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Rotational Analysis of the 2900A Band of CO_2^+

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A rotational analysis of the CO_2^+ doublet band near λ2896 and λ2882 has been made. The band was photographed in the third order of the 30-foot grating spectrograph at Ryerson Laboratory with a dispersion of 0.22A/mm and a resolving power of 300,000. The structure is explained by a $^2\Sigma^+_u \rightarrow {}^2\Pi_g$ (case *a*, inverted) transition, where the $^2\Pi_g$ is the ground state of CO_2^+. Alternate lines are missing as expected for $^2\Sigma$ in view of the zero spin of the oxygen nuclei. A number of perturbations are observed, which involve displacements and weakening of the lines. These are probably caused by higher vibrational levels of a $^2\Pi_u$ state which lies about 0.8 volts below the $^2\Sigma^+_u$. The values found for the molecular constants of the lower $^2\Pi_g$ state ($B_1 = 0.3795$ cm^{-1}, $B_2 = 0.3813$ cm^{-1} and the Λ-doubling coefficient $p = 0.004$ cm^{-1}) agree with those found by Mrozowski. For the upper $^1\Sigma^+_u$ state, $B = 0.3784$ cm^{-1} and the spin-doubling coefficient $\gamma = 0.019$ cm^{-1}. The spin-orbit coupling coefficient A for the $^2\Pi_g$ state is -159.5 cm^{-1}.

INTRODUCTION

THE spectrum of CO_2 has been the object of considerable investigation. From studies of the infra-red and Raman spectra Martin and Barker[1] were able to show that the normal CO_2 molecule is linear, confirming the previous results of Eucken[2] and of Stuart.[3]

Among the first to study the emission spectrum were Fox, Duffendack, and Barker,[4] who found extensive systems of bands from λ2800 to λ5000. They observed that the bands centered at λ2882 and λ2896 (see Fig. 1) were the strongest in the spectrum and presented a different appearance from the other bands. Duffendack and Smith[5] concluded that most of the observed bands could be ascribed to CO_2^+ as the emitter, and estimated the excitation potential of the strong λ2900 doublet band at 19 volts.

This band was first photographed under high dispersion by Duncan.[6] He used a 65-volt arc at 6–15 ma with flowing CO_2 at a pressure of 0.1 mm. His dispersion with a 21-foot grating was 1.2A/mm in the second order. This, however, was not sufficient to resolve the structure fully, but from its appearance he believed that each of the two sub-bands consists of a positive, a negative, and a zero branch. The zero branches he identified with the strong, rather wide lines at 34,517.54 cm^{-1} and 34,678.25 cm^{-1} marked (*b*) and (*a*) in Fig. 1. He concluded, in agreement with Duffendack and Smith, that the excitation potential for the bands must be about 19 volts, and thus correspond to ionization of the molecule.

Schmid[7] photographed the λ2900 band with a 21-foot grating in this laboratory, using a continuous flow of CO_2 through a Back box with magnetic field, and also a hollow cathode without field. He concluded that the transition was a (0,0) band of a $^2\Pi$ (case *a*)$\rightarrow{}^2\Pi$ (case *b*) electronic transition in a linear CO_2^+ molecule,[8] although his resolving power did not permit a satisfactory analysis. He also arranged the lines in P and R branches, again identifying a Q branch in each sub-band with each of the two strong lines mentioned above.

The emitter of the band was more definitely identified as CO_2^+ by Roy and Duffendack.[9] They employed a low voltage arc in mixtures of CO_2 and O_2, with and without the addition of rare gases. Accepting the electron impact value of $I = 14.4$ volts given by Smyth[10] for the minimum

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[1] P. E. Martin and E. F. Barker, Phys. Rev. **41**, 291 (1932).

[2] A. Eucken, Zeits. f. Physik **37**, 714 (1926).

[3] H. Stuart, Zeits. f. Physik **47**, 457 (1928).

[4] G. W. Fox, O. S. Duffendack, and E. F. Barker, Proc. Nat. Acad. Sci. **13**, 302 (1927).

[5] O. S. Duffendack and H. L. Smith, Phys. Rev. **34**, 68 (1929).

[6] J. F. Duncan, Phys. Rev. **34**, 1148 (1929).

[7] R. F. Schmid, Zeits. f. Physik **83**, 711 (1933).

[8] The notation and formulas for diatomic molecules are applicable to linear triatomic molecules [cf. R. S. Mulliken, Phys. Rev. **42**, 364 (1932)].

[9] A. S. Roy and O. S. Duffendack, Proc. Nat. Acad. Sci. **19**, 497 (1933).

[10] H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931).

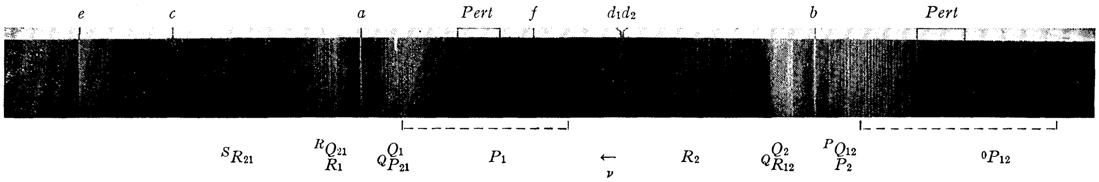

FIG. 1. Spectrogram of the λ2900 doublet band of CO_2^+. The sub-bands are centered near (*a*) ($\nu = 34{,}678.25$ cm^{-1}) and (*b*) ($\nu = 34{,}517.54$ cm^{-1}). The meaning of the letters is given in the text. The portions of the branches shown by dashed brackets under *Pert* are shown enlarged in Fig. 4, while the solid brackets include the lines which show the greatest perturbations.

ionization potential of CO_2, they obtained a value of $I = 18.7$ volts for the excitation potential of the λ2900 band.

From a pair of Rydberg series in the ultraviolet absorption spectrum of CO_2, Henning[11] and Rathenau[12] found an ionization potential of 18.00 ± 0.03 volts which should presumably correspond to ionization of an inner electron.

On the basis of theoretical considerations as to the electron configuration of CO_2, and taking into account the experimental data available, Mulliken[13] concluded that the λ2900 band is most probably a $^2\Sigma^+_u \rightarrow {}^2\Pi_g$ transition, with the $^2\Pi_g$ as the normal state of CO_2^+. The electron configuration he gives for the normal state of CO_2 is the following:

$$(1s)^2(1s)^2(1s)^2(2s)^2(2s)^2(\sigma+s+\sigma, \sigma_g)^2(\sigma-\sigma+\sigma, \sigma_u)^2 \times(\pi+\pi+\pi,\ \pi_u)^4(\pi-\pi,\ \pi_g)^4,\ {}^1\Sigma^+_g.$$

By identifying the ionization potential of 18 volts as that required for the removal of one of the σ_u electrons from the normal molecule (thus resulting in a $^2\Sigma^+_u$ state for the ion) he was able to predict a minimum I of 13.72 volts for CO_2, a value which is lower than the electron impact values of Mackay[14] and of Smyth.[10] Mulliken's estimate is in exact agreement with the $I = 13.73 \pm 0.01$ volts found later by Price and Simpson[15] from an additional Rydberg series. This energy would then correspond to that required for the removal of a π_g electron from the CO_2 molecule giving the normal state of CO_2^+. The absence of vibrational excitation in Henning's Rydberg series indicates that CO_2^+ in the $^2\Sigma^+_u$ state is linear, and it is reasonable to assume that the same is true for the normal state.

The present writer, in 1936–37, obtained a series of plates in the second order of the 30-foot grating in Ryerson Laboratory, using a water-cooled hollow cathode. The experiments were resumed in 1940 when a new grating with higher resolving power was available, and, with an improved hollow cathode, excellent third-order plates were obtained. These permitted the rotational analysis to be made, confirming Mulliken's prediction. The transition is, in fact, a $^2\Sigma^+_u \rightarrow {}^2\Pi_g$ transition in a linear molecule, where the $^2\Pi_g$ is case *a*, inverted.

EXPERIMENTAL

A large portion of the experimental work was done in collaboration with Dr. S. Mrozowski in Ryerson Laboratory in a joint program to cover the complete CO_2 spectrum from λ2800 through the visible.

The λ2900 band was photographed on Eastman Process plates. During the exposures, many of 50-hour duration, constant observation of the barometric pressure was required, since changes of over 2.5 mm Hg cause an appreciable shift of the lines at the high dispersion used. For similar reasons the temperature of the grating was kept constant to within 0.1°C. A bromine filter was used to cut out the second-order spectrum.

The dispersion was 0.22A/mm and the resolving power exceeded 300,000. The theoretical resolving power of 450,000 could not be attained because of the Doppler width of the lines at the high current density used. To obtain a rough estimate of the half-intensity width due to Doppler broadening, an approximate temperature of emission was determined as follows. The J value of the most intense line in each branch was

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[11] H. J. Henning, Ann. d. Physik 5, **13**, 599 (1932).

[12] G. Rathenau, Zeits. f. Physik **87**, 32 (1933).

[13] R. S. Mulliken, J. Chem. Phys. **3**, 720 (1935).

[14] C. A. Mackay, Phys. Rev. **24**, 319 (1924).

[15] W. C. Price and D. M. Simpson, Proc. Roy. Soc. **A169**, 501 (1939).

obtained, and an average value of $J_{\max}=38$ was found. There was considerable uncertainty in this determination because of the perturbations discussed later, but the average value should be sufficiently good for the rough approximation desired. The usual formula for the intensity of a line is[16] $I=Cie^{-BJ(J+1)/0.7T}$. The intensity factor i for a given transition may approximately be taken as $(aJ+b)$ (where a and b are small, since the summation rule for the intensity factor of all permissible transitions to or from a given level J requires that $\sum i \sim (2J+1)$). For high J values we may neglect the small additive quantities b in the expression for i and the 1 in the numerator of the exponent of the intensity formula. This approximation gives $T \backsimeq 2BJ_{\max}^{2}/0.7$. With $B=0.38$ cm^{-1} as shown later and $J_{\max}=38$, the effective rotational temperature of emission is found to be about 1600°K. The half-intensity Doppler breadth of the lines is then given by

$$\delta=1.67(\lambda_0/C)(2RT/\mu)^{\frac{1}{2}} \backsimeq 0.012\text{A},$$

corresponding to a resolving power of 2900/0.012 $\backsimeq$240,000, and indicating that the estimated temperature is probably somewhat high.

The source used was a water-cooled hollow cathode operated from a 2000-volt d.c. generator at currents up to 2.3 amperes. At pressures below 1 mm, the discharge was very steady and the CO and CO$^+$ bands were relatively weak. At higher pressures the discharge became very bright and arc-like, but the added intensity was mainly due to CO.

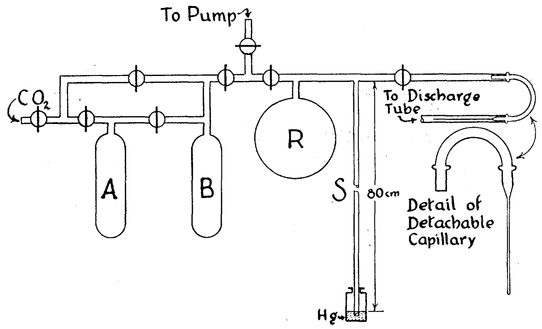

FIG. 2. Diagram of purifying system and flow control. Commercial CO$_2$ was purified by sublimation and resublimation between A and B by liquid nitrogen. The reservoir R and the capillary permitted regulation of the rate of flow of CO$_2$ into the discharge tube.

A series of exposures with flowing and stagnant gas was made with a Hilger E-3 quartz spectrograph to determine the effect that the rate of flow would have on the relative intensities of the CO$_2^+$ and CO bands. For the stagnant series the 3-liter discharge tube was filled with CO$_2$ to the proper pressure and then isolated from the pump. A 2-second exposure was taken as soon as the power was turned on and successive 2-second exposures were taken after the discharge had been going for 10 seconds, 1 minute, 5 minutes, 25 minutes and 2 hours without changing the gas. No change was found in the relative intensities of the CO$_2^+$ and CO bands in the various exposures. This indicated that equilibrium between the two gases is almost instantly attained and then maintained. Thus it was seen to be useless to keep a fast flow of CO$_2$ through the discharge tube, and in the subsequent exposures only a small amount was admitted through a leak to replenish that removed by the clean-up action of the discharge. This was a decided advantage considering the long exposures required and the time involved in the purification of the CO$_2$.

The arrangement shown in Fig. 2 was used to keep the pressure in the discharge tube constant. Commercial CO$_2$ was purified by sublimation and resublimation between A and B by liquid nitrogen, and stored as solid in B. In this manner no trouble was experienced from impurities and even the λ3064 OH band was absent. A Pyrex capillary was made as shown in the inset. It was held in place as shown in Fig. 2 by Picein wax and could easily be removed to alter its length for adjustment of the rate of flow. Further adjustment was provided by the 2-liter reservoir R into which CO$_2$ was admitted from B when required, so that the pressure registered by the barometer and safety-valve S at the head of the capillary would permit the proper flow. With this arrangement the tube operated for several hours without attention and required only occasional small additions of CO$_2$ into the reservoir to maintain its pressure constant within 3–5 cm Hg.

It was hoped that the band might appear more intensely in the presence of helium. However, a series of exposures made with various concentrations of the two gases at various pressures did not show any appreciable increase in the intensity of the CO$_2^+$ bands.

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[16] Cf. R. S. Mulliken, Rev. Mod. Phys. 3, 89 (1931).

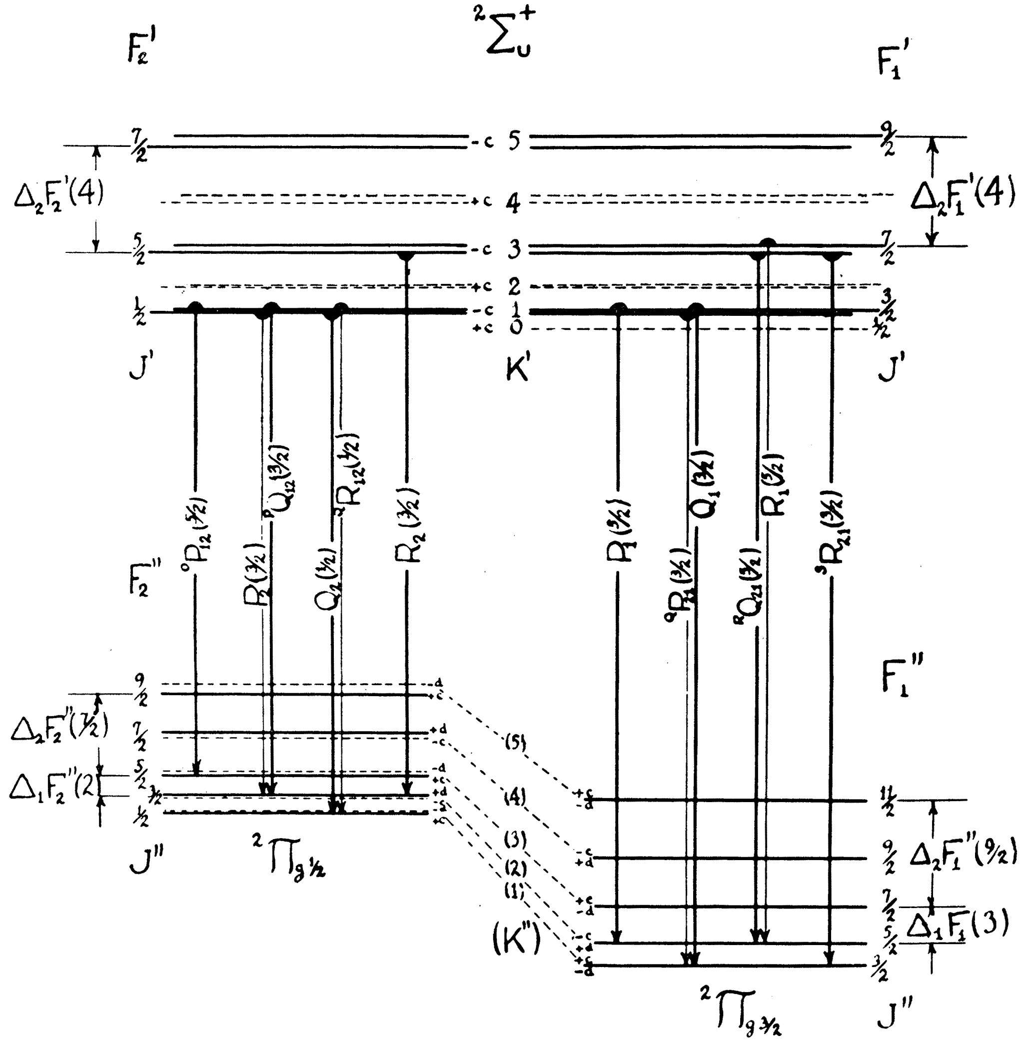

FIG. 3. Energy level diagram of the $^2\Sigma^+_u \rightarrow {}^2\Pi_g$ (inverted case *a*) transition. The + levels of the $^2\Sigma^+_u$ and the − levels of the $^2\Pi_g$ are missing. They are shown by dotted lines. The first line of each branch is given. The Λ-doubling of the $^2\Pi_{1/2}$ and the spin doubling of the $^2\Sigma^+_u$ are greatly exaggerated.

Three plates with different exposures were measured on a linear dispersion scale at the Massachussetts Institute of Technology with Professor Harrison's machine. The second-order iron lines at λ4352.738 and λ4315.087, one near the beginning and the other near the end of the band, were used to set the machine to the proper dispersion and wave-length range. Six readings were obtained for each line, since the plates were measured both forward and backwards. The average of the six readings was then taken, corrected for the non-linearity of the dispersion of the grating, and reduced to vacuum. The correction curve for the deviation from true linear dispersion was obtained directly from the grating formula. The scarcity of standard iron lines in the region covered by the band did not permit the construction of an experimental correction curve, but the theoretical curve used should be sufficiently good to give the absolute wave numbers of the lines to a few hundredths of a wave number throughout the 30A region which includes the band. A greater reliability than this cannot be expected, as the measurements of S. Mrozowski on other bands of CO_2^+ over a wide spectral region have shown. The combination

TABLE I. *Wave numbers in 2900*A *band of* CO_2^+.

OBSERVED WAVE NUMBERS OF LINES	INT.†	ASSIGNMENT*		
34404.48	1	$^{O}P_{12}$		
11.17	2*w*	——		
11.66	1			
14.50	1			
15.59	1			
16.82	1			
21.56	1	74		
22.47	1			
23.34	1			
24.50	1			
24.91	2	72		
26.11	1			
27.96	1	70		
28.56	1			
29.08	1			
30.91	1	68		
31.78	1			
32.95	1			
33.83	2	66		
35.11	1			
36.42	2	64		
37.17	1			
37.66	1			
38.74	1			
39.30	2	62		
40.37	1			
41.05	1			
42.01	2	60		
42.63	1			
44.61	2	58		
45.33	1			
47.22	3	56		
48.12	1			
49.80	4	54		
51.47	1			
52.26	4	52		
54.83	4	50		
56.16	1			
57.40	5	48		
59.90	5	46		
62.45	5	44		
65.00	5	42		
67.80	5	40		
68.34	1			
70.56	1	38		
71.91	5	36		
75.00	4	34		
75.96	3	32		
78.96	2	30	$^{P}Q_{12}$	P_2
81.51	1		——	—
81.71	5	28	69	
82.95	1		67	
84.44	5	26	65	
85.31	2		63	
85.55	1			59
86.94	6*vw*	24	61	
87.88	6		59	57
89.01	6		57	55
89.73	6	22		
90.06	7		55	53
91.14	7		53	51
92.18	8		51	49
92.52	6	20		
93.21	8		49	47
94.21	8		47	45
94.68	5			
95.14	8*w*		45	43
95.86	5			
96.31	9		43	41
97.30	9		41	39
98.44	8*w*		39	37
99.54	8*w*		35	35
34500.52	8		31	33
01.16	8		33	
01.68	8			31
02.13	8		29	
02.90	8			29
03.33	9		27	
03.98	7			
04.28	7			27?
04.54	9		25	
04.92	7			
05.59	9		23	
05.81	8			25?
06.04	8			
06.81	9		21	23?
07.11	6*w*			
07.72	7			
08.07	8*w*			
08.41	5			
08.77	6			
09.07	6			
09.41	8			
09.91	7			
10.28	8			
10.78	7			
11.32	7			
11.78	6			
12.21	8			
12.46	7			
12.94	5			
13.50	6			
13.75	5			
14.16	5			
14.50	4			
14.68	6			
15.06	7			
15.44	5			
15.98	6			
16.35	7			
17.06	8			
17.54	10*vvw*		(*b*)	
18.48	7*vw*			
19.28	6			
20.06	6			
20.80	6*vw*			
21.35	6			
21.94	6			
22.39	8	$^{Q}R_{12}$	Q_2	
22.84	8	——	—	
23.01	9			
23.28	8	20?		
23.56	8	22		
23.81	8			
24.12	8	24		
24.38	8	26	20	
24.72	8	28, 30	22	
25.48	10*vvw*		24, 26, 28	
25.76	10		30	
26.14	9		32	
26.67	10*w*	32, 34	34	
27.08	9		36	
27.61	9		38	
28.10	9		40	
28.57	9	38	42	
29.09	9	40	44	
29.60	9	42	46	
30.00	9	44	48	
30.53	9	46	50	
31.03	9	48	52	
31.50	9	50	54	
31.83	9	52	56	
32.21	8	54		
32.82	8			
33.05	7			
33.51	7			
33.93	6*w*			
34.27	5			
34.81	5			
35.29	2			
35.69	3			
36.13	3			
36.33	3			
36.64	3			
37.04	3			
37.66	2			
38.15	3			
38.38	2			
39.19	3			
39.64	3			
40.11	2			
40.76	3			
41.29	4			
41.97	4	R_2		
42.33	2	—		
42.80	5	21		
43.28	3			
43.95	6	23		
44.78	2			
45.35	6	25		
46.16	2			
47.05	7*w*	27		
47.74	2			
48.08	3			
48.93	7	29		
49.33	4			
49.75	2			
50.13	2			
50.80	7	31		
51.33	3			
51.99	3			
52.52	2			
52.84	7	33		
53.49	2			
54.13	3			
54.82	8	35		
55.55	4*w*			
56.32	4			
56.79	7	37		
57.30	3			
57.61	3			
58.01	3			
58.30	2			
58.82	7	39		
59.62	2			
60.04	1			
60.33	2			
60.46	2			
60.83	5	41		
61.30	2			
61.59	2			
61.99	2			
62.84	7*w*	43		
63.36	3			
63.97	4			
64.84	7	45		
65.25	4			
65.51	2			
66.00	2			
66.47	4			
66.83	6	47		
67.25	3			
68.85	6	49		
69.31	2			
69.61	3			
69.91	3			
70.33	1			
70.79	5	51		
71.36	3			
71.68	4			
72.31	1			
72.76	5	53		
73.64	2*vw*			
74.67	5	55		
75.12	2			
75.65	3			
76.08	1			
76.51	4	57		
78.35	3			
78.66	2	59		
79.50	2			
80.13	3			
80.45	2			
80.87	2			
81.12	2			
81.77	4			
82.25	3*w*			
82.95	3*w*			
83.28	5			
83.73	5			
84.16	4			
85.17	6*vw*	(d_1)		
85.88	6*vw*	(d_2)		
86.46	1			
86.87	2			
87.24	2			
87.59	2			
87.99	1	P_1		
88.44	2	——		
88.97	2	76		
89.81	2*w*			
90.14	2*w*			
91.05	1			
91.41	1			
91.93	2	74		
92.23	2			
92.80	1			
93.09	1			
93.37	1			
94.26	1			
94.70	2	72		
96.34	2			
97.26	3	70		
97.60	2			
97.77	2			
99.02	3			
99.72	3	68		
34600.29	2			
00.93	1			
01.29	1			
01.78	1			
02.21	3	66		
02.74	1			
03.16	1			
03.42	1			
03.30	3*w*	64		
05.43	1			
06.09	2			
06.75	4	62		
07.15	3			
07.74	3			
08.61	2			
09.01	4	60		
09.52	2			
10.41	1			
11.17	4	58		
11.89	1			
12.19	2			
12.83	2			
13.38	5	56		
14.56	1			
15.10	2			
15.55	6	54		
16.14	3		(*f*)	
16.53	5			
17.72	6	52		
18.22	2			
18.82	2			
19.89	7	50		
21.35	1			
21.71	2			
22.09	6	48		
23.02	2			
23.52	2			
24.25	7	46		
25.60	1			
26.47	7	44		
27.30	2			
28.72	6	42		
29.52	1			
29.96	2			
30.18	1			
31.23	6	40		
32.69	2			
33.70	1	38		
34.76	6	36		
35.24	1			
37.58	6	34		
38.28	4	32		
39.54	1			
40.22	1			
41.08	4	30		
41.45	2			
42.71	1			
43.11	2			
43.60	7	28		
44.75	3			
45.29	2*w*			
46.15	6	26		
46.60	1			
47.50	3			
48.16	1		Q_1	
48.47	7	24	——	
48.77	4			
49.10	2			
49.37	2		71	
50.01	3			
50.47	4		69	
51.08	7	22		
51.48	4		67	
51.97	4			
52.35	5		65	
52.69	2			$^{Q}P_{21}$
53.11	5		63	——

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† The letters *w*, *vw*, and *vvw* after the intensities mean wide, very wide and very very wide.

* Under the heading of "Assignment" the *J* numbering for the lines of the various branches is given. For example, 41 means $J = 41\frac{1}{2}$. The letters in parentheses have the meanings given in the text.

TABLE I—*Continued.*

Observed Wave Numbers of Lines	Int.†	Assignment*		
53.29	4			
53.68	7	20		59
53.95	6		61	
54.45	5			57
54.79	7		59	
55.20	5			55
55.37	7		57	
55.84	6			53
56.12	8		55	
56.41	7			51
56.77	8		53	
57.14	7			49
57.47	8		51	
57.88	6			47
58.12	8		49	
58.62	6			45
58.82	8		47	
59.32	6			43
59.46	9		45	
60.01	6			41
60.17	9		43	
60.72	7			39
60.88	9		41	
61.42	8			37
61.92	9		39	
62.39	9		35	35
62.95	9*w*		37, 31	33
63.31	7			
63.74	8		33	
63.99	8			31
64.27	8		29	
64.68	6			
65.02	9			29
65.12	9		27	
65.79	8*vw*			
66.00	8			27
66.55	8			
67.07	9		23	
67.51	8			25
68.13	9		21	
68.76	6			23?
69.23	9*w*		19?	
69.75	5			21?
69.99	5			
70.43	8			
70.73	7			
71.01	6			
71.29	5			
71.68	7			
72.27	5			
72.70	6			
72.99	7*w*			
73.72	4			
74.16	6			
74.63	3			
75.30	5			
76.34	5			
76.70	6			
77.11	4			
77.48	6			
78.25	10*vvw*	(*a*)		
79.16	2			
79.73	2			
80.06	3			
81.52	2			
81.99	3			
82.52	3			
83.02	5*w*			
83.44	5	R_1	$^RQ_{21}$	
83.71	6	——	——	
84.06	6	18		
84.44	7	20		
84.89	7	22		
85.59	7	24	18	
86.10	8	26?	20	
86.92	10*vw*	30	22, 24, 26	
87.38	9		28	
87.59	6			
87.88	9		30	
88.47	9		32	
89.24	10*vw*	32, 34	34	
89.93	9		36	
90.70	9		38	
91.47	9	36	40	
91.87	7	38		
92.34	9*w*	40	42	
93.13	9	42	44	
93.96	9	44	46	
94.77	8		48	
95.62	8		50	
96.44	8		52	
87.27	8	54		
98.11	7*w*	56		
98.79	7			
99.14	6			
99.52	6			
99.81	6			
34700.19	6			
00.59	7			
01.22	6			
01.38	5			
01.79	6			
02.12	7*w*	$^SR_{21}$		
03.08	6*w*	——		
03.52	5			
03.82	5	21?		
04.11	6			
04.78	3			
05.46	7	23		
06.16	3			
07.07	5*w*	25		
08.12	3			
08.98	7	27		
09.67	2			
10.09	3			
11.01	7	29		
12.05	4			
13.09	7	31		
13.81	3			
14.32	2			
14.75	4			
15.39	7	33		
16.41	3			
16.82	4			
17.26	4			
17.58	7	35		
18.06	3			
18.79	3			
19.18	4			
19.87	7*w*	37		
20.45	4			
21.16	3			
22.17	6	39		
22.83	5			
23.43	3			
23.91	5			
24.46	6	41		
24.92	6			
25.48	3			
25.94	5			
26.82	7	43		
27.20	4			
27.51	3			
27.91	3			
28.50	4			
29.12	6	45		
29.40	5			
30.28	4			
30.90	3			
31.44	5	47		
32.06	4			
32.87	3			
33.77	5	49		
35.51	2			
36.14	4*w*	51		
36.85	3			
37.38	2			
37.83	2			
38.48	5	53		
39.11	4			
39.58	4			
40.96	4*w*	55		
41.58	5			
42.11	4			
42.66	4			
43.09	5	57		
43.59	5			
43.88	5			
44.35	5			
44.81	6			
45.41	5*vvw*	59	(*c*)	
46.39	3			
46.81	3			
47.44	3*w*	61		
48.74	3			
49.56	4			
50.10	2			
50.91	3			
51.58	3			
52.03	2			
53.01	3			
53.52	2			
54.12	2			
54.71	1			
55.06	3*w*			
55.85	1			
56.27	1			
57.11	4			
58.26	2			
58.94	2*w*			
60.63	2			
61.07	4			
62.33	3			
62.61	3			
63.21	3			
63.62	3			
63.96	4			
64.49	4			
64.78	4			
65.58	4*w*			
66.10	3			
66.67	5			
67.21	4*vw*			
67.72	4			
68.52	6			
69.23	3			
69.63	4			
70.27	5			
70.59	5			
71.40	4*w*			
72.15	4			
72.69	5			
73.45	5			
73.97	5			
74.52	5			
74.95	5			
75.38	4			
75.70	3			
76.02	4			
76.43	5			
76.67	6			
77.04	6			
77.50	6			
77.81	6			
78.06	6			
78.67	9	(*e*)		

differences [see Eqs. (3) and (4)] should show a greater accuracy since they involve lines which are closer together than the interval between the iron standards. Two other iron lines, namely λ4325.768 and λ4307.91 provided a check on the accuracy of the corrections. Table I gives the wave numbers of the lines, together with the estimated intensities, obtained from the amplitudes on the photometric trace.

ANALYSIS

General considerations

The schematic energy level diagram (Fig. 3) shows the first line of each branch for a $^2\Sigma^+{}_u \rightarrow {}^2\Pi_g$ transition with case *a* inverted $^2\Pi_g$. The antisymmetric levels should be missing because of the zero spin of the oxygen nuclei. These levels are indicated by dotted lines; they correspond to the + rotational levels in the $^2\Sigma^+{}_u$ and to the − rotational levels in the $^2\Pi_g$ state.

In accordance with the selection rules $\Delta J = 0$ or ± 1 and $+ \rightleftarrows -$, the band should consist of two sub-bands with six branches in each, the separation between the two sub-bands being approximately equal to A, the spin-orbit coupling coefficient for the $^2\Pi_g$ state. The coefficient A is negative for inverted $^2\Pi$ ($^2\Pi_{3/2}$ lies deeper). The P_2, $^PQ_{12}$ and the Q_2, $^QR_{12}$ branches in the ($^2\Sigma$, $^2\Pi_{1/2}$) sub-band and the $^QP_{21}$, Q_1 and the $^RQ_{21}$, R_1 branches in the ($^2\Sigma$, $^2\Pi_{3/2}$) sub-band should form four series of close pairs [cf. Fig. 3 and Eqs. (1)] with separations $\Delta\nu_{12}(K)=\gamma(K+\frac{1}{2})$ where γ is a small constant; $\Delta\nu_{12}$ corresponds to the spin doubling of the $^2\Sigma^+{}_u$ levels.[17]

The total energy terms are given by[16,17]

$$^2\Pi_{1/2}\colon\ T_{2c}(J)=(T_0''-\tfrac{1}{2}A-\tfrac{1}{4}B_2)-\tfrac{1}{2}p(J+\tfrac{1}{2})+B_2J(J+1)+DJ^2(J+1)^2\cdots, \tag{1a}$$

$$^2\Pi_{1/2}\colon\ T_{2d}(J)=(T_0''-\tfrac{1}{2}A-\tfrac{1}{4}B_2)+\tfrac{1}{2}p(J+\tfrac{1}{2})+B_2J(J+1)+DJ^2(J+1)^2\cdots, \tag{1b}$$

$$^2\Pi_{3/2}\colon\ T_{1c}(J)=(T_0''+\tfrac{1}{2}A-\tfrac{9}{4}B_1)+B_1J(J+1)+DJ^2(J+1)^2\cdots=T_{1d}(J), \tag{1c}$$

$$\begin{aligned}^2\Sigma;\ J=K+\tfrac{1}{2}\colon\ T_1(J)&=T_0'+\tfrac{1}{2}\gamma K+BK(K+1)+DK^2(K+1)^2\cdots\\&=T_0'+\tfrac{1}{2}\gamma(J-\tfrac{1}{2})+B(J-\tfrac{1}{2})(J+\tfrac{1}{2})+D(J-\tfrac{1}{2})^2(J+\tfrac{1}{2})^2\cdots,\end{aligned} \tag{1d}$$

$$\begin{aligned}^2\Sigma;\ J=K-\tfrac{1}{2}\colon\ T_2(J)&=T_0'-\tfrac{1}{2}\gamma(K+1)+BK(K+1)+DK^2(K+1)^2\cdots\\&=T_0'-\tfrac{1}{2}\gamma(J+\tfrac{3}{2})+B(J+\tfrac{1}{2})(J+\tfrac{3}{2})+D(J+\tfrac{1}{2})^2(J+\tfrac{3}{2})^2\cdots\end{aligned} \tag{1e}$$

where γ is as given above and p is the Λ-doubling constant [$\Delta\nu_{dc}(J)=p(J+\frac{1}{2})$ with p positive in this case; the Λ-doubling of the $^2\Pi_{3/2}$ is expected to be negligibly small[17]]. Schaffer[18] has shown that for linear triatomic molecules D is given by the same type of formula $D=4B^3/\omega^2$ as for diatomic molecules, where here ω refers to the totally symmetrical vibration frequency. Using $B=0.38$ cm^{-1} as shown later, and $\omega=1305$ cm^{-1},[19] one obtains $D=1.3\times10^{-7}$ cm^{-1} for the $^2\Pi_g$ state, and may expect nearly the same for the $^2\Sigma^+{}_u$ state, since the B values of the two states are almost equal.

The equations for the band lines of the ($^2\Sigma^+{}_u$, $^2\Pi_{1/2}$) sub-band in such a transition are:[16,17]

$$\begin{aligned}^OP_{12}(J)=T_1'(J-1)-T''_{2c}(J)&=\nu_2+\tfrac{1}{4}(p-3\gamma+3B)-(2B+B_2-\tfrac{1}{2}p-\tfrac{1}{2}\gamma)J\\&\quad+(B-B_2)J^2-2(2D'+D'')J^3\cdots,\end{aligned} \tag{2a}$$

$$\begin{aligned}P_2(J)=T_2'(J-1)-T''_{2d}(J)&=\nu_2-\tfrac{1}{4}(p+\gamma+B)-(B_2+\tfrac{1}{2}p+\tfrac{1}{2}\gamma)J\\&\quad+(B-B_2)J^2-2D''J^3\cdots,\end{aligned} \tag{2b}$$

$$^PQ_{12}(J)=T_1'(J)-T''_{2d}(J)=\nu_2-\tfrac{1}{4}(p+\gamma+B)-(B_2+\tfrac{1}{2}p-\tfrac{1}{2}\gamma)J+(B-B_2)J^2-2D''J^3\cdots, \tag{2c}$$

$$\begin{aligned}Q_2(J)=T_2'(J)-T''_{2c}(J)&=\nu_2+\tfrac{1}{4}(p-3\gamma+3B)+(2B-B_2+\tfrac{1}{2}p-\tfrac{1}{2}\gamma)J\\&\quad+(B-B_2)J^2+2(2D'-D'')J^3\cdots,\end{aligned} \tag{2d}$$

$$\begin{aligned}^QR_{12}(J)=T_1'(J+1)-T''_{2c}(J)&=\nu_2+\tfrac{1}{4}(p+\gamma+3B)+(2B-B_2+\tfrac{1}{2}p+\tfrac{1}{2}\gamma)J\\&\quad+(B-B_2)J^2+2(2D'-D'')J^3\cdots,\end{aligned} \tag{2e}$$

$$\begin{aligned}R_2(J)=T_2'(J+1)-T''_{2d}(J)&=\nu_2-\tfrac{1}{4}(p+5\gamma-15B)+(4B-B_2-\tfrac{1}{2}p-\tfrac{1}{2}\gamma)J\\&\quad+(B-B_2)J^2+2(4D'-D'')J^3\cdots.\end{aligned} \tag{2f}$$

The equations for the band lines of the ($^2\Sigma^+{}_u$, $^2\Pi_{3/2}$) sub-band are obtained from these by replacing the subscripts of T'', ν_2 and B_2 by 1 and putting $p=0$ since the Λ-doubling for the $^2\Pi_{3/2}$ state is negligible. The notation for the branches is then P_1, $^QP_{21}$, Q_1, $^RQ_{21}$, R_1, and $^SR_{21}$, respectively, in order of increasing frequency, as in Eqs. (2). The difference $\nu_1-\nu_2$ is approximately A, as mentioned in the second paragraph of this section. The branches of both sub-bands should have intensities $Q_i>R_i>P_i$;[16] thus the close pairs should consist of lines of different intensity. The coefficient D will introduce a correction of significance only in the J^3 terms of the equations for the band lines, as given above, and then only for high J values. The J^2 term produces a contribution of the order of only 10^{-3} cm^{-1} for $J=70$, while the J^4 term has $(D'-D'')$ as coefficient, and this is very nearly equal to zero.

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[17] Cf. R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

[18] W. H. Schaffer, unpublished work.

[19] S. Mrozowski, private communication.

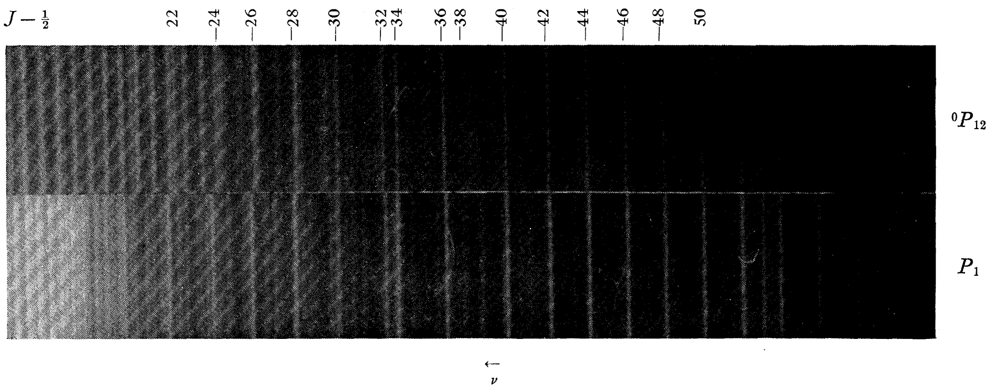

FIG. 4. Enlargement of the perturbed regions of the $^{O}P_{12}$ and P_1 branches (see Fig. 1 and the text), showing displacements and weakenings between $J=28\frac{1}{2}$ and $J=42\frac{1}{2}$.

Adjacent lines in a branch correspond to a difference in J of two units on account of the missing levels. If we assume[13] $B \backsimeq B_1 \backsimeq B_2$ and neglect the small constants γ and p and the terms in D, the spacing between the lines is seen to be $6B$, $2B$, $2B$, $-2B$, $-2B$, and $-6B$, respectively, in the order given above for the various branches of each sub-band.

Observed spectrum

The observed spectrum (see Fig. 1) is in agreement with these features. It consists of two well-defined sub-bands with six branches in each. The outer branches in each sub-band have fairly wide separation between lines and are free from overlapping above $J=20\frac{1}{2}$,[20] but the inner branches, which may be identified with the series of pairs mentioned previously, do not present such a simple appearance. This would be anticipated on account of their closer spacing, the small spin doubling of the $^2\Sigma^+{}_u$, and the presence of the low J members of the widely spaced branches, all of which effect a considerable overlapping. Indeed, the weak member of each pair is usually fused with a strong line of slightly different J. The weak branch $^{Q}P_{21}$ is, however, well resolved from its companion Q_1 at high J values, and a few lines of R_1 begin to be resolved beyond $J=52\frac{1}{2}$.

The nearly uniform spacing of the lines in each of the various branches (aside from the perturbations discussed later) and the consequent absence of heads (see Fig. 1), at once indicates approximate equality in the rotational constants of the upper and lower states. The observed spacing is approximately three times as large for the wide branches as for the close branches, in agreement with the theoretical considerations given above.

Combination relations

After we had thus established the plausibility of a $^2\Sigma^+{}_u \rightarrow {}^2\Pi_g$ transition, the normal line of attack was followed to confirm the belief. The first step usually consists of getting the double-differences [see Fig. 3 and Eqs. (2)] from combination relations. Those for the lower state are

$$^2\Pi_{1/2}:\ \Delta_2 F_{2c}''(J) \equiv T_{2c}''(J+1) - T_{2c}''(J-1) = {}^{Q}R_{12}(J-1) - {}^{O}P_{12}(J+1) \quad \text{with } (J+\tfrac{1}{2}) \text{ even,} \tag{3a}$$

$$:\ \Delta_2 F_{2d}''(J) \equiv T_{2d}''(J+1) - T_{2d}''(J-1) = R_2(J-1) - P_2(J+1) \quad \text{with } (J+\tfrac{1}{2}) \text{ odd,} \tag{3b}$$

$$^2\Pi_{3/2}:\ \Delta_2 F_1''(J) \equiv T_1''(J+1) - T_1''(J-1) = R_1(J-1) - P_1(J+1) \quad \text{with } (J+\tfrac{1}{2}) \text{ even,} \tag{3c}$$

$$:\ \Delta_2 F_1''(J) \equiv T_1''(J+1) - T_1''(J-1) = {}^{S}R_{21}(J-1) - {}^{Q}P_{21}(J+1) \quad \text{with } (J+\tfrac{1}{2}) \text{ odd.} \tag{3d}$$

By virtue of the missing levels, each of these expressions gives only a set of alternate and not consecutive $\Delta_2 F''$'s, as shown by the designation $(J+\frac{1}{2})$ odd (or even). This means that an

---

[20] As usual, J is written for J''.

unambiguous selection of $\Delta_2 F'''$s cannot be made directly from them since they are all different and so cannot be used in a mutual comparison.

A more favorable situation results when the double-differences for the upper state are considered. With the combination relations

$$
\begin{aligned}
{}^2\Sigma^+{}_u:\ \Delta_2 F_1'(K=J-\tfrac{1}{2}) &\equiv T_1'(K+1) \\
&\quad -T_1'(K-1) = {}^QR_{12}(J) - {}^OP_{12}(J) \\
&\quad = R_1(J) - P_1(J) \text{ with } K \text{ even}, \qquad (4a) \\
:\ \Delta_2 F_2'(K=J+\tfrac{1}{2}) &\equiv T_2'(K+1) \\
&\quad -T_2'(K-1) = R_2(J) - P_2(J) \\
&\quad = {}^SR_{21}(J) - {}^QP_{21}(J) \text{ with } K \text{ even}, \qquad (4b)
\end{aligned}
$$

there is the possibility of a check, as indicated. Each of the $\Delta_2 F_1''$s can be obtained in two ways, which should presumably enable one to make the correct identifications. In the actual analysis, however, many possible differences were found which agreed within the error of measurement and no final choice could be made with certainty by using Eqs. (4).

Another factor which greatly increased the difficulty of a correct determination is the following. It can be seen from Eqs. (3) and (4) that the double-differences are to be obtained by combining lines of the wide branches with lines of the *weak* component of the double branches. The latter, as already mentioned, were not readily identified initially because they are usually merged with lines of the stronger branch. Further uncertainty was at first introduced by the perturbations which affect the upper state.

TABLE II.

$J-\frac{1}{2}$	$P_1(J)$ $-{}^OP_{12}(J)$	${}^RQ_{21}(J)$ $-Q_2(J)$	Av. $\Delta(J)$	$\Delta(J+2)$ $-\Delta(J)$
20	161.16	161.21	161.18	
22	161.35	161.38	161.36	0.18
24	161.53		161.53	0.17
26	161.71		161.71	0.18
28	161.89	161.90	161.90	0.19
30	162.10	162.12	162.11	0.21
32	162.32	162.33	162.32	0.21
34	162.58	162.57	162.58	0.26
36	162.85	162.85	162.85	0.27
38	163.14	163.09	163.12	0.27
40	163.43	163.37	163.40	0.28
42	163.72	163.77	163.74	0.34
44	164.02	164.04	164.03	0.29
46	164.55	164.36	164.36	0.33
48	164.69	164.77	164.73	0.37
50	165.06	165.09	165.08	0.35
52	165.46	165.41	165.44	0.36
54	165.75	165.77	165.76	0.32
56	166.16			
58	166.56			
60	167.00			
62	167.45			
64	167.88			
66	168.38			

Identification of the lines

Fortunately, however, the perturbations observed in the ${}^OP_{12}$ and the P_1 branches (see Fig. 4) permitted an identification of lines of equal J' in these two branches, though not a determination of their absolute J numbering. The correct ordering of lines according to J was found by taking the differences [see Eqs. (1) and (2)]

$$
\begin{aligned}
\Delta(J) &= P_1(J) - {}^OP_{12}(J) = T_{2c}''(J) - T_1''(J) \\
&= [-A + \tfrac{9}{4}B_1 - \tfrac{1}{4}B_2] - \tfrac{1}{2}p(J+\tfrac{1}{2}) \\
&\quad + (B_2 - B_1)J(J+1) \text{ with } (J+\tfrac{1}{2}) \text{ odd} \\
&= \text{const.} + aJ + bJ^2. \qquad (5a)
\end{aligned}
$$

The values $\Delta(J)$ should change smoothly with J (giving constant second differences) and thus provide an identification of corresponding lines in the two branches even in the region of the perturbations, since the relations are independent of the upper state and the lower state is not perturbed. The values of $\Delta(J)$ and also of $\Delta(J+2)-\Delta(J)$ are given in Table II, which was obtained after ordering the lines so as to give Δ's varying with J in the predicted manner. Exactly the same values should, according to Fig. 3, be obtained from the combination ${}^RQ_{21}(J)-Q_2(J)$, and were actually obtained, thus providing a combination relation check. In this manner it was possible, for example, to locate the very weak and strongly displaced lines, ${}^OP_{12}(38\tfrac{1}{2})$ and $P_1(38\tfrac{1}{2})$, whose existence was not suspected from an inspection of the spectrograms (cf. Fig. 4).

Similarly, the combinations

$$
\begin{aligned}
\Gamma(J) &= {}^SR_{21}(J) - R_2(J) = Q_1(J) - {}^PQ_{12}(J) \\
&= T_{2d}''(J) - T_1''(J) \text{ with } (J+\tfrac{1}{2}) \text{ even} \qquad (5b)
\end{aligned}
$$

establish a correct ordering for the lines of these four branches. Unfortunately, however, these two sets of orderings are independent of each other and do not help to determine relations between the J values of the two sets of branches.

Assignment of J values

After one had obtained the proper ordering for the lines in each of the strong branches it was

TABLE III.

$^2\Pi_{1/2}$: VALUES OF $\Delta_1 F''_{2d}(J) - \Delta\nu_{dc}(J+\frac{1}{2})$				$^2\Pi_{3/2}$: VALUES OF $\Delta_1 F_1''(J)$			
J	CALC.*	$^PQ_{12}(J-\frac{1}{2})$ $-{}^OP_{12}(J+\frac{1}{2})$	$R_2(J-\frac{1}{2})$ $-Q_2(J+\frac{1}{2})$	J	CALC.*	$^SR_{21}(J-\frac{1}{2})$ $-{}^RQ_{21}(J+\frac{1}{2})$	$Q_1(J-\frac{1}{2})$ $-P_1(J+\frac{1}{2})$
20	15.55	15.55	15.56	18	14.04	13.93	14.02
22	17.07	17.08	17.13	20	15.56	15.69	15.55
24	18.58	18.65	18.60	22	17.08	17.19	17.05
26	20.11	20.10	20.10	24	18.59	18.54	18.60
28	21.62	21.62	21.61	26	20.11	20.15	20.05
30	23.14	23.17	23.17	28	21.62	21.60	21.59
32	24.63	24.56	24.66	30	23.14	23.13	23.19
34	26.15	26.16	26.17	32	24.66	24.62	24.67
36	27.67	27.63	27.74	34	26.12	26.15	26.16
38	29.19		29.18	36	27.69	27.65	27.63
40	30.71	30.64	30.72	38	29.15	29.17	29.25
42	32.21	32.30	32.26	40	30.71	30.70	30.69
44	33.72	33.86	33.75	42	32.12	32.12	32.16
46	35.24	35.24	35.24	44	33.75	33.69	33.70
48	36.73	36.81	36.83	46	35.26	35.16	35.21
50		38.31	38.32	48	36.77	36.67	36.73
52		39.86	39.76	50	38.23	38.15	38.23
54		41.33	41.26	52		39.70	39.75
56		42.84	42.84	54		41.21	41.22
58		44.40	44.30	56		42.85	42.74

* This column was calculated from Mrozowski's $\Delta_2 F''$'s with the help of Eqs. (6), (7), and (8).

possible to obtain the combination differences[21]

$$\begin{aligned} {}^2\Pi_{1/2}\colon\ & {}^PQ_{12}(J-\tfrac{1}{2}) - {}^OP_{12}(J+\tfrac{1}{2}) \\ & = R_2(J-\tfrac{1}{2}) - Q_2(J+\tfrac{1}{2}) \\ & = T''_{2c}(J+\tfrac{1}{2}) - T''_{2d}(J-\tfrac{1}{2}) \\ & = \Delta_1 F''_{2c}(J) - \Delta\nu_{dc}(J-\tfrac{1}{2}) \\ & = \Delta_1 F''_{2d}(J) - \Delta\nu_{dc}(J+\tfrac{1}{2}), \end{aligned} \tag{6a}$$

$$\begin{aligned} {}^2\Pi_{3/2}\colon\ & Q_1(J-\tfrac{1}{2}) - P_1(J+\tfrac{1}{2}) \\ & = {}^SR_{21}(J-\tfrac{1}{2}) - {}^RQ_{21}(J+\tfrac{1}{2}) \\ & = T_1''(J+\tfrac{1}{2}) - T_1''(J-\tfrac{1}{2}) \\ & = \Delta_1 F_1''(J), \text{ since } p_1 = 0, \end{aligned} \tag{6b}$$

which seemed especially suitable for the determination of J, since in each case a combination relation check is offered and the sequence of the lines was unambiguously known from the combination relations (5). But, even so, there were several combination sets in sufficiently close agreement so that no definite selection could be made. Nevertheless, a tentative assignment of J could be made for these branches.

Fortunately, another line of inquiry was available by this time. Mrozowski,[22] working concurrently with the writer in this laboratory, as already mentioned, had been able to obtain a rotational analysis of a series of longer wavelength CO_2^+ bands previously studied by Smyth[23] and by Schmid.[24] His system of bands belongs to a $^2\Pi_u \rightarrow {}^2\Pi_g$ transition, and because he has been able to identify several members of a v' progression his $\Delta_2 F''$'s and rotational constants for the lower state ($^2\Pi_g$) are very accurate. The values he obtained[19] are: $B_1'' = 0.3796$ cm^{-1}, $B_2'' = 0.3812$ cm^{-1} and $p = +0.004$ cm^{-1} (Λ-doubling coefficient for the $^2\Pi_{1/2g}$ levels).

It was hoped that Mrozowski's lower $^2\Pi_g$ state would be the same as that for the λ2900 band. Since the double-differences [Eqs. (3)] were not reliable, no comparison with his $\Delta_2 F''$'s was possible at first. Instead, $\Delta_1 F''$'s were calculated from Mrozowski's double-differences and his B values with the help of the equations [cf. Eqs.

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[21] It will be noticed that this is not the usual definition of the single-differences (i.e., $F(J+\frac{1}{2}) = T(J+1) - T(J)$) in which the assignment of J is that of the lower level involved. The number J used here is the average value of the J's of the two rotational levels whose separation is given, just as in the case of the usual definition of the double-differences. This designation is preferred here by virtue of its greater consistency with that for $\Delta_2 F(J)$ and the greater symmetry of the resulting equations.

[22] S. Mrozowski, Phys. Rev. **59**, 923A (1941).

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

[24] R. F. Schmid, Phys. Rev. **41**, 732 (1932).

TABLE IV.

$^2\Pi_{1/2}$: VALUES OF $\Delta_2F_2''(J)$						$^2\Pi_{3/2}$: VALUES OF $\Delta_2F_1''(J)$					
$J-\frac{1}{2}$	$\Delta_2F_{2c}''(J)$*	${}^QR_{12}(J-1)$ $-{}^OP_{12}(J+1)$†	$J-\frac{1}{2}$	$\Delta_2F_{2d}''(J)$*	$R_2(J-1)$ $-P_2(J-1)$†	$J-\frac{1}{2}$	$\Delta_2F_1''(J)$*	$R_1(J-1)$ $-P_1(J+1)$†	$J-\frac{1}{2}$	$\Delta_2F_1''(J)$*	${}^SR_{21}(J-1)$ $-{}^QP_{21}(J+1)$†
19	30.48	30.49	22	35.08	34.99	17	27.34	27.30	22	34.92	35.06
21	33.54	33.55	24	38.13	38.14	19	30.37	30.38	24	37.94	37.95
23	36.60	36.62	26	41.18	41.07	21	33.40	33.36	26	40.98	41.07
25	39.63	39.69	28	44.22	44.15	23	36.43	36.42	28	44.01	
27	42.67	42.67	30	47.27	47.25	25	39.46	39.44	30	47.04	47.02
29	45.73	45.76	32	50.31	50.28	27	42.50		32	50.08	50.14
31	48.77	48.76	34	53.34	53.30	29	45.53		34	53.11	53.00
33	51.81		36	56.41	56.41	31	48.56		36	56.14	56.16
35	54.87		38	59.45	59.49	33	51.60	51.66	38	59.16	59.15
37	57.92		40	62.49	62.51	35	54.62		40	62.18	62.17
39	60.95		42	65.52		37	57.65	57.77	42	65.20	65.20
41	64.00	64.09	44	68.53	68.63	39	60.67	60.64	44	68.26	68.20
43	67.01	66.95	46	71.57	71.63	41	63.69	63.62	46	71.28	71.24
45	70.04	70.10	48	74.60	74.65	43	66.72	66.66	48	74.30	74.30
47	73.08	73.13	50	77.66	77.71	45	69.77	69.71	50	77.32	77.36
49	76.13	76.20	52	80.69	80.73	47	72.79	72.75			
51	79.17	79.20	54	83.73	83.75	49	75.81	75.81			
			56	86.77	86.79	51	78.84	78.83			
						53	81.86	81.85			
						55	84.88	84.87			
						57	87.91	87.97			

* Obtained from Mrozowski's analysis of his bands. Values above $J=50\frac{1}{2}$ have been extrapolated.
† Some values are missing because blends make their determination too uncertain.

(3) and (6)]

$$^2\Pi_{1/2}\text{: } \Delta_2F''_{2i}(J)=T''_{2i}(J+1)-T''_{2i}(J-1)$$

$$=4B_2(J+\tfrac{1}{2})\pm p+8DJ^2(J+\tfrac{3}{2})\cdots, \quad (7\text{a})$$

$$\text{: } \Delta_1F''_{2i}(J)=T''_{2i}(J+\tfrac{1}{2})-T''_{2i}(J-\tfrac{1}{2})$$

$$=2B_2(J+\tfrac{1}{2})\pm p/2$$

$$+4DJ^2(J+\tfrac{3}{2})\cdots, \quad (7\text{b})$$

where the + sign in front of p applies when i is d and the − sign applies when i is c. For $^2\Pi_{3/2}$ the subscripts 2 of F, T, and B are to be replaced by 1, and here $p=0$. Since, in general, $\Delta_2F_i(J)=\Delta_1F_i(J+\frac{1}{2})+\Delta_1F_i(J-\frac{1}{2})$, one obtains, neglecting the small quantity p,

$$\Delta_1F_i(J+\tfrac{1}{2})=\tfrac{1}{2}[\Delta_2F_i(J)]\pm B\pm 3DJ(J+1), \quad (8)$$

in which the last term may be neglected for reasons already given. The Δ_1F'''s thus calculated were corrected for the Λ-doubling, in the case of the $^2\Pi_{1/2}$, to correspond to Eq. (6a), and were used uncorrected for the $^2\Pi_{3/2}$ [cf. Eq. (6b)]. An excellent agreement was at once found for one set of combinations for each sub-band (see Table III), proving that both band systems do have the same lower $^2\Pi_g$ state, and making possible a definite assignment of J values for the λ2900 band through the use of Mrozowski's analysis of the other system.

Only alternate Δ_1F'''s are found from the combination relations (6), namely those for which J is even (see Fig. 3), a fact which proves that the upper state is a $^2\Sigma$ with missing levels.[25] A similar procedure involving Eqs. (6), (7) and (8) was now applied to the P_2, ${}^QR_{12}$, ${}^QP_{21}$ and R_1 branches. From this we obtained the Δ_1F'''s with J odd, and it was thus possible to assign correct J values for these branches, though with some uncertainty in many cases because of blends.

Having determined the position and numbering of many of the lines of the weak branches, it was then possible to get Δ_2F's for both the upper and lower states corresponding to Eqs. (4) and (3). The agreement of the latter with Mrozowski's is very good, as can be seen from Table IV, but his values for the lower state are certainly more precise because he obtained the average of several bands which are free from the serious overlapping of the present case.

Mrozowski's double-differences were also used to get more precise Δ_2F''s by employing relations

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[25] That the upper level is common to both sub-bands is also shown by the identical perturbations in the ${}^OP_{12}$ and P_1 branches (see Fig. 4).

TABLE V.

$^2\Sigma^+_u$: VALUES OF $\Delta_2F_1'(K)$: $J=K+3/2$

K	$\Delta_2F_{2c}''(J)$ $+[{}^OP_{12}(J+1)$ $-{}^OP_{12}(J-1)]$*	$\Delta_2F_1''(J)$ $+[P_1(J+1)$ $-P_1(J-1)]$*	${}^QR_{12}(K+1/2)$ $-{}^OP_{12}(K+1/2)$†	$R_1(K+1/2)$ $-P_1(K+1/2)$†
20	30.75	30.81	30.76	30.76
22	33.80	33.82	33.83	33.81
24	37.13	37.14	37.18	37.12
26	39.96	39.95	39.94	
28	43.00	43.01	43.01	
30	45.75	45.76	45.76	45.74
32	50.85	50.90		50.96
34	51.76	51.80	51.71	51.66
36	56.57	56.59		56.71
38	58.19	58.20	58.24	58.17
40	61.20	61.18	61.29	61.11
42	64.46	64.37		64.41
44	67.49	67.55	67.55	67.49
46	70.58	70.63	70.63	70.59
48	73.63	73.61	73.63	73.61
50	76.59	76.67	76.67	76.66
52	79.69	79.69		79.68
54	82.66	82.71		82.70
56	85.60	85.70		
58	88.70	88.77		
60	91.63	91.70		
62	94.50	94.53		

$^2\Sigma^+_u$: VALUES OF $\Delta_2F_2'(K)$: $J=K-3/2$

K	$\Delta_2F_{2d}''(J)$ $+[R_2(J+1)$ $-R_2(J-1)]$*	$\Delta_2F_1''(J)$ $+[{}^SR_{21}(J+1)$ $-{}^SR_{21}(J-1)]$*	$R_2(K-1/2)$ $-P_2(K-1/2)$†	${}^SR_{21}(K-1/2)$ $-{}^QP_{21}(K-1/2)$†
24	36.23	36.27		
26	39.53	39.55	39.54	39.49
28	42.88	42.89	42.77	42.98
30	46.09	46.04	46.03	45.99
32	49.14	49.12	49.12	49.10
34	52.35	52.38	52.32	52.44
36	55.32	55.30	55.28	
38	58.38	58.44	58.35	58.45
40	61.48	61.48	61.52	61.45
42	64.50	64.48		64.46
44	67.53	67.55		67.50
46	70.53	70.56	70.63	70.50
48	73.56	73.60	73.62	73.56
50	76.62	76.63	76.67	76.63
52	79.60	79.69	79.65	79.73
54	82.66	82.69	82.70	82.64
56	85.64		85.66	85.76
58	88.61	88.53	88.63	88.64
60	91.65		91.72	91.73

* The Δ_2F'''s were obtained from Mrozowski's analysis of his bands. Values above $J=50\frac{1}{2}$ have been extrapolated.
† In such a symbol as ${}^QR_{12}(K+1/2)$, the number in parentheses of course means, as usual, the value of J'' for the line in question. Some of the values in columns 3, 4 and 5 are missing because blends make the determination too uncertain.

of the type

$$\Delta_2F_1'(K=J-3/2)=\Delta_2F_2''(J)+[{}^OP_{12}(J+1)-{}^OP_{12}(J-1)]. \quad (9)$$

(See Fig. 3.) The bracketed term is the interval between successive lines in a branch, and, since it could be very accurately determined, this set of Δ_2F''s is probably better than the one obtained directly from the combination differences (4) which depend on measurements of weak, blended lines. Both sets are given in Table V, and it may be seen that they agree well.

It was not possible to extend the analysis with certainty to lower J values than those given in the tables because of the extensive overlapping of various branches, and also because of perturbations in the branches originating from T_2' which alter their spacing and intensity below $J=27\frac{1}{2}$.

Evaluation of molecular constants

The rotational constants for the $^2\Pi_g$ state were determined from Eqs. (7) and the double-differences given by Eqs. (3). The B'' values obtained agree closely with Mrozowski's,[19] as would be expected, but certainly his are more accurate for the reasons pointed out above. Similarly, his value of p (the Λ-doubling coefficient) is more reliable than the one that could be obtained from the λ2900 band. That his p value is positive in sign and is very good is supported by the fact that it was used in Eq. (6a) as a correction of his single-differences to get the combination differences which show such an excellent agreement with those obtained directly (see Table III). Therefore, no independent evaluation of these constants need be given.

The value of the rotational constant for the $^2\Sigma^+_u$ state was found to be $B'=0.3784$ cm^{-1}, which is only slightly smaller than B''. The B value of the ground state of neutral CO_2 is[26] $B_0=0.3895$ cm^{-1}. The close similarity of all these values indicates that the σ_u electron missing in the $^2\Sigma^+_u$ state, as well as the π_g electron which is missing in the $^2\Pi_g$ state, are almost non-bonding, a rather surprising result. B' was obtained, from equations of the same type as Eq. (7), from the Δ_2F_1''s above $J=40\frac{1}{2}$ and from the Δ_2F_2''s above $J=28\frac{1}{2}$, since only for these J values is the

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[26] G. Herzberg, unpublished work.

spacing of the lines fairly uniform and apparently free from perturbations.

The spin-coupling constant γ for the ${}^2\Sigma^+{}_u$ state was found to be 0.019 cm^{-1} from relations of the type

$$\begin{aligned}\Delta\nu_{12}(K)&=\gamma(K+\tfrac{1}{2})\\&={}^PQ_{12}(K=J-\tfrac{1}{2})-P_2(K=J-\tfrac{1}{2})\\&={}^QR_{12}(K=J+\tfrac{1}{2})-Q_2(K=J+\tfrac{1}{2}),\qquad(10)\end{aligned}$$

where, as in determining B', only the lines apparently free from perturbations were used. This value of γ, however, may not have much meaning, since it is possible that the perturbations have produced for the higher J values a permanent shift in the relative positions of T_1 and T_2.

By extrapolating the differences given by Eq. (5) to $J=0$, one gets for the spin-orbit coupling constant $A=-160.3+2B=-159.5$ cm^{-1}. The ${}^2\Pi_g$ is, therefore, a very good case a even to the highest J values observed since $Y=A/B=-419.5$.[27] The ${}^OP_{12}$ and ${}^SR_{21}$ branches, which would be forbidden by the selection rule $\Delta K=0$, ± 1 for case b, remain intense to very high J values, as they should in view of the good approximation of the ${}^2\Pi_g$ to case a.[13]

Equation (5) was also used to evaluate the difference (B_2-B_1) between the rotational constants for the ${}^2\Pi_{1/2}$ and ${}^2\Pi_{3/2}$ sub-levels. Remembering that successive intervals correspond to a change in J of two units, one gets for the difference between $\Delta(J+2)$ and $\Delta(J)$ the value $p+2(B_2-B_1)(2J+3)$, where again p may be neglected (see column 4, Table V). Taking the mean of 17 such differences, and using the average J associated with it, one finds the value of (B_2-B_1) equal to 0.0018 cm^{-1}. From the equation[27, 28] $B_i=B(1\pm B/A)$, one gets $(B_2-B_1)=2B^2/A=2(0.38)^2/160=0.0018$ cm^{-1}, in perfect agreement with the experimental value. This is somewhat higher than the value $(B_2-B_1)=0.0016$ cm^{-1} obtained by Mrozowski,[19] but still the agreement is good. The present method of determining the value of the difference between the two rotational constants is very accurate since (B_2-B_1) appears directly as the coefficient of $J(J+1)$, whereas the value obtained by Mrozowski relies on the independent determination of B_2 and B_1. Using $B=\tfrac{1}{2}(B_1+B_2)=0.3804$ cm^{-1}, from Mrozowski's values, and $(B_2-B_1)=0.0018$ cm^{-1}, one gets the probably better values $B_1=0.3795$ cm^{-1} and $B_2=0.3813$ cm^{-1}.

PERTURBATIONS

The perturbations in the ${}^OP_{12}$ and P_1 branches (see Fig. 4) between the lines $J=28\tfrac{1}{2}$ and $J=42\tfrac{1}{2}$ show not only displacements but also considerable weakening of some of the lines, especially for $J=30\tfrac{1}{2}$, $32\tfrac{1}{2}$, and $38\tfrac{1}{2}$ of both branches, corresponding to lines originating from T_1' at $K=29$, 31, and 37 (see Fig. 3). The lines $J=25\tfrac{1}{2}$ and $J=41\tfrac{1}{2}$ of the branches ${}^SR_{21}$ and R_2 (originating from T_2' at $K=27$ and $K=43$), although not appreciably displaced, are also weakened. The same is true for the corresponding lines of the other branches. A few very faint extra lines appear near the weakened lines, but even the sum of intensities of the regular and extra lines is less than normal. Besides, it was not found possible to fit any of the extra lines into the perturbation, which indicates that they, just as many other additional lines which appear throughout the band, may, at least some of them, have a different origin. Further perturbations appear in the ${}^SR_{21}$ and R_2 branches below $J=27\tfrac{1}{2}$. At this point the spacing between the lines becomes smaller and their intensity is reduced, but it was difficult to carry out a detailed investigation of these perturbations, since the lines merge with the high J members of the Q branches. It seems very probable that these perturbations are caused by higher vibrational levels of the ${}^2\Pi_u$ state of Mrozowski's bands, since the zero vibrational level of the latter lies only about 0.8 volt below that of the ${}^2\Sigma^+{}_u$ state. Several quanta, and not all of the totally sym-

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[27] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1923).

[28] Cf. R. S. Mulliken, Rev. Mod. Phys. **2**, 113 (1930). Carrying the expansion of Hill and Van Vleck's formula for the rotational term values of the components of doublet states (reference 27) one step farther one gets (for $|A|\gg 4$)

$$B^*=B[1\pm B/A\Lambda\mp(B^3/A^3\Lambda^3)(J+\tfrac{1}{2})^2\cdots].$$

The third term then might preferably be included as a correction term for D, giving $D^*=D(1\mp B^4/A^3\Lambda^3\cdots)$. In the present case $B^4/A^3\Lambda^3=5.1\times 10^{-9}$ cm^{-1}, or about 4 percent of D.

metric vibration, would be needed to give the proper perturbing $^2\Pi_u$ vibronic states.

The diminished intensity of some of the lines means, according to accepted ideas,[29] that the perturbation is accompanied by accidental predissociation. However, this does not seem possible in the present instance, since the dissociation energy of CO_2^+ is, in the most favorable case, about one volt higher than the energy (4.3 volts) of the perturbed levels. The lowest energies of dissociation would be

$$CO_2^+ \rightarrow CO + O^+ - 5.27 \text{ volts} \quad (11a)$$

$$CO_2^+ \rightarrow CO^+ + O - 5.82 \text{ volts} \quad (11b)$$

$$CO_2^+ \rightarrow C^+ + O_2 - 6.98 \text{ volts} \quad (11c)$$

$$CO_2^+ \rightarrow C + O_2^+ - 7.96 \text{ volts.} \quad (11d)$$

Equation (11b) is based on $I(CO) = 14.1$ volts (from electron impact), while (11c) and (11d) depend on $C_{\text{solid}} \rightarrow C_{\text{gas}} - 5.4$ volts. A higher heat of sublimation of carbon would give an even higher value for the heat of dissociation in (11c) and (11d). To make (11b) fit the idea of accidental predissociation would require $I(CO) = 12.6$ volts. The lowest value (11a) cannot be altered since $I(O) = 13.55$ volts and the heats of formation of CO and CO_2 are accurately known.

A possible explanation of the weakening was suggested by Professor Mulliken and Dr. H. Beutler, as follows. The perturbing $^2\Pi_u$ rotational levels may have a high probability of transition to levels of several vibrational states of the $^2\Pi_g$ electronic state with which the $^2\Sigma^+{}_u$ rotational levels involved cannot combine with appreciable intensity because of the Franck-Condon principle. If the radiation lifetime of the $^2\Pi_u$ levels is much shorter than that of the perturbed $^2\Sigma^+{}_u$ levels, as seems plausible,[30] the perturbed levels of the latter would have their population seriously depleted, and there would be a corresponding weakening of the lines originating from them.

Further study will be required before a detailed explanation of the perturbations can be given.

Unexplained Features of the Band

The two strong "lines" $\nu = 34678.25$ cm^{-1} and $\nu = 34517.54$ cm^{-1} marked (a) and (b) in Fig. 1, which were assumed by Duncan[6] and by Schmid[7] to be the zero branches of the transition, are always associated with the band and are not atomic lines. They appear with the same relative intensity in all the plates taken under various conditions and may perhaps be branches of a weaker member of the same sequence as the band studied. The preponderating intensity of the band analyzed as compared with other possible bands in the same system suggests that there is very little vibration in the upper state. This may be caused by the operation of the Franck-Condon principle in the excitation process, since the B values of the CO_2 ground state and of the $^2\Sigma^+{}_u$ state of CO_2^+ are almost equal, and the molecule is linear in both states. From this $^2\Sigma^+{}_u$ state radiation is very strong only to the vibrationless $^2\Pi_g$ level, because both B values are likewise equal, and the molecule is also linear in the lower state. However, detailed attempts to account for these "lines" as, for example, Q branches, or heads of branches, have not been successful.

The heads marked (c) ($\nu = 34745.45$ cm^{-1}) and (d_1, d_2) ($\nu_1 = 34585.88$ cm^{-1} and $\nu_2 = 34585.17$ cm^{-1}) have a separation of about 160 cm^{-1}, but their structure is too weak and diffuse for precise measurements. Presumably they also represent transitions between higher vibrational levels of the same electronic states.

A similar separation of 162.14 cm^{-1} exists between (e) ($\nu = 34778.67$ cm^{-1}) and (f) ($\nu = 34616.53$ cm^{-1}), but the sharp, clear-cut appearance of the latter and its smaller intensity does not seem to justify the same correlation. The latter may be the atomic line λ2887.91 of O^+, since the wavelength from the present plate measurements is 2887.95A.

Acknowledgment

This investigation was made possible by the grant of a Latin-American Fellowship by the John Simon Guggenheim Memorial Foundation. The work was conducted under the direction of Professor R. S. Mulliken, whose continuous

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[29] G. P. Ittmann, Naturwiss. **22**, 118 (1934).

[30] Both on the basis of theoretical intensity calculations [cf. R. S. Mulliken, J. Chem. Phys. **3**, 720 (1935)] and in view of the fact that the total observed emission intensity of the $^2\Pi_u \rightarrow {}^2\Pi_g$ system is much greater than that of the single $^2\Sigma^+{}_u \rightarrow {}^2\Pi_g$ band.

encouragement and suggestions permitted a successful solution of the problem. The author is also greatly indebted to Dr. S. Mrozowski for his collaboration in the experimental work and for the use of his unpublished data, and to Dr. H. Beutler for his help and advice in various phases of the work. Thanks are also due to Professor G. R. Harrison, of the Massachusetts Institute of Technology, for the careful measurement of the plates.

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Note on the Photoelectric Threshold of Bismuth Films of Measured Thickness

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The photoelectric threshold wave-length change with thickness in aged bismuth films deposited on Pyrex at room temperature in vacuum is investigated further with some important modifications in apparatus and method including measurement of the average film thickness and extension of the temperature range in which the DuBridge analysis is applied. The data show that the bismuth films are characterized by: (1), an initial value of the threshold wave-length (2497A average) fairly independent of film thickness for the first 44 atom layers; (2), a definite shift toward higher threshold wave-lengths occurring between 44 and 111 atom layers thickness; followed by (3), a steady increase of threshold wave-length with film thickness above about 111 atom layers. These results are in general agreement with the previous preliminary work but show some differences which are discussed briefly.

In preliminary experiments[1] an increase of the photoelectric threshold wave-length with increasing film thickness was observed for aged bismuth films deposited on glass at room temperature. This note describes a further investigation of this effect with some important improvements in apparatus and method including measurement of the film thickness and extension of the temperature range in which the DuBridge[2] analysis is applied.

Apparatus. Procedure

In the first experiments[1] the photoelectric cell was constructed with a molybdenum evaporation trough containing the bismuth close to the condensation surface (inclined to the vapor stream), a design resulting in deposits of uneven thickness. The proximity of the evaporation trough to the condensation surface resulted also in undesirable heating of the lower section of the surface.

The experimental tube shown by Fig. 1 and described in the accompanying legend eliminated these defects and, following the determination of the vapor pressure of bismuth,[3] made it possible to measure the average thickness of the bismuth deposits (unknown in the earlier experiments[1]). The electrodes E, used for electrical contact with the deposited metal in these experiments, also were useful in measuring the electrical conductance of the bismuth films in a later investigation.[4] A total obstruction charcoal trap was connected between the experimental tube and the vacuum pumps and was immersed continuously in liquid air during the experiments. The experimental tube and associated glass apparatus was subjected to the usual preliminary cleaning and outgassing. The photoelectric currents were measured with a Compton electrometer and the light source was the same as that described previously.[1] The illumination of the film (dimensions between electrodes about 0.5 cm×1 cm) was confined to a central circular area of diameter about 3.35 mm.

The temperature of the bismuth films on P

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[1] A. H. Weber, Phys. Rev. **53**, 895 (1938).

[2] L. A. DuBridge, Phys. Rev. **39**, 108 (1932).

[3] A. H. Weber, Phys. Rev. **57**, 1042 (1940).

[4] A. H. Weber and D. F. O'Brien, following paper.

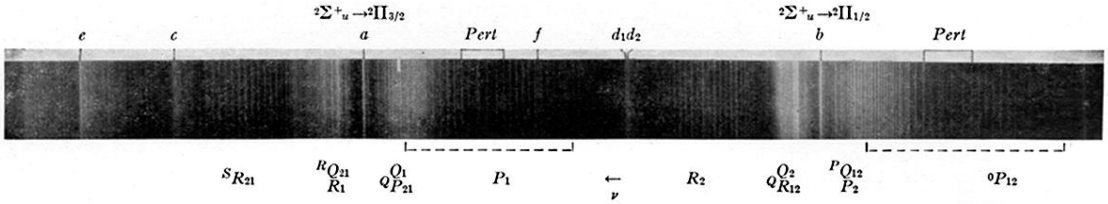

FIG. 1. Spectrogram of the λ2900 doublet band of CO_2^+. The sub-bands are centered near (*a*) ($\nu = 34{,}678.25$ cm^{-1}) and (*b*) ($\nu = 34{,}517.54$ cm^{-1}). The meaning of the letters is given in the text. The portions of the branches shown by dashed brackets under *Pert* are shown enlarged in Fig. 4, while the solid brackets include the lines which show the greatest perturbations.

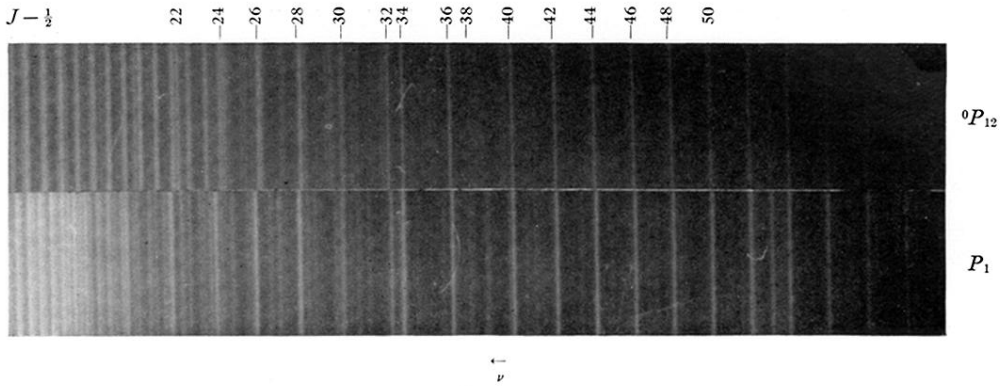

FIG. 4. Enlargement of the perturbed regions of the $^{O}P_{12}$ and P_1 branches (see Fig. 1 and the text), showing displacements and weakenings between $J=28\frac{1}{2}$ and $J=42\frac{1}{2}$.