Analysis of the (0,0) $^2\Pi \rightarrow {}^2\Sigma$ CN Band at 9168A

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The rotational structure of the 0,0 band of the red CN system has been analyzed by means of spectrograms taken in the first order of a 21-foot grating. The values obtained for the various constants are $B_0'' = 1.8906$ cm^{-1}, $B_0' = 1.6907$ cm^{-1}, $D_0' = -6.07 \times 10^{-6}$ cm^{-1}, $A = -53.3$ cm^{-1}, $p_0 = 0.009$ cm^{-1} and $q_0 = -0.0008$ cm^{-1}. These are in agreement with the values obtained by Jenkins, Roots and Mulliken for transitions which involve higher vibrational levels of the $^2\Pi$ state. The origin of the band is at 10905.12 cm^{-1}.

INTRODUCTION

RECENTLY Kiess[1] has reported the existance of strong carbon bands in the infrared beyond 9000A. It seemed desirable to photograph these as they might or might not be the 0, 0 and 1, 1 bands of the $^2\Pi \rightarrow {}^2\Sigma$ CN band system whose position has been determined by Asundi and Ryde.[2] Analysis of the bands shows them to be these transitions. The results obtained are in agreement with those of Jenkins, Roots and Mulliken[3] who have analyzed transitions involving higher vibrational levels of the $^2\Pi$ state.

EXPERIMENTAL PROCEDURE

The source used was a 220 volt d.c. arc drawing 9 amperes. Spectrograms were obtained upon xenocyanine plates recently developed by the Eastman Kodak Company. These plates were hypersensitized with ammonia and exposed for nine hours in order to obtain sufficiently strong spectrograms. The dispersive apparatus was a 21-foot grating mounted stigmatically. Plates were taken in the first order, the dispersion for this region being 4.78A per mm. Second and third order iron lines were used for the comparison spectrum.

ROTATIONAL ANALYSIS

The rotational analysis of the 0, 0 band yields the six main branches. The satellite, ${}^oP_{12}$ and ${}^sR_{21}$, branches are not strong enough to permit of identification. In the region to the violet of the 1, 1 band, the six principal branches of the 0, 0 band account for virtually all the lines observed. For the equations giving the term values and for the combination relations reference is made to the article of Jenkins, Roots and Mulliken. Table I gives the wave-numbers of the various branches of the 0, 0 band. The appearance of the bands is quite similar to that of the 8, 3 band of which a reproduction is shown in reference three.

[1] C. C. Kiess, Bureau of Standards, Journal of Research **8**, 393 (1932).
[2] R. K. Asundi and J. W. Ryde, Nature **124**, 57 (1929).
[3] F. A. Jenkins, Y. K. Roots and R. S. Mulliken, Phys. Rev. **39**, 16 (1932).

TABLE I.

K''	R_2	Q_2	P_2	R_1	Q_1	P_1
0	10,931.83					
1	33.62	10,929.69			10,878.25	
2	35.05	27.10			79.08	
3	36.13	24.42			79.48	
4	36.82	21.48			79.08	
5	37.27	18.26			78.05	
6	37.27	14.97		10,901.80	76.62	
7	36.82	10.89		02.90	74.65	
8	36.13	06.59		03.71	72.44	
9	35.05	02.02		04.18	69.59	
10	33.62	897.19		04.18	66.43	
11	31.83	92.02		03.71	62.65	
12	29.77	86.39		02.72	58.56	
13	27.27	80.42		01.17	53.89	
14	24.42	74.28		899.64	48.86	
15	21.23	67.66		97.77	43.37	
16	17.63	60.73		95.11	37.55	
17	13.69	53.38		92.02	31.02	
18	09.35	45.67		88.36	24.20	
19	04.66	37.55		84.60	17.01	
20	899.60	29.18	10,762.19	80.42	09.39	
21	94.08	20.35	50.06	75.49	01.20	
22	88.36	11.19	37.44	70.21	792.72	
23	82.09	01.57	24.54	64.60	83.80	10,705.83
24	75.49	791.71	11.36	58.56	74.38	693.19
25	68.48	81.37	697.39	52.05	64.62	80.09
26	61.07	70.69	83.49	45.15	54.44	66.59
27	53.38	59.62	68.99	37.55	43.87	52.63
28	45.15	48.16	54.20	30.15	32.86	38.17
29	36.63	36.30	38.94	21.98	21.44	23.46
30	27.68	24.01	23.46	13.40	09.64	08.35
31	18.31	11.36	07.43	04.45	697.39	592.74
32	08.66	698.33	591.11	795.07	84.78	76.78
33	798.50	84.78	74.37	85.32	71.65	60.52
34	88.00	77.16	57.36	75.04	58.13	43.72
35	77.11	56.95	39.69	64.62	44.27	26.46
36	65.76	42.41		53.33	29.97	08.89
37		27.41		41.93	15.28	490.72
38		12.13		30.03	00.25	71.89
39		596.31		17.60	584.76	
40		80.22		05.10	68.81	
41		63.68		692.07	52.60	
42		46.68		78.62	35.86	
43		29.34		64.60	18.76	
44		11.64		50.31	01.27	
45		493.61		35.56	483.32	
46		75.08		20.50	65.03	
47		56.13		04.94	46.31	
48		36.92		589.16	27.23	
49		17.24		72.73	07.66	
50		397.09		55.98	387.78	
51		76.79		38.76	67.51	
52		55.89		21.16	46.77	
53		34.60			25.67	
54		12.98			04.17	

TABLE I. (*Cont.*)

K''	R_2	Q_2	P_2	R_1	Q_1	P_1
55		290.91			282.27	
56		68.54			60.05	
57		45.77			37.30	
58		22.51			14.27	
59		198.90			190.77	
60		74.90			66.89	
61		50.53			42.60	
62		25.76			17.95	
63		00.63			092.84	

The combination differences for the $^2\Sigma$ state have been computed from the expression

$$R_1(K-1) - P_1(K+1) = \Delta_2F_1''(K).$$

The values obtained have been compared with those for the 0, 0 transition of the violet CN band system as determined by Uhler and Patterson.[4] Unfortunately the greater portion of the $\Delta_2F_1''(K)$ values available from the $^2\Pi \rightarrow {}^2\Sigma$ transition are not obtainable from the violet band. The reason for this is that the P lines necessary for the determination of the combination differences are, for the most part, those in the immediate vicinity of the head of the band and Uhler and Patterson were unable to resolve them. There is good agreement between those values of $\Delta_2F_1''(K)$ which are available from both band systems. The value of B_0'' obtained is 1.8906 cm^{-1} which is to be compared with 1.8904 cm^{-1}, the value predicted from the B_v'' equation given by Jenkins, Roots and Mulliken.

TABLE II. *Combination differences Δ_2F_i' for the $v=0$ level of the $^2\Pi$ state.*

J	$R_2(J)-P_2(J)$	$R_1(J)-P_1(J)$
$19\frac{1}{2}$	137.41	
$20\frac{1}{2}$	144.02	
$21\frac{1}{2}$	150.92	
$22\frac{1}{2}$	157.55	
$23\frac{1}{2}$	164.13	158.77
$24\frac{1}{2}$	171.09	165.37
$25\frac{1}{2}$	177.58	171.90
$26\frac{1}{2}$	184.39	178.56
$27\frac{1}{2}$	190.95	
$28\frac{1}{2}$	197.69	191.98
$29\frac{1}{2}$	204.22	198.52
$30\frac{1}{2}$	210.88	205.05
$31\frac{1}{2}$	217.55	211.71
$32\frac{1}{2}$	224.13	218.29
$33\frac{1}{2}$	230.64	224.80
$34\frac{1}{2}$	237.42	231.32
$35\frac{1}{2}$		238.16
$36\frac{1}{2}$		244.44
$37\frac{1}{2}$		251.21
$38\frac{1}{2}$		258.14

[4] H. S. Uhler and R. A. Patterson, Astrophys. J. **42,** 434 (1915).

Table II contains the combination differences for the $^2\Pi$ state. By means of these values the various constants have been determined by the same methods as those used by the above mentioned authors. The values are

$$B_0^{*}{}_{,-1/2} = 1.7404 \text{ cm}^{-1}$$
$$B_0^{*}{}_{,1/2} = 1.6410 \text{ cm}^{-1}$$
$$B_0' = 1.6907 \text{ cm}^{-1}$$
$$D_0' = -6.07 \times 10^{-6} \text{ cm}^{-1}$$
$$A = -53.3 \text{ cm}^{-1}$$
$$p_0 = 0.009 \text{ cm}^{-1}$$
$$q_0 = -0.0008 \text{ cm}^{-1}$$
$$\nu_0 = 10905.12 \text{ cm}^{-1}.$$

The value of B_0' is in excellent agreement with the value, 1.6903 cm^{-1}, obtained by extrapolation from the results of the analysis of other bands of this system. There is considerable inaccuracy in the determination of the values of p_0 and q_0 as the P branches could not be measured in the region of low K values. Furthermore the value of A is slightly higher than that obtained from the higher vibrational levels of this electronic state.

The analysis of the 1, 1 band has not been carried out due to the fact that the lines of low K value were absent from the spectrograms obtained. The two Q branches are easily identified and may be followed to quite high K values. There is also evidence of the R branches.

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