

other can be readily followed by simple inspection. There are no missing lines at the center of the band.

Preliminary data have been obtained in five other regions of absorption shown in Coblenz' curves. In some of these the measurements have progressed quite far but they will not be discussed at present, for it is desired to repeat them and possibly increase their refinement by improvements in some parts of the apparatus.

¹ E.g., Sleator, W. W., *Astrophys. J.*, **48**, 1918 (125-143).

² *Physik. Zeitschr.*, **12**, 1912 (870-873).

³ Coblenz, W. W., *J. O. S. A.*, **5**, 1921 (356-362).

⁴ *Ibid.*, Publications of the Carnegie Institution of Washington, **35**, 1905 (166-169).

THE SPECTRUM OF CO₂

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In the course of an investigation of the spectrum of carbon monoxide¹ it became necessary to determine whether or not any of the observed bands might be assigned to the carbon dioxide molecule. Existing data upon the subject cannot be considered conclusive, for the spectra observed in both gases under ordinary conditions of excitation are identical. A continuous flow method previously employed for the study of HCl² makes it possible, however, to distinguish between the spectra due to a given gas and to its dissociation products. The application of this method to the study of CO₂ has revealed a band spectrum apparently not observed previously which may be ascribed with confidence to the CO₂ molecule. A few of the most intense heads did appear rather faintly on the earlier CO plates; hence it appears that in the electrical discharge through stagnant gas the reaction $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ occurs.

A supply of CO₂ free from CO was obtained by dropping H₂SO₄ upon CaCO₃ in an evacuated flask (Fig. 1). Both reagents were as pure as could be obtained. The gas was collected in a trap immersed in liquid air, pumping being continued meanwhile. After the generator was shut off a fraction of this condensed gas was allowed to expand into a reservoir where it was stored at a pressure of about two atmospheres: the remainder was released through the generator. From the reservoir CO₂ was admitted slowly into the discharge tube and subjected to electron bombardment in a force free space before reaching the filament. The tube is provided with a tightly fitting diaphragm having an aperture about 2×6 mm. in front of the filament, the aperture being covered with a fine platinum gauze.

The exciting electrons are accelerated between the filament and the gauze in a direction opposite to the flow of the gas. When the proper rate of pumping is maintained—the pressure in the tube being about 0.1 mm.—there is no indication of carbon monoxide appearing in the excitation chamber, either by diffusion from the region around the filament or by dissociation of CO_2 through electron impacts. The spectra, photographed through a quartz window at one side of the tube, show none of the bands ordinarily assigned to CO. As soon as pumping ceases and the flow is stopped, however, the character of the discharge rapidly changes and the CO_2 bands disappear. This effect is observed even with an oxide-coated filament operating at a comparatively low temperature. The discharge in the

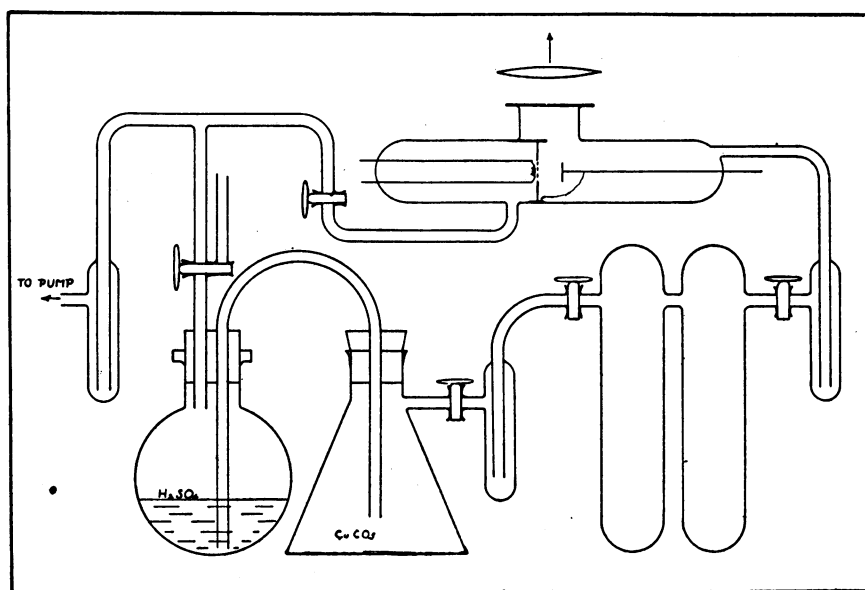


FIGURE 1
Diagram of apparatus.

flowing gas produces a violet glow between the gauze and plate which changes rapidly to the familiar sky blue color characteristic of CO when the flow is stopped. Further evidence that no dissociation products found their way into the impact region lies in the fact that the 2537 mercury line appears only very faintly on the spectrograms, even though no liquid air was applied to the trap between the discharge tube and pump. In fact the line as observed would be expected because of the mercury vapor which was known to exist in the CO_2 storage reservoirs.

Reproductions of the spectrum of the discharge through flowing CO_2 are shown in plate I. The spectrogram *A* was taken with a Hilger E2

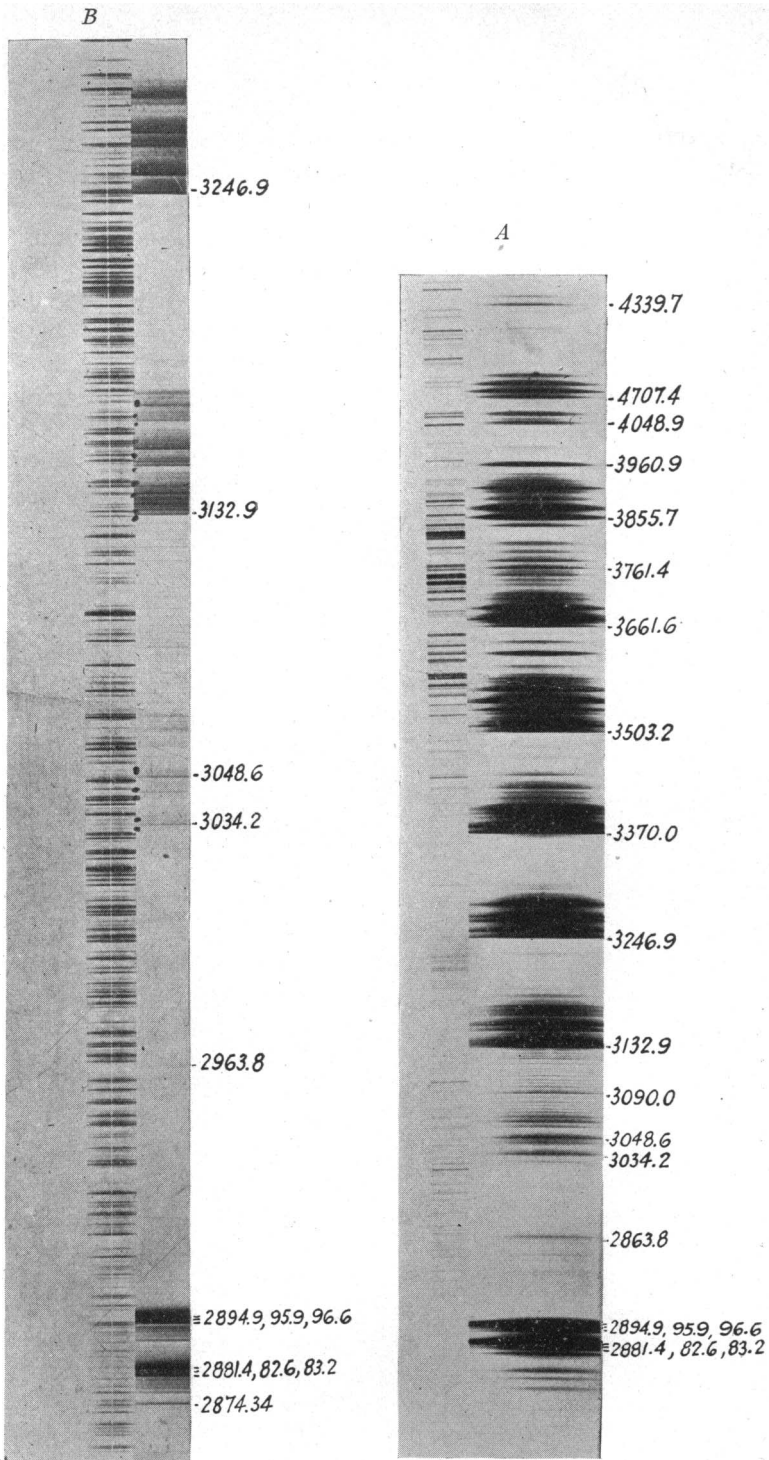
quartz spectrograph while *B* was taken with the E1 model. The spectrum consists of bands of several different types, as revealed in the reproductions, and extends from approximately 5000 Å to 2800 Å, the bands at the ends being too faint to reproduce. For the most part, the bands are degraded toward the red and have sharp edges. The fine structure is not resolved near the edges by the E1 spectrograph nor is it revealed by a three-fold enlargement of the spectrogram in which a dispersion of approximately 1 Å per mm. is attained.

The bands constituting the strong groups consist of two or more band systems which overlap one another to some extent. Some progress has been made in the analysis of these groups and it seems certain that one system consists of the bands listed in table 1.

λ	ν (VAC.)	$\Delta\nu$
3027.0	33026.3	
3132.9	31910.1	1116.2
3246.9	30789.8	1120.3
3370.0	29665.1	1124.7
3503.2	28537.2	1127.9
3647.8	27406.0	1131.2

This system probably extends farther than indicated in the table both in the direction of greater and in the direction of shorter wave-lengths, but the bands are fainter and are difficult to pick out of the overlapping groups. The nature of the groups associated with these edges suggests that several of the edges involve the same electronic transitions, but the frequency differences within the groups are quite irregular. We have not been able to analyze the groups on the basis of transitions between sets of multiple vibrational levels. It seems fairly certain that the bands listed in table 1 originate in a set of initial vibrational levels, the final state consisting of a single vibrational level. The related edges in the groups may result from multiple electronic terms or from a structure of the molecule such that more than one moment of inertia is involved.

The bands with edges near 2880 and 2895 are distinctly different from the others in structure. The spectrogram *A* shows two intensity maxima in this region which are resolved by the larger spectrograph into double-edged bands as shown in spectrogram *B*. Each band has two oppositely degraded branches with sharp inner edges between which a very narrow band appears. These oppositely degraded bands have some resemblance to the ammonia bands at 3360 and 3370 Å, but in ammonia the narrow band between the edges does not appear. This narrow band may be due to a zero branch which is not extensively developed. No relation between these bands and those constituting the groups has been discovered. They



Spectrogram A. The spectrum of flowing CO₂ taken with a Hilger E2 quartz spectrograph. Iron comparison spectrum. Spectrogram B. A portion of the spectrum of flowing CO₂ taken with a Hilger E1 quartz spectrograph. Iron comparison.

will have to be photographed with an instrument of considerably greater dispersion before any definite conclusions can be drawn as to their nature.

Table 2 gives a list of the wave-lengths and intensities of most of the band edges. Those marked * were measured only on a spectrogram taken with the E2 instrument and may be in error by as much as 1 Å as it was difficult to locate the edge exactly with such small dispersion. The wave-lengths not marked were measured on spectrograms taken with the E1 spectrograph and are probably correct to at least 0.1 Å. The iron lines were used for comparison. As none of these bands are absorbed in normal CO₂, the normal state of the molecule is not their final state. Whether they belong to an excited molecule or to an ion was not determined.

TABLE 2

λ	INTEN.	λ	INTEN.	λ	INTEN.
*2849.5	4	64.6	9	40.3	5
* 56.4	5	69.9	10	49.1	4
* 62.5	6	80.5	3	49.7	4
74.3	7	83.3	4	56.4	2
77.2	5	84.3	8	61.4	6
78.2	5	85.8	3	74.6	6
80.7	6	87.7	3	89.3	5
82.1	10	92.6	4	3805.4	5
82.6	9	3301.1	4	09.8	5
83.1	10	70.0	10	38.8	6
90.4	7	72.5	5	53.2	4
95.4	10	75.2	3	53.8	4
95.9	9	77.5	10	55.7	9
96.4	10	82.2	5	66.8	3
*2907.5	0	86.2	3	70.5	5
* 10.2	0	88.9	7	72.7	7
* 16.3	0	94.5	7	74.5	6
* 19.1	0	3396.9	3	90.4	5
* 24.8	1	99.4	4	99.3	5
* 25.2	1	99.9	3	3904.5	3
* 28.3	1	3400.9	3	14.1	7
* 29.4	1	02.2	1	20.2	4
* 33.1	3	04.3	1	22.2	4
* 35.7	3	13.3	3	27.3	4
* 45.2	2	26.6	3	59.4	3
* 49.4	4	43.5	2	60.9	7
* 56.8	0	* 64.5	0	64.1	5
* 58.7	2	* 71.0	0	*4002.3	2
* 61.8	2	3503.2	7	* 25.0	1
* 63.8	5	10.8	9	48.9	3
* 88.6	2	17.1	7	50.5	5
* 90.3	2	28.3	4	58.6	4
*3005.3	3	33.8	9	68.1	5
* 07.3	3	45.9	10	70.7	5
* 17.8	2	51.4	7	71.7	4
* 19.6	0	62.2	9	95.7	3

* 22.6	1	65.5	6	4103.4	3
27.0	3	81.1	4	07.9	7
34.2	6	83.3	2	09.2	5
43.9	5	86.0	2	20.8	6
48.6	6	* 99.1	6	22.6	8
* 58.3	5	3615.8	3	37.6	7
* 63.5	5	16.9	3	40.1	3
* 67.7	5	18.6	3	44.7	2
* 72.1	4	21.0	7	59.5	4
* 90.0	5	34.3	2	70.5	2
3132.9	8	37.7	6	* 85.3	2
34.6	8	38.5	6	* 96.6	0
35.7	6	47.8	3	*4208.6	1
36.7	9	61.6	7	* 64.0	3
39.2	9	68.1	6	* 81.6	4
42.4	5	70.1	6	4308.4	3
49.5	6	74.1	9	23.8	4
50.7	6	79.6	7	39.7	6
55.2	9	83.1	2	41.0	5
64.9	5	87.9	2	4359.6	5
70.1	7	3690.9	4	64.7	3
74.3	5	91.8	8	67.4	3
3246.9	10	3708.0	3		
53.9	10	13.9	3		

¹ Duffendack and Fox, *Nature*, 118, 12 (1926); *Science*, 64, 277 (1926); *Astrophys. J.*, in press.

² Barker and Duffendack, *Phys. Rev.*, 26, 339 (1925).

THE ENTROPY OF RADIATION

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The very close agreement between the formula of Planck and the measured distribution of black body radiation has led to numerous attempts to provide a theoretical basis for this formula. Of these the one receiving widest acceptance is that of Einstein,¹ who obtains the Planck formula by assuming merely that the chance of emission from an excited atom is increased by the presence of other light, of the same frequency as that which the atom emits, and that the increase is proportional to the concentration of that light.

I shall now approach this problem in a way which seems to me even more fundamental. The distribution of radiant energy in thermal equilibrium may be calculated as soon as we know the entropy of radiation as a function of concentration and of frequency. The notion of entropy may in turn