected by the field and concluded that they came from an excited ion of very short lifetime or from a neutral molecule. The balance of the evidence seems to be in favor of CO_2^+ as the originator of this whole band system.

A second emission spectrum has been found by Kondratjew[11] who studied the spectrum of CO burning in O_2. He photographed a group of diffuse bands in the same general region as the emission bands discussed above and believes them due to CO_2. They are arranged in series with wave number differences of approximately 600 cm^{-1}. These bands probably form an entirely separate system from those considered here. Besides these emission spectra an absorption spectrum in the Schumann region was reported by Leifson;[12] it consisted of a number of bands, only four of which he was able to measure. These have never been observed in emission.

The object of the present work has been three-fold. First, to study the emission spectrum by high speed electron impact in flowing gas in order to confirm its origin and possibly to get a simplified intensity distribution. Second, to obtain the absorption spectrum in emission, and finally to extend some regularities already observed in the wave numbers of the known spectrum. Of these aims only the last has met with much success but the entire work will be reported in full.

PART I. EXPERIMENTAL

Apparatus and procedure

The excitation chamber in which the spectrum was observed was the same as that used by Smyth and Arnott[1] and the arrangement of filament, transverse magnetic field, and so on were very similar. Figure 1 is repeated from their previous paper but will not be discussed here.

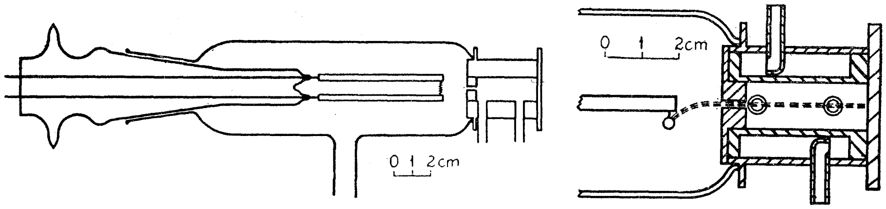

Fig. 1. (a) Schematic diagram of electron beam apparatus. (b) Details of filament, electron beam and water-cooled anode.

Commerical carbon dioxide was resublimed twice in vacuum with liquid air and then stored over phosphorous pentoxide. It was admitted through an artificial leak and during an exposure flowed steadily through the apparatus. Besides CO_2 a small amount of stop-cock grease vapor and a varying amount of mercury vapor were present. Traces of the CH bands were observed in some of the spectrograms. The mercury lines could be varied at will from moderate intensity almost to the vanishing point without any effect on the CO_2 spectrum.

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[11] Kondratjew, Zeits. f. Physik **63,** 322 (1930).

[12] Leifson, Astrophys. J. **63,** 73 (1926).

Of three different spectroscopes used, a constant deviation glass Hilger covered the range from 7000A down to 4000, with Ilford panchromatic, Wratten and Wainwright hypersensitive panchromatic, and Ilford Golden Iso-zenith plates; for the region down to 2000A a medium size quartz Hilger, (E 315), with Iso-zenith plates proved very satisfactory; and finally for the Schumann region, a fluorite window was sealed on the excitation chamber and a small fluorite vacuum spectrograph of the type described by Cario and Schmidt-Ott[13] was attached to the apparatus; Schumann plates obtained from the Hilger were used in this instrument. With these spectroscopic arrangements the entire spectrum from about 6500 to about 1400AU was studied though none of it at very high dispersion.

The nature of the luminosity in excitation chamber was of two distinct types. At low pressures, (0.04 mm as measured by a McLeod connected to the excitation chamber) and small currents (5 to 30 m.a. in the main discharge) a sharply defined beam of a deep purple color extended from the orifice of the main discharge tube across the excitation chamber toward the window. The magnetic field was usually adjusted so that this beam was bent downwards striking the wall of the chamber just short of the window. Under these conditions the rest of the excitation chamber was dark. We will refer to this condition as the beam discharge. If the pressure was raised or the current increased the sharp beam became fuzzy and eventually the entire excitation chamber was filled with luminosity as if from a secondary discharge. We will refer to this condition as the high pressure discharge.

Observed spectra

As we had hoped the "beam discharge" showed no trace of the CO spectrum in the visible and near ultraviolet. Long exposures brought out the "first negative" CO^+ bands and traces of the OH band at 3300 and the CH bands at around 4200; a few bands of the 4th positive group appeared faintly on some of the plates taken with the fluorite spectrograph. By far the most prominent feature of the spectrum was the CO_2 band spectrum already mentioned as observed by Fox, Duffendack and Barker.[5] This was so intense that a plate could be obtained with the quartz spectrograph in an hour's exposure even when the current in the discharge tube was only 20 or 30 milliamperes. Apart from this spectrum no bands not definitely attributable to CO were observed between 6500 and 1400 except the CH and OH bands already mentioned.

A particular effort was made to get in emission the bands reported by Leifson in absorption. In spite of variations of the field accelerating the electrons from 700 volts down to 60 and of increases of pressure and current up to the high pressure condition where the 4th positive bands of CO came out prominently no trace of CO_2 emission bands was observed in this region. On some of the first spectrograms there did appear to be bands, though of different wave-length from those given by Leifson, but more careful adjustment of the spectrograph and measurement of the plates showed them to be groups of

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[13] Cario and Schmidt-Ott, Zeits. f. Physik **69,** 719 (1931).

TABLE I.

NOTE: The meaning of the designations given in the fourth column and of the values of $\nu_c-\nu_0$ in the fifth column are explained in the text of part II. When they are enclosed in parentheses they refer to the wave numbers in column six.

Wave-lengths and wave numbers in columns one and two marked with asterisks are accurate only to 1.0A or 10 cm^{-1} respectively. All wave numbers in column six are accurate only to 10 cm^{-1}.

Fox, Duffendack and Barker				This Paper			
λ	ν_0	Int.	Desig.	$\nu_c-\nu_0$	ν_0	Int.	
					37,662	1	
					623	1	
					35,433	0	
					410	1	
			a_8?		284	1	
					115	0	
2849.5*	35,084*	4	b_8*	−4*	090		
56.4*	34,999*	5	d_{10}*	0*	008	1	
62.5*	924*	6	n_9*	+29*	34,930	2	
—	—	—			916	00	
—	—	—	j_{10}	+27	831	00	
			e_{10}	+9			
74.3	781	7	r_9	−6	783	5	
77.2	746	5			758	3	
78.2	734	5	k_{10}	−6	—	—	
80.7	704	6			705	10	
82.1	687	10			—	—	
82.6	681	9			—	—	
83.1	675	10			675	11	
					600	4	
90.4	587	7			—	—	
—	—	—			561	4	
—	—	—	(l_{10})?	(+19)?	545	11	
95.4	527	10			—	—	
95.9	522	9			—	—	
96.4	516	10			515	10	
2907.5*	34,384*	0			—	—	
10.2*	352*	0			—	—	
16.3*	280*	0			—	—	
19.1*	247*	0	m_{11}*	+10*	—	—	
24.8*	180*	1			—	—	
25.2*	175*	1			—	—	
2928.3*	34,139*	1	a_7*	−1*	—	—	
29.4*	127*	1			—	—	
33.1*	085*	3			34,082	2	
35.7*	054*	3	c_8*	+4*	063	2	
45.2*	33,944*	2	b_7*	+27*	33,951	1	
49.4*	895*	4	d_9*	+3*	900	2	
56.8*	810*	0			—	—	
58.7*	789*	2	g_{10}*	+6*	785	1	
61.8*	753*	2	j_9*	0*	750	0	
63.8*	731*	5	e_9*	+4*	732	2	
			(r_8)	(+20)	649	0	
			(k_9)	(−23)	490	00	
88.6*	451*	2	l_9*	+6*	—	—	
90.3*	432*	2			420	0	
—	—	—			404	00	
3005.3*	265*	3			263	1	
07.3*	243*	3	f_{11}*	−23*	236		
17.8*	127*	2	m_{10}?	+32*	122	00	
19.6*	107*	0			—	—	
22.6*	075*	1			080	2	
—	—	—			060	1	
—	—	—			039	0	
27.0	026	3	a_6	−1	026	2	2nd Neg. C
—	—	—			32,990	0	λ3030?
34.2	32,948	6	c_7	+1	949	4	
—	—	—			858	1	
43.9	843	5	b_6	+15	837	3	
48.6	792	6	d_8	0	791	5	
58.3*	688*	5	g_9*	+5*	689	4	
63.5*	633*	5	e_8	−4*	640	4	
			j_8	+2*			
67.7*	588*	5	r_7*	−27*	587	2	
72.1	542*	4	k_8*	−21*	537	2	
—	—	—	(k_8)	(+10)	510	1	
—	—	—			498	00	OH?
—	—	—			475	00	
—	—	—			461	00	
—	—	—	(p_9)	(−7)	442	0	
—	—	—			422	0	
—	—	—			403	0	
—	—	—			380	0	
3090.0*	3235*	5	l_8*	+2*	32,355	2	
					323	1	
—	—	—			301	1	OH band?
—	—	—			283		
					257	2	
—	—	—	(h_9?)	(+5)	221	2	
—	—	—			185	2	
—	—	—			148	1	
—	—	—	(f_{10}??)	(−3)	125	0	
—	—	—			095	0	
—	—	—	(m_9)	(−6)	064	1	
—	—	—			043	00	
—	—	—			014	2	
—	—	—			31,985	3	
—	—	—			921	2	
3132.9	31,910	8	a_5	−2	909	4	
34.6	893	8			886	4	
35.7	882	6					
36.7	871	9			869	5	
39.2	846	9	c_6	−6	? 856	4	
					835	5	
42.4	814	5			—	—	
49.5	742	6	b_5	0	743	4	
50.7	730	6			—	—	2nd Neg C
55.2	685	9	d_7	−2	690	5	λ3153
64.9	588	5	g_8	0	588	3	55
70.1	536	5	e_7?		530	3	59
			j_7	+6			
74.3	494	5			488	3	
—	—	—	(r_6)	(+4)	443	1	
—	—	—	(k_7)	(+9?)	402	2	
					382		
—	—	—	(p_8)	+4	325	0	
					291		
—	—	—	(l_7)	(−7)	255	0	
—	—	—	(h_8?)	(?)	150	00	
					100		
—	—	—	(f_9?)	(−15)	035	00	
—	—	—	(f_9?)	(+26)	30,994	1	
—	—	—	(m_8)	(−21)	972	2	
—	—	—			901	0	
—	—	—			854?	00	
—	—	—			831?	00	2nd Neg C
3246.9	30,790	10	a_4	−1	790	6	λ3249.4
53.9	723	10	c_5	−3	716	6	51.0
64.6	623	9	b_4	−1	621	5	54.6
69.9	573	10	d_6	−2	568	5	70.5
—	—	—	(n_5)	(+19)	490	0	
80.5	474	3	g_7	+4	468	3	
83.3	448	4			—	—	
84.3	439	8	j_6	−10	439	5	
85.8	425	3		+4	—	—	
87.7	408	3	e_6	−1	—	—	
92.6	363	4	r_5?		371	1	
3301.1	284	4	k_6?	+14	279	1	
—	—	—	(p_8)	0	220	0	
—	—	—	(l_6)	(+22)	111	00	
—	—	—	(h_7)	(−1)	013	00	
—	—	—	(f_8)	(+3)	29,911	1	
—	—	—	(m_7)	(−1)	844	1	
—	—	—			692	0	
3370.0	29,665	10	a_3	0	665	8	2nd Neg C
72.5	643	5			—	—	λ3372.8
75.2	619	3			—	—	75.4
77.5	599	10	c_4	+1	594	8	77.9
82.2	558	5			—	—	
86.2	523	3			—	—	
88.9	500	7	b_3	−2	492	4	
94.5	451	7	d_5	+3	450	4	
96.9	439	3			—	—	
99.4	409	4			—	—	
99.9	404	3			—	—	
3400.9	396	3	n_4	−7	398	5	
02.2	384	1			—	—	
04.3	366	1	g_6	0	—	—	
3413.3	29,289	3	e_5	+2	29,280	1	
—	—		(r_4)	(0)	211	0	
26.6	175	3	k_5	+7	176	2	
43.5	032	2	l_5?	−13	025	2	
—	—	—			28,988	1	
—	—	—	(h_6)	(−4)	902	00	

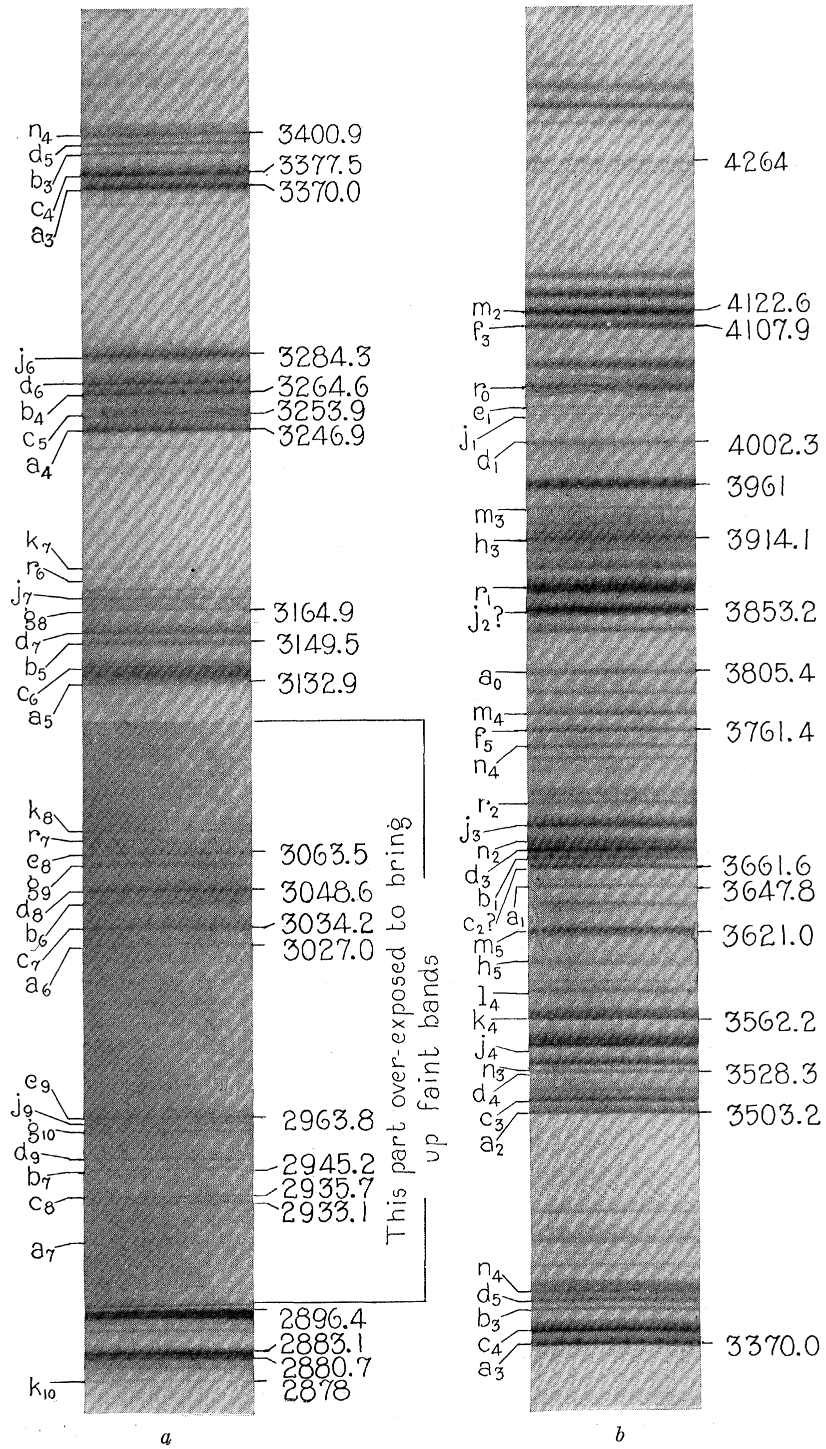
TABLE I. (*Continued*).

Fox, Duffendack and Barker					This Paper		
λ	ν_0	Int.	Desig.	$\nu_c-\nu_0$	ν_0	Int.	
64.5*	28,856*	0			?820	0	
71.0*	802*	0	f_7*	+3*			
—	—	—	(m_6)	(+9)	721	1	2nd Neg C
3503.2	537	7	a_2	0	537	3	λ3503.6
10.8	475	9	c_3	+1	470	3	06.8
17.1	424	7			—	—	11.5
—	—	—			408	1	
—	—	—	(b_2)	+5	365	0	
28.3	334	4	d_4	0	324	2	
33.8	290	9	n_3?	−25	287	4	
45.9	194	10	j_4	−3	201	7	
51.4	150	7	e_4?	+21 (+12)	163	6	
62.2	065	9	r_3? k_4	−2	061	6	
65.5	039	6			032	5	
81.1	27,916	4			27,915	3	
83.3	899	2	l_4	0	—	—	
86.0	878	2			871	2	
99.1*	777*	6	h_5*	+5*	756?	3	
3615.8	649	3	f_6??		—	—	
16.9	640	3			642	7	
18.6	635	3			—		
21.0	609	7	m_5	+5	600		
34.3	508	2			—	—	
37.7	482	6			—	—	
38.5	476	6			468	4	
47.8	406	3	a_1	0	390	3	2nd Neg C.
61.6	303	7	c_2??		302	5	3663.0
68.1	254	6			—	—	
70.1	240	6	b_1	0	242	2	3671
74.1	210	9	d_3	0	200	5	3674.9
79.6	169	7			—	—	
83.1	143	2	n_2	−6	151	2	
87.9	108	2	g_4?	+19	—	—	
90.9	086	4			—	—	
91.8	072	8	j_3 e_3?		074	6	
3708.0	26,961	3	r_2	−2	26,960	3	
13.9	918	3	k_3?	+17	910	2	
—	—	—	(p_4)	+1	870		
—	—	—	(l_3)	−5	780	1	
40.3	729	5			718	2	
49.1	666	4			—	—	
49.7	661	4	h_4	+1	661	3	
56.4	614	2			—	—	
61.4	578	6	f_5	−2	576	4	
74.6	485	6	m_4	+9	483	4	
89.3	383	5			373	2	
3805.4	271	5	a_0	0	266	3	
09.8	241	5	c_1?	−22	—	—	
—	—	—	b_0??		152	0	
—	—	—	(d_2)	(−3)	085	2	
38.8	042	6	n_1?		039	4	2nd Neg C.
53.2	25,945	4	j_2	−4	25,950	6	λ3849.5
53.8	941	4		0	—	—	52.9
55.7	928	9	e_2	−9	—	—	
66.8	854	3			—	—	
70.5	829	5	r_1	−1	824	7	
72.7	815	7	k_2	−4	—	—	
74.5	803	6			—	—	
90.4	697	5			690	4	
99.3	638	5	l_2	+9	—	—	
3904.5	604	3	p_2?	+15	593	2	
14.1	541	7	h_3	−3	—	—	
—	—	—			523	3	
20.2	502	4			—	—	
22.2	489	4			—	—	
27.3	456	4	f_4	0	—	—	
—	—	—			434		
—	—	—	(m_3)	(+19)	351	2	
59.4	249	3			—	—	
60.9	240	7			241	7	
64.1	219	5			—	—	
4002.3*	24,979*	2	d_1*	−28*	24,970	3	
25.0*	838*	1	j_1*	−28*	830	2	
—	—	—	(e_1)	(+10)	778	2	
48.9	691	3	r_0	+2	691	5	
50.5	681	5	k_1	−2	—	—	
58.6	632	4			—	—	
68.1	575	5			—	—	
70.7	559	5			568	5	
71.7	553	4			—	—	
—	—	—			452	2	
95.7	409	3	h_2	+1	401	1	
4103.4	363	3			—	—	
07.9	337	7			335	5	
09.2	329	5	f_3	+3	—	—	
20.8	260	6			260	6	2nd Neg C.
22.6	250	8	m_2	−8	—	—	λ4125?
37.6	162	7			158	6	
40.1	147	3			—	—	
44.7	120	2			—	—	
59.5	035	4			045	5	
70.5	23,971	2			—	—	
85.3*	886*	2			23,901	1	
96.6*	822*	0	d_0*	−6*	—	—	
4208.6*	23,754*	1	g_1*	−8*	23,752	0	
64.*	496*	3					
81.6*	349*	4	l_0*	+32*			
4308.4	204	3	f_2	0			
23.8	121	4	m_1	−10			
39.7	038	6					2nd Neg C.
41.0	030	5					λ4340?
59.6	22,932	5					
64.7	905	3					
67.4	891	3					

carbon lines. A further study of this part of the spectrum with different types of excitation is desirable.

The appearance of the 4th positive bands of CO when the discharge was in the "high pressure" condition has been mentioned. A similar condition photographed with the glass spectrograph and panchromatic plates showed the Angstrom bands of CO very strong but the CO_2 bands remained as strong as ever.

In the experimental work up to this point only the electron beam method of excitation had been tried but the anticipated simplification of the spectrum had not been obtained. Furthermore, in spite of the implication of Duffendack and his collaborators that the spectrum which they observed was new, the author came to a different conclusion. After a careful review of the literature, he became convinced that the spectrum under consideration was identical with the second negative bands of carbon although much richer and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d_5
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a_4
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3253.9
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2883.1
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k_{10}
This part over-exposed to bring up faint bands
a
4264
m_2
f_3
4122.6
4107.9
r_0
e_1
j_1
d_1
4002.3
3961
m_3
h_3
3914.1
r_1
j_2?
3853.2
a_0
3805.4
m_4
f_5
n_4
3761.4
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c_2?
a_1
3661.6
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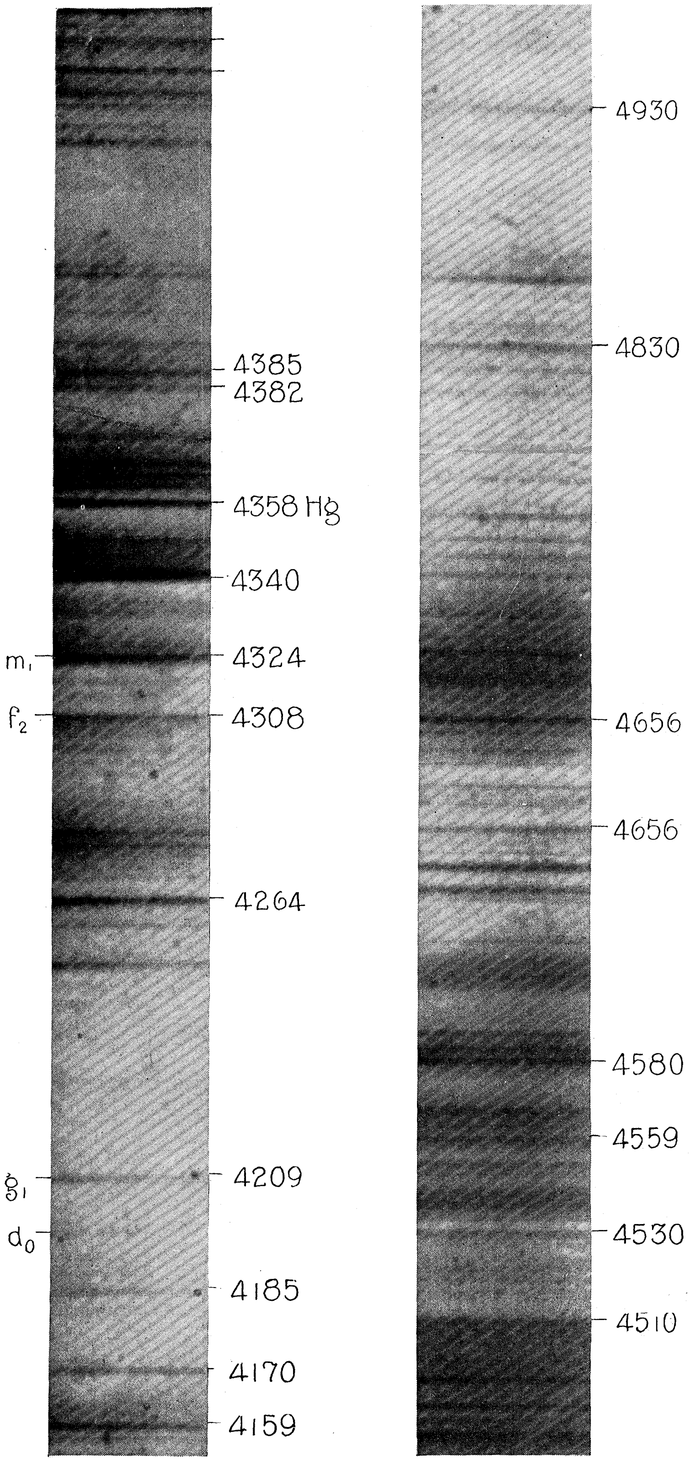
b

Fig. 2.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c Fig. 2. *d*

more extensive than the older work on them indicated. It seemed desirable therefore to try a much simpler method of excitation. The test was easily made. A discharge tube of the simplest type was connected to an old vacuum system. CO_2 from a tank was run through with no particular effort at purification. A high potential outfit was connected to the tube and the flow of gas adjusted until a bright discharge was running smoothly. A spectrogram of the negative glow was taken and showed the complete CO_2 spectrum that had been studied by the electron beam method. It should be added that the Angstrom bands and probably also some other CO bands were quite strong so that this method of excitation is not as clean cut as that previously described. Nor was the intensity as high. Obviously, since this is exactly the method of excitation used in older work to get the second negative bands of carbon and since nearly all wave-lengths given in previous lists of that spectrum are found on our plates the two spectra are identical. It remains a question why the older work reports such a small number of bands.

If the reproductions given in Figs. 2a and 2b be compared with that of Fox, Duffendack and Barker* they will be seen to be almost identical except for the presence of the OH 3300 and CH 4300 bands. The general run of intensity is the same on our plates as on the older ones and therefore the hope that this method of excitation would give a simplified intensity distribution was not justified. Figs. 2c and 2d showing as they do the long wave-length end of the spectrum photographed by the small glass Hilger, indicate that there are a great many more bands than are given in Fox, Duffendack and Barker's list but the measurements on these small dispersion plates did not seem of sufficient accuracy to be included in the list of wave numbers used below for analysis. The measurements from the plate taken with the medium Quartz Hilger which is reproduced in Figs. 2a and 2b should be accurate to about ten wave number units and therefore are a useful check on the more accurate measurements of Fox, Duffendack and Barker on plates taken with the El Quartz Hilger. The probable accuracy which they estimate for their wave-lengths is 0.1A in most cases and 1.0A for bands which they were unable to study with the large instrument. Converted to wave number units these errors are about 1 and 10 cm^{-1} for the region concerned. To allow a detailed comparison of the old results and the new and to serve as a basis for an analysis Table I has been prepared giving both sets of measurements and including also the wave-lengths of the 2nd negative bands.

PART II. ANALYSIS

First inspection of the spectra shows that from λ2900 to λ3500 the bands occur in five well-defined groups of similar but not identical structure; then from 3500 to 4000 is a terrific tangle; then two more groups appear at about λ4100 and λ4270; then another confused array of bands petering out to the end of the spectrum at about λ5000. On the violet side are the two strong bands at λ2893 and λ2883, resolved by Duncan into fine structure, and be-

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* The writer is very much obliged to Professor Duffendack who was kind enough to send him one of his CO_2 plates.

yond them some weaker bands that appear again like the groups around λ3000. Fox, Duffendack and Barker arranged six of the strong bands at the violet edges of these groups in a progression. The author has been able to extend their analysis very considerably. His results will be presented first in an entirely empirical way and then possible interpretations will be discussed.

Adding one band on either end of the set arranged by Fox, Duffendack and Barker we get the series given in Table II and find the observed wave numbers very accurately expressed by the formula $\nu=\nu_a+1136.85v-1.85v^2$ where $\nu_a=26{,}271.0$ and $v=0, 1, \cdots 7$. This implies transitions from a series of vibrational levels of an upper electronic state to a single lower level. This is to be considered merely as a convenient working assumption. The bands in this progression will be designated $a_0, a_1, a_2 \cdots a_0$ and the upper levels $A_0, A_2, A_3 \cdots A_7 \cdots$ where the values of the levels are calculated from the formula. These levels could be adjusted to get a slightly better fit with the a-progression but such an adjustment makes greater errors later on.

TABLE II. *a-series.*

Desig. of band	λ	νobs.	Int.	νcal.	νcal. − νobs.	Desig. of level
a_0	3805.4	26.271.0	5	26,271.0	0	A_0
a_1	3647.8	27,406.0	3	27,406.0	0	A_1
a_2	3503.2	28,537.2	7	28,537.3	+0.1	A_2
a_3	3370.0	29,665.1	10	29,664.9	−0.2	A_3
a_4	3246.9	30,789.8	10	30,788.8	−1.0	A_4
a_5	3132.9	31,910.8	8	31,909.0	−1.8	A_5
a_6	3027.0	33,026.3	3	33,025.5	−0.8	A_6
a_7	2928.3*	34,139.5*	1	34,138.3	−1.2	A_7
				35,247.4		A_8
				36,352.8		A_9
				37,454.5		A_{10}
				38,552.5		A_{11}

Further examination of the spectrum shows that most of the strong bands in the separate groups and many bands in the more confused part of the spectrum can be represented by transitions between the A-levels and different lower levels, i.e., by formulas of the type $\nu=\nu_a-\nu_x+1136.85v-1.85v^2$. Such bands may be symbolically represented by $A_i-\nu_x$, e.g. A_4-2454 would be a band represented by the above formula if ν_x were put equal to 2454 cm^{-1} and $v=4$. As may be seen from the small coefficient of the quadratic v-term the differences between successive A-levels are very nearly the same and therefore it is difficult to be certain of the proper v-values unless the bands observed in a progression are very accurately measured. This means that the value of ν_x may in some cases be too large or too small by approximately 1130 cm^{-1} or even by integral multiples of that number.

In order to save space the results of the analysis have been included in Table I where column four shows the assignment of the bands to various progressions and column five gives the errors of the wave numbers calculated by the use of the various values of ν_x given in Table V below. But to illustrate their nature more clearly two progressions will be presented separately in detail. The first, the d-progression is the most satisfactory one of all except the intial a-series. As may be seen from Table III below, the value of ν_x is fixed within very narrow limits, probably 2454 to 2456 and the agreement with observed values is excellent except in one or two cases. In this table, as in Table I and elsewhere except Table II, tenths of cm^{-1} have been ignored.

TABLE III. *d-progression.* $A_i - 2454$.

Desig.	ν_c	ν_0	$\nu_c - \nu_0$	Intensity F. D. & B.	This paper
d_0	23,816	23,822*	−6*	0	—
d_1	24,951	24,979*	−28*	2	3
d_2	26,082	(26,085)	(−3)	—	2
d_3	27,210	27,210	0	9	5
d_4	28,334	28,334	0	4	2
d_5	29,454	29,451	+3	7	4
d_6	30,571	30,573	−2	10	5
d_7	31,683	31,685	−2	9	5
d_8	32,792	32,792	0	6	5
d_9	33,898	33,895*	+3*	4	2
d_{10}	34,999	34,999*	0*	5	1

* Indicates accuracy of only ±10.

( ) Indicates wave number from author's plate. All others are from Fox, Duffendack and Barker.

As typical of the other extreme, a value of ν_x has been chosen that was suggested by other combinations. The agreement with observed ν's is very poor, perhaps not more than chance, and ν_x could certainly be altered by ±20 or even by ±1130 as discussed above without making it much worse.

TABLE IV. *n-progression.* $A_i - 1400$.

Desig.	ν_c	ν_0	$\nu_c - \nu_0$	Intensity F. D. & B.	This paper
n_0	24,871	—	—		
n_1	26,006	26,042	−36	6	4
n_2	27,137	27,143	−6	2	—
n_3	28,265	28,290	−25	9	4
n_4	29,389	29,396	−7	3	—
n_5	30,509	(30,490)	+19	—	0

The whole gamut of progressions is given in Table V where the values of ν_x are in column one and the intensities of the bands of the corresponding progression follow along the row. If an intensity is given and unmarked it is the intensity of a band in Fox, Duffendack and Barker's list whose wave number agrees to within 10 cm^{-1} with that calculated. If it is marked with an asterisk it is one of Fox, Duffendack and Barker's less accurately measured bands and if in parentheses it is from the author's plate and does not appear on Fox, Duffendack and Barker's list. In either of these last two cases the $\nu_c - \nu_0$ may be as great as 30 cm^{-1}. The values of ν_x are taken empirically to give the best agreement throughout each particular progression and the ± error indicates the limits outside of which there is noticeably poorer agreement. In most cases this error could be considerably exceeded without bringing the disagreement about 10 cm^{-1} or 30 cm^{-1} for the two grades of accuracy of measurement respectively. The actual value of $\nu_c - \nu_0$

TABLE V.

Desig.	ν_x	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	A_{11}
a	0	5	3	7	10	10	8	3	1*				
b	167 ± 2	—	6	(0)	7	9	6	—	2*	5	—	—	—
c	1189 ± 2	—	—	—	9	10	10	9	6	3	—	—	—
n	1400 ± 20	—	—	2	—	3	(0)	—	—	—	—	—	—
r	1578 ± 10	3	5	3	—	(0)	—	(1)	5*	(0)	7		
d	2454 ± 2	0	2*	(2)	9	4	7	10	9	6	4	5	
j	2596 ± 4	—	1*	4	8	10	—	3	7	5*	2*		
e	2618 ± 10	—	(2)	9	—	(6)	3	3	7	5*	5*	(00)	
k	2727 ± 10	—	5	7	—	9	3	—	(2)	4*	(0)	5	
l	2890 ± 10	4*	—	5	(1)	2	2	—	(0)	5	2	?	
g	3660 ± 7	—	1*	—	—	—	—	1	3	5	5*	2*	
p	3918 ± 20	—	—	—	—	(1)	—	—	(0)	(0)	(0)	—	
h	4127 ± 4	—	—	3	7	4	6	(00)	(00)	(00)	(2)	—	
m	4295 ± 10	—	4	8	(2)	6	7	(1)	(1)	(2)	(1)	—	0* ?
f	5333 ± 4	—	—	3	5	4	6	—	0*	(0)	(1)	(0)	3*

for each particular band is given in column five of Table I. In the fourth column of Table I and in Figs. 2a and 2b the assignments of the bands are given and in many cases even where the $\nu_c - \nu_0$ is obviously too large an assignment is still given indicating the approximate location expected for that particular band of that progression. In making these assignments fifteen different progressions have been used and in the neighborhood of a hundred bands accounted for. Of these fifteen progressions, all but four (m, n, r, p) were found independently of the scheme of energy levels now preferred for their representation and are the residue of some thirty odd different trial values of ν_x, both positive and negative, suggested by various observed regularities in the spectrum. They are believed to be established with reasonable certainty. Of the four progressions, m, n, r, p, only two, m and r, seem pretty good; the other two, n and p, are decidedly wobbly. The reason for including them will emerge from explanation of these progressions which will be advanced presently.

The most striking of the progressions are the a, b, c, d and e, having ν_x values of 0, 167, 1189, 2454 and 2618. It will be noted that the difference between the first two and between the last two is approximately the same, 166 cm^{-1}. Furthermore this difference occurs quite frequently elsewhere in the spectrum, for example between the k and l and the h and m progressions. For a long time the writer[14] believed this separation to indicate a splitting of one of the electronic levels. This point of view made it possible to explain all but one of the values of ν_x in terms of combinations of two fundamental modes of vibration with quadratic anharmonic terms.[15] But this explanation never seemed really satisfactory particularly as two strong progressions, the c and g, could not be associated with others at separations of 167, that seemed to have any reality. Therefore, in spite of its attractive simplicity and initial success, it has been abandoned.

Before advancing the present explanation it is necessary to review some of the recent work on the infrared spectrum of CO_2. Dennison[16] has recently

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[14] Smyth and Chow, Phys. Rev. **37**, 1023 (1931).

[15] Smyth and Chow, Phys. Rev. **37**, 1710 (1931).

[16] Dennison, Revs. of Mod. Phys. **3**, 280 (1931).

discussed the normal modes of vibration to be expected in triatomic molecules of various types. He shows that in a linear molecule there are four normal modes of vibration instead of three. This arises from the fact that the vibration of the central atom perpendicular to the axis of symmetry is not confined to a particular line but merely to a plane. To characterize this motion completely two quantum numbers, v_2 and l, are necessary. To a first approximation the energy of the molecule is independent of l but if the assumption that the motion of the atoms is infinitesimal compared with the equilibrium distances between them is given up the energy becomes dependent on l. Dennison gives the following equation for the total energy:

$$W/h = \text{const.} + v_1\nu_1 + v_2\nu_2 + v_3\nu_3 + x_{11}v_1^2 + x_{22}(v_2^2 - \tfrac{1}{3}l^2) + x_{33}v_3^2 + x_{12}v_1v_2 + x_{13}v_1v_3 + x_{23}v_2$$

where $v_1v_2v_3$ are quantum numbers, the coefficients x_{11}, x_{12} etc. are constants and l has the values v_2, v_2-2, $\cdots$ 0. This expression differs from the general formula for the vibrational energy of a triatomic non-collinear molecule only in the presence of the factor $(1/3)l^2$.

At the last Washington meeting of the American Physical Society, Martin and Barker[17] reported the application of these ideas to the explanation of the observed infrared and Raman spectra of CO_2. Professor Barker has been kind enough to send the writer the frequencies and energy level diagram which he showed on the screen at that time. The frequencies are $\nu_1 = 1361$ cm^{-1}, $\nu_2 = 668$ cm^{-1} and $\nu_3 = 2350$ cm^{-1}. The $v_2 = 2$ level splits into two ($l = 2$ and $l = 0$) in the manner described above and the amount of splitting, determined from Raman lines, is 102 cm^{-1}. The similar spread of the $v_2 = 3$ level is 147 cm^{-1}. The Raman lines correspond to changes of two in v_2.

How can this be applied to the present problem? Obviously not directly since this emission spectrum does not involve the normal state of the molecule. Very possibly the initial and final electronic configurations are such that the molecule is no longer linear; particularly as it seems likely that the spectrum comes from CO_2^+. But the frequencies that emerged in the empirical analysis are of the order of magnitude of the ν_1, $2\nu_2$ and ν_3 given above, which suggests that the shape and binding forces of the excited molecule or ion may be similar to those of the molecule in its normal state.

Working from this point of view it is suggested that the various progressions are all v_1' progressions. That is that the ν_1 of the upper state is about 1140 cm^{-1}. The observed separation of 166 cm^{-1} between a number of pairs of progressions is interpreted as a splitting of the $v_2' = 2$ level. On this basis the $v_2' = 2$, $l' = 0$ and $v_2' = 2$, $l' = 2$ levels have values 1029 and 1195 cm^{-1} respectively above the lowest vibration state of the upper electronic level. The value of ν_3' remains undetermined as there appears no ν_x that requires a v_3' different from zero. In the lower electronic state are four vibration levels besides the zero. Three, at 1400, 2727, and 4127 are probably $v_1'' = 1$, 2 and 3, respectively. The fourth at 2456 is $v_3'' = 1$, probably; perhaps it is $v_1'' = 2$ and

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[17] Martin and Barker, Phys. Rev. **37,** 1708 (1931).

2727 is $v_3''=1$, 4127 then being a combination, $v_1''=1$ and $v_3''=1$. In this state no values of v_2'' other than zero appear and therefore v_2'' remains undetermined. The complete absence of any transitions from the $v_2'=1$ state is an unexplained difficulty with this whole arrangement. Perhaps it is the result of some selection rule which an extension of Dennison's analysis to electronic transitions might explain.

In the scheme of levels as shown in Fig. 3, the $v_1'>0$ levels have been omitted so that each transition shown represents an entire progression. The levels are labeled by letters to avoid any insistence on their suggested interpretation. Their numerical values are chosen to give the most general agreement with the observed ν_xs. That this agreement is good in most cases can be seen from Table VI. A slightly different choice of separations of the levels gives a good deal better agreement for all but the *g* and *h* progressions. This may be accidental or as seems more likely the scheme may be over simplified. In any case the values given in Table VI which represent exactly combinations of the levels in Fig. 3 give computed wave numbers that agree within 10 cm^{-1} with sixty-two of the more accurately measured bands in Fox, Duffendack and Barker's table, within 30 cm^{-1} with twenty-eight of the less accurately measured bands and within 30 cm^{-1} with seventeen bands that were observed on the author's plate but not by Fox, Duffendack and Barker.

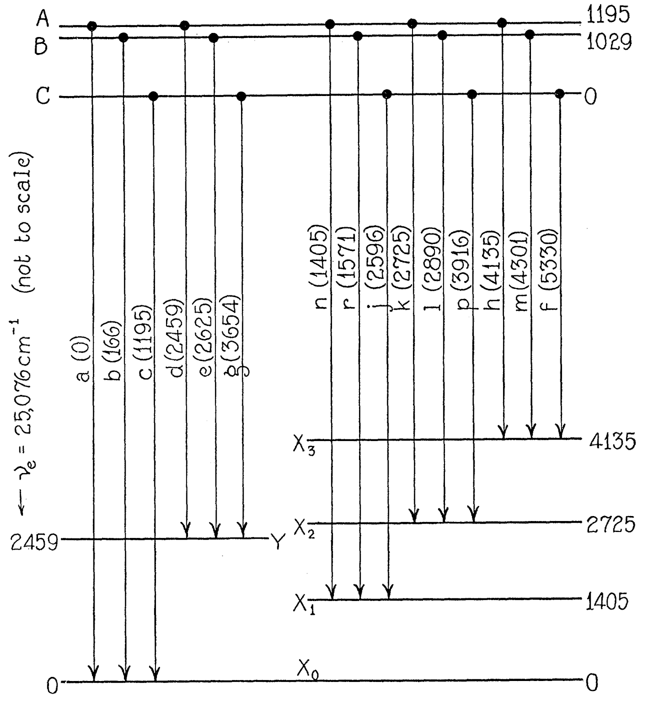

Fig. 3.

If the empirical values of ν_x are used only some half dozen more bands are brought within the limits of error but the average value of $\nu_c - \nu_0$ is very considerably reduced. Furthermore, if the doubtful n and p progressions and the A_0 and A_{10} combinations are omitted only twenty-three of the 117 predicted bands are not observed within the limits of error. Considering the overlapping of the bands, their varying intensity and the fact that the measurements are of edges, often ill-defined, rather than of origins, this agreement seems good.

TABLE VI.

Progression	Empirical	Calc.	Diff.	Transition
a	0	0	—	$A-X_0$
b	167	166	−1	$B-X_0$
c	1189	1195	6	$C-X_0$
d	2454	2459	5	$A-Y$
e	2618	2625	7	$B-Y$
f	5333	5330	−3	$C-X_3$
g	3660	3654	−6	$C-Y$
h	4127	4135	8	$A-X_3$
j	2596	2596	0	$C-X_1$
k	2727	2725	−2	$A-X_2$
l	2890	2891	1	$B-X_2$
m	4295	4301	6	$B-X_3$
n	1400	1405	5	$A-X_1$
p	3918	3916	−2	$C-X_2$
r	1578	1572	−6	$B-X_1$

Obviously this scheme of levels is not the only possible way of explaining the observed regularities. The observed A-progressions can not even be assigned with certainty to the upper electronic state. They are cut off at either end about equally sharply, as is the spectrum, so that the A_{10} level may well be actually a $v_1'' = 0$ level. That this was the case was assumed by the author in papers presented to the Physical Society at the New York[14] and Washington[15] meetings. But this now seems unlikely and attempts to construct a satisfactory energy level scheme on this basis have met with no success.

Granted the A-progressions are ν_1' progressions it might still be expected that all three normal modes of vibration of both upper and lower states should be present in the spectrum. Analytically the spectrum would then be represented by the difference between two equations like that of Dennison's given above, with an electronic term added in. This would give eighteen undetermined constants and could certainly be adjusted to give the observed regularities but it would also predict many regularities that are not observed. Attempts to apply such formulas have not been successful.

There remain a number of bands in Table I, among them the two strongest in the spectrum, which have not been fitted into the scheme. Separations of about 160 cm^{-1} and about 1400 cm^{-1} occur in them with fair regularity showing signs of something like a ν_1'' progression but no definite analysis has been achieved as yet. There also seem to be smaller differences of the order of 10 cm^{-1} that are repeated but these are too near the limits of accuracy of measurement to be dependable.

In connection with some data[18] on the ionization of CO_2 it is of interest to consider the energies of excitation of the upper levels here postulated. The ν_e, that is the energy to go from zero vibration in the lower state to zero vibration in the upper state, is $25{,}076\ cm^{-1} = 3.1$ volts while the excitation of the A_{10} level requires 4.6 volts. The interpretation of a particular secondary ionization process in CO_2 suggests the existence of an excitation level in the ion (or molecule) at about 4.5 volts.

It should also be pointed out that the long wave-length end of the spectrum from 4000 to 5000 has hardly been touched. The bands included in Table I are only a small part of what is shown on plates taken with the glass spectrograph (see Figs. 2c and 2). In fact the bands in this region are so thick that much greater dispersion is necessary before an analysis can be convincing. For this reason no great weight is given to the fact that some of the progressions given above can be extended in this region and such extensions have not been included in the discussion.

It is probable that the analysis presented above will have to be considerably revised as our knowledge of this spectrum is increased. Yet it seems significant and encouraging that so large a proportion of the observed bands can be fitted into a plausible and not very complicated scheme. If this can be done with an emission spectrum not involving the normal state, it may be possible to do even better in cases where absorption spectrum data can be applied. Such a case is offered by SO_2 whose absorption spectrum has recently been partly analyzed by Watson and Parker.[19] Chow and the author[20] have already pointed out an interesting correlation between this analysis and an emission spectrum previously observed and are beginning a systematic study of the emission spectrum.

In conclusion I wish to thank Miss Janet MacInnes and Mr. T. C. Chow for their help in various phases of this work.

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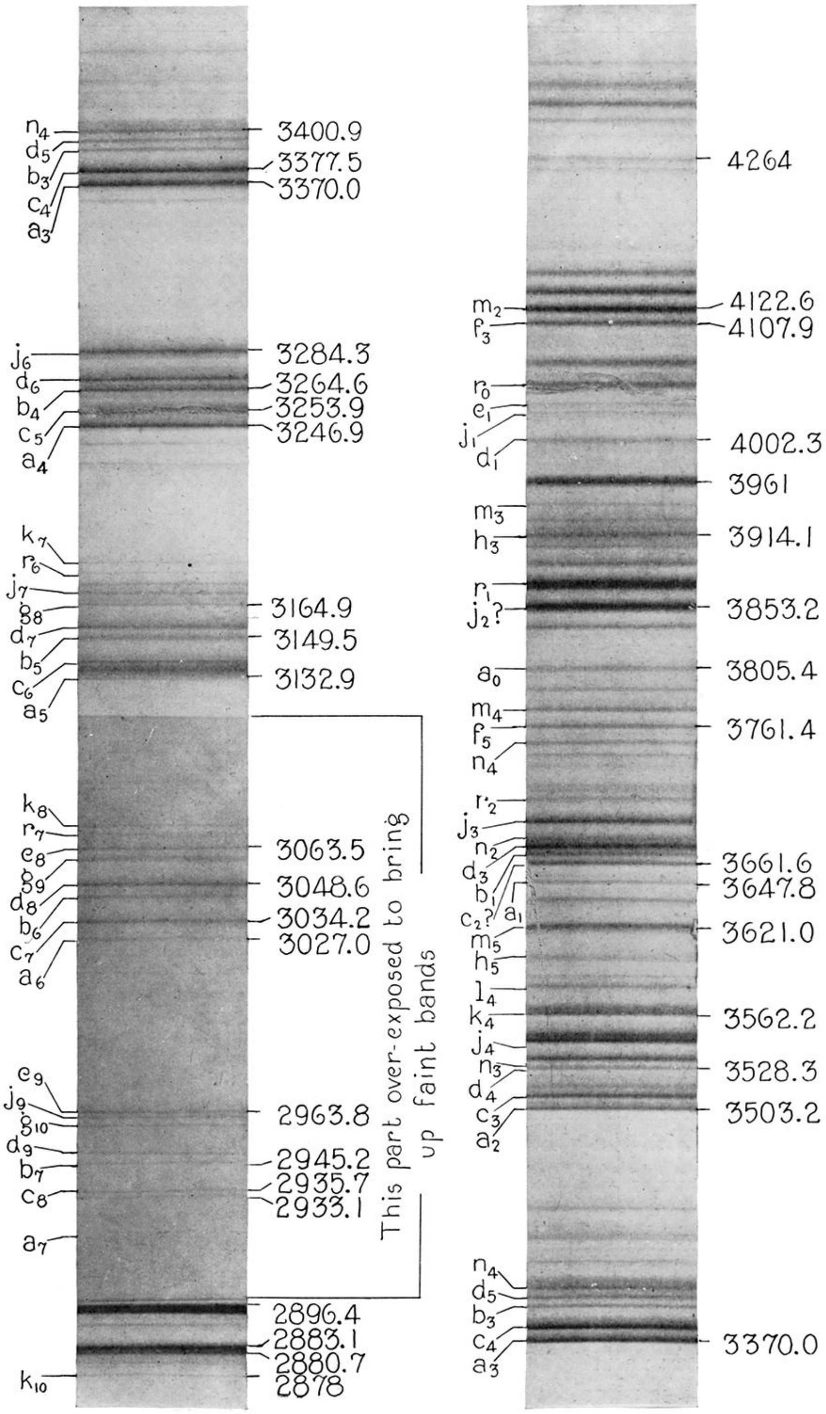
[18] Smyth, Revs. of Mod. Phys. **3**, 382 (1931).

[19] Watson and Parker, Phys. Rev. **37**, 1484 (1931).

[20] Chow and Smyth, Phys. Rev. **38**, 838 (1931).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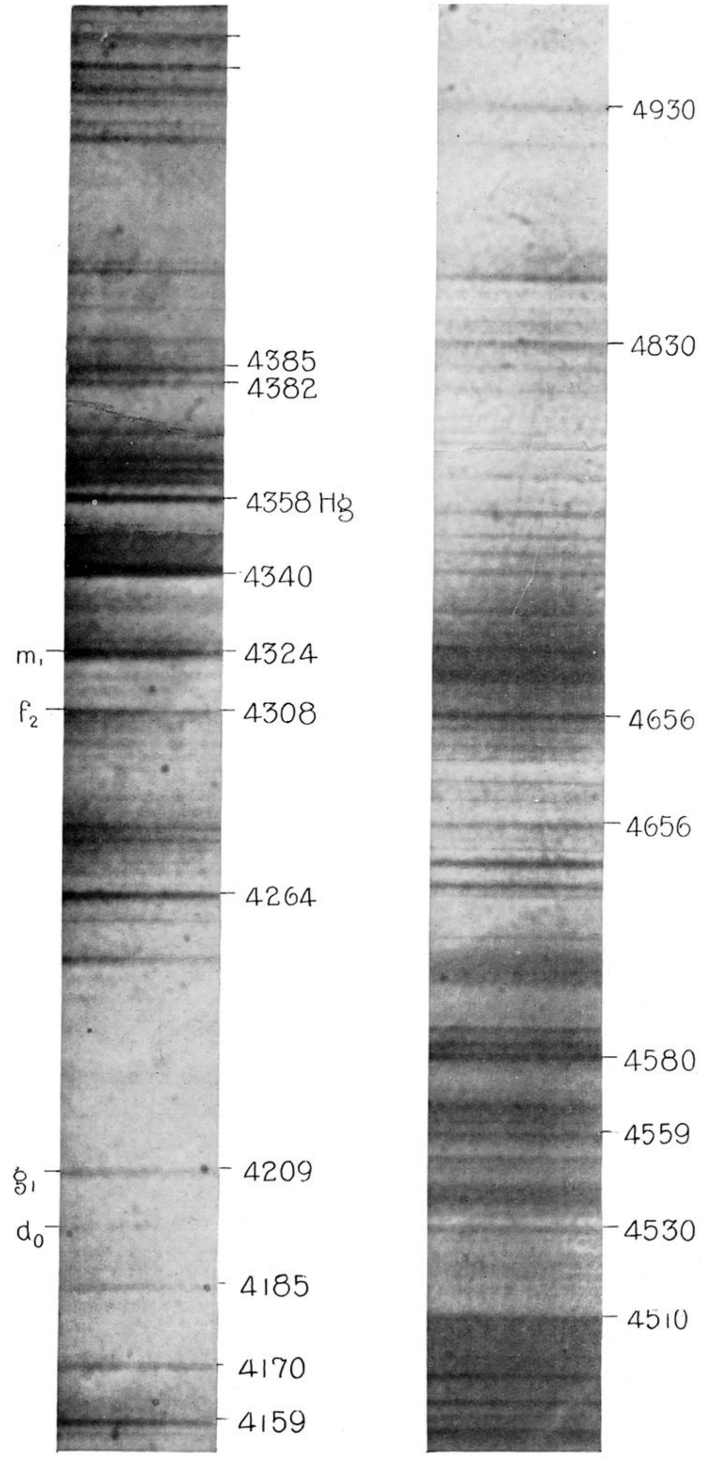
a

b

Fig. 2.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g_1
4209
d_0
4185
4170
4159
4930
4830
4656
4656
4580
4559
4530
4510

c Fig. 2. *d*