Rotational Analysis of the First-Negative Bands of the CO^+ Molecule

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(Received August 19, 1932)

By using the light of a graphite hollow cathode in a CO_2 atmosphere, the $^2\Sigma \rightarrow {}^2\Sigma$ (first-negative) CO^+ bands at λλ2299.7, 2325.2, 2419.4, 2445.8, 2474.2, 2504.5, 2577.7, 2607.2, 2638.7 and 2672.3A have been photographed in the second and third order of a 21 foot Rowland grating. The analysis gives the rotational constants: $B_e' = 1.778$ cm^{-1}, $\alpha' = 0.032$ cm^{-1} and $B_e'' = 1.954$ cm^{-1}, $\alpha'' = 0.019$ cm^{-1}. The ρ-type doubling of both of the upper and lower $^2\Sigma$ states seems to be very small. Only lines with high rotational quantum numbers show broadenings and sometimes measurable doublings. Definite perturbations could not be observed.

THE first attempt at a rotational analysis of the first-negative group of CO^+ was made by Blackburn.[1] He photographed the bands in the light of a helium discharge tube and measured mostly in the first order of a 21 foot grating. Since he did not publish his measurements and because the rotational constants given by him seem to be erroneous, new measurements seemed desirable. For that purpose a $1 \times 1 \times 1$ inch graphite block with a cylindrical hollow (3 mm width) was put in a bulb with a quartz window, and using a CO_2 atmosphere at 0.1 mm pressure a direct current of about 700 milliamperes was led through. A smaller piece of graphite served as anode. The cathode became red hot and the hollow gave a very bright blue colored light, which contained the whole CO^+ spectrum in considerable intensity and also some CO and CO_2 bands. In 50 hour exposures good second and third order pictures were obtained.

TABLE I. λ = *2299.69A 0→1 band.*

K	P	K	R	K	P	K	R
		1	43,456.0	19	43,319.0	25	43,434.4
1	43,445.6	2	458.6	20	309.1	26	429.3
2	441.2	3	461.7	21	298.6	27	423.8
3	436.6	4	464.0	22	287.9	28	418.0
4	431.7	5	465.8	23	276.6	29	412.1
5	426.5	6	467.4	24	265.1	30	405.5
6	421.0	7	468.5	25	253.2	31	398.3
7	415.1	—	—	26	241.2	32	391.1
8	409.0	14	468.5	27	228.7	33	383.6
9	402.5	15	466.9	28	216.0		
10	395.7	16	465.3	29	202.7	34	{375.5
11	388.5	17	463.2	30	189.4		{375.0
12	381.0	18	460.8	31	175.4		
13	373.1	19	457.8	32	161.6	35	{367.7
14	365.0	20	455.1	33	147.0		{366.8
15	356.6	21	451.6	34	131.9		
16	347.7	22	447.8			36	{359.3
17	338.5	23	443.7				{358.4
18	329.0	24	439.2				
						37	349.7?

[1] C. M. Blackburn, Proc. Nat. Acad. **11**, 28 (1925).

TABLE II. λ = *2419.39A 0→2 band.*

K	*P*	*K*	*R*	*K*	*P*	*K*	*R*
1	41,292.4	1	41,303.1	18	41,182.2	27	41,285.0
2	288.4	2	306.1	19	173.2	28	280.6
3	284.0	3	308.8	20	163.9	29	275.3
4	279.3	4	311.1	21	154.4	30	269.9
5	274.2	5	313.3	22	144.1	31	264.1
6	268.7	6	314.9	23	134.0	32	257.9
7	263.0	—	—	24	123.4	33	251.1
8	257.3	17	315.9	25	112.5		
9	251.1	18	314.2	26	101.3		
10	244.6	19	312.2	27	89.8		
11	237.9	20	309.8	28	78.4		
12	230.8	21	307.1	29	66.2		
13	223.3	22	304.2	30	53.8		
14	215.6	23	301.0	31	41.3		
15	207.9	24	297.5	32	28.3		
16	199.8	25	293.7	33	15.0		
17	191.2	26	289.4	34	1.4		

TABLE III. λ = *2325.17A 1→2 band.*

K	*P*	*K*	*R*	*K*	*P*	*K*	*R*
4	42,956.9	12	42,993.4	21	42,820.5	29	42,925.9
5	952.3	13	992.3	22	809.4	30	918.9
6	946.8	14	990.8	23	797.7	31	911.0
7	940.8	15	989.0	24	785.7	32	903.0
8	934.5	16	986.9	25	773.5	33	894.5
9	927.7	17	984.3	26	760.6		
10	920.7	18	981.6	27	747.8	34	885.7
11	913.4	19	978.3	28	734.5		885.0
12	905.8	20	975.0	29	720.7		
13	897.6	21	971.2	30	706.7	35	878.2
14	889.2	22	966.9				876.3
15	880.4	23	961.9				
16	871.5	24	956.5			36	868.0
17	861.8	25	951.0				867.1
18	852.2	26	945.6				
19	841.9	27	939.3			37	858.5
20	831.5	28	932.6				875.6

TABLE IV. λ = *2445.84A 1→3 band.*

K	*P*	*K*	*R*	*K*	*P*	*K*	*R*
1	40,848.4	0	40,856.3	16	40,754.0	23	40,849.4
2	844.3	1	859.3	17	744.9	24	845.3
3	839.6	2	862.1	18	735.8	25	840.8
4	835.0	3	864.6	19	726.2	26	836.0
5	829.8	4	866.8	20	716.4	27	830.8
6	824.8	5	868.7	21	706.5	28	825.5
7	819.0	—	—	22	696.2	29	819.8
8	812.9	15	870.5	23	685.1	30	813.3
9	806.7	16	869.2	24	674.2	31	806.9
10	799.9	17	867.5	25	663.2	32	800.1
11	792.9	18	865.4	26	651.3		
12	785.7	19	863.0	27	639.2		
13	778.1	20	859.9	28	626.6		
14	770.1	21	856.7	29	614.6		
15	762.1	22	853.1	30	602.3		

TABLE V. λ=*2577.68A 1→4 band.*

K	P	K	R	K	P	K	R
2	38,750.6	1	38,765.4	22	38,612.7	29	38,743.0
3	746.7	2	768.5	23	603.0	30	738.2
4	742.0	3	771.3	24	592.9	31	732.8
5	737.4	4	773.7	25	581.0	32	727.2
6	732.0	5	776.0	26	517.7	33	721.4
7	726.8	6	777.6	27	561.0	34	715.1
8	721.0	7	779.3	28	550.0	35	708.9
9	715.1	—	—	29	538.3	36	702.4
10	708.9	17	779.8	30	526.6	37	695.9
11	702.4	18	778.4	31	514.7	38	687.7
12—	696.5	19	776.7	32	502.1	39	679.9
13	688.5	20	774.6	33	489.5	40	671.9
14	681.2	21	772.3	34	476.5		
15	673.6	22	769.5	35	463.6		
16	665.7	23	766.6	36	450.0		
17	657.7	24	763.5	37	436.1		
18	649.1	25	759.9	38	422.1		
19	640.5	26	756.1	39	407.8		
20	631.5	27	752.1	40	393.5		
21	622.2	28	747.6	41	378.1		
				42	362.7		

TABLE VI. λ=*2474.21A 2→4 band.*

K	P	K	R	K	P	K	R
2	40,377.2	1	40,391.5	25	40,190.3		
3	372.9	2	394.6	26	178.0	30	40,336.3 / 335.3
4	368.0	3	397.1	27	165.4		
5	362.9	4	399.1	28	152.6		
6	357.5	5	401.0	29	139.4	31	329.4
7	351.5	—	—	30	125.9		
8	345.5	13	403.0	31	111.9	32	322.6 / 321.3
9	339.1	14	401.8	32	97.6		
10	332.6	15	400.2	33	82.8		
11	325.2	16	398.1			33	314.8
12	317.7	17	395.8	34	68.0 / 67.0		
13	310.0	18	393.3			34	307.0 / 305.8
14	301.9	19	390.3				
15	293.6	20	386.9	35	52.7 / 51.2		
16	284.7	21	383.3				
17	275.7	22	379.2				
18	266.2	23	375.3	36	37.0 / 34.4		
19	256.5	24	370.1				
20	246.0	25	365.1				
21	235.6	26	359.7	37	21.0 / 19.2		
22	224.8	27	353.7				
23	213.5	28	347.7				
24	202.0	29	341.1	38	6.2 / 4.5		

TABLE VII. λ=2607.16A 2→5 band.

K	P	K	R	K	P	K	R
7	38,290.4			28	38,105.9	33	38,270.6
8	284.6	13	38,343.9	29	93.6	34	263.6
9	278.5	14	343.3	30	81.4	35	256.3
10	272.0	15	342.1	31	68.6	36	248.5
11	265.3	16	340.9	32	55.5	37	240.7
12	258.4	17	339.2	33	42.3	38	232.3
13	251.1	18	337.3	34	28.4	39	223.5
14	243.5	19	335.0	35	14.4	40	214.5
15	235.5	20	332.5	36	0.2	41	205.1
16	227.4	21	329.8	37	37,985.5	42	195.5
17	218.9	22	326.6	38	970.7		(double)
18	210.1	23	323.1	39	955.4		
19	201.1	24	319.1				
20	191.7	25	315.1	40	{939.7 938.8		
21	182.0	26	310.8				
22	172.1	27	306.0				
23	161.7	28	301.0	41	{923.9 922.7		
24	151.4	29	295.6				
25	140.4	30	289.9				
26	129.1	31	283.7	42	907.3		
27	117.8	32	277.3				
				43	{890.9 889.2		

TABLE VIII. λ=2504.48A 3→5 band.

K	P	K	R	K	P	K	R
9	39,852.0	12	39,914.6	21	39,745.1		
10	845.1	13	913.5	22	733.9	24	{39,876.5 875.4
11	838.0	14	911.9				
12	830.1	15	909.9				
13	822.2	16	907.5	23	{725.7 724.4		
14	813.8	17	904.8			25	{870.7 869.2
15	805.2	18	901.6				
16	795.8	19	898.2				
17	786.7	20	894.3			26	{865.1 863.3
18	776.6	21	890.1				
19	766.5	22	885.7				
20	756.0	23	881.2			27	{858.8 857.0

TABLE IX. λ=2638.72A 3→6 band.

K	P	K	R	K	P	K	R
9	37,821.6	13	37,844.5	23	37,700.5	27	37,839.2
10	815.2	14	883.4	24	689.5	28	833.6
11	808.0	15	881.9	25	678.4	29	827.6
12	800.7	16	880.1	26	666.0	30	820.9
13	793.3	17	878.1	27	654.0	31	813.9
14	785.5	18	875.8	28	642.1	32	807.0
15	777.5	19	873.1	29	629.1	33	799.2
16	768.8	20	870.0	30	616.3	34	791.8
17	760.0	21	866.8	31	602.9	35	783.6
18	751.0	22	863.1	32	589.1	36	774.7
19	741.5	23	858.9	—	—	37	766.1
20	731.7	24	854.5	36 (?)	467.5		(double)
21	721.7	25	849.6				
22	711.4	26	844.6	37 (?)	{450.2 449.2		

TABLE X. λ=*2672.31A 4→7 band.*

K	P	K	R	K	P	K	R
2	37,383.8	2	37,400.9	17	37,283.4	23	37,377.0
3	379.4	3	403.1	18	274.0	24	372.0
4	375.1	4	404.9	19	264.3	25	366.8
5	369.9	5	407.0	20	254.1	26	361.1
6	364.7	—	—	21	243.7	27	355.0
7	358.9	13	407.6	22	232.8	28	384.4
8	353.1	14	406.0	23	221.7	29	341.7
9	346.5	15	404.2	24	210.1	30	334.4
10	339.9	16	401.9	25	198.0	31	326.9
11	332.9	17	399.6	26	186.1	32	319.1
12	325.5	18	396.8	27	174.0	33	310.8
13	317.8	19	393.6	28	160.8		
14	309.7	20	389.9	29	147.4		
15	301.2	21	385.9	30	133.6		
16	292.3	22	381.5	31	119.9		

TABLE XI. *Upper state combinations.* $R(K)-P(K)$.

v'	0	0	1	1	1	2	2	3	3	4
v''	1	2	2	3	4	4	5	5	6	7
K										
1	10.4	10.7		10.9						
2	17.4	17.7		17.8	17.9	17.4				17.1
3	25.0	24.8		25.1	24.6	24.2				23.7
4	32.3	31.8		31.7	31.6	31.1				29.9
5	39.3	39.1		38.9	38.6	38.1				37.2
6	46.4	46.2			45.6					
7	53.4				52.5					
—										
12			87.6					84.5		
13			94.7			93.0	92.8	91.3	91.2	89.8
14	103.6		101.6			99.8	99.8	98.1	97.8	96.4
15	110.3		108.6	108.4		106.6	106.6	104.6	104.4	103.0
16	117.6		115.4	115.1		113.3	113.5	111.7	111.3	109.6
17	124.7	124.7	122.5	122.6	122.1	120.1	120.2	118.1	118.1	116.1
18	131.8	131.9	129.4	129.6	129.3	127.1	127.2	125.0	124.8	122.8
19	138.7	139.0	136.5	136.8	136.2	133.7	134.0	131.7	131.6	129.3
20	145.9	145.9	143.5	143.5	143.1	140.9	140.8	138.4	138.3	135.8
21	153.1	152.7	150.6	150.2	150.1	147.8	147.8	145.0	145.2	142.2
22	160.0	160.0	157.5	156.9	156.8	154.5	154.5	151.9	151.6	148.7
23	167.1	167.0	164.2	164.3	163.6	161.8	161.3		158.5	155.4
24	174.0	174.2	170.8	171.2	170.6	168.1	167.7		165.0	161.8
25	181.2	181.2	177.5	177.6	178.9	174.8	174.7		171.2	168.7
26	188.2	188.1	185.0	184.7	184.4	181.6	181.7		178.6	175.0
27	195.0	195.2	191.6	191.6	191.0	188.3	188.2		185.1	181.0
28	202.0	202.2	198.1	198.9	197.6	195.1	195.1		191.5	187.6
29	209.4	209.1	205.2	205.2	204.8	201.7	202.0		198.5	194.3
30	216.1	216.2	212.3	211.0	211.6	209.5	208.5		204.6	200.7
31	222.8	222.8			218.1		215.1		211.1	207.1
32	229.6	229.6			225.1		221.8		217.9	
33	236.6	236.1			232.9		228.4			
34					239.6		235.2			
35					245.3		242.0			
36					252.4		248.3			
37					259.9		255.2			
38					265.7		262.6			
39					272.2		268.2			
40					278.4					

TABLE XII. *Lower state combinations.* $R(K-1)-P(K+1)$.

v'	0	0	1	1	1	2	2	3	3	4
v''	1	2	2	3	4	4	5	5	6	7
K										
1				12.0?						
2	19.4	19.0		19.7?	18.8	18.6				
3	26.8	26.8		27.1	26.5	26.6				25.9
4	35.1	34.6		34.8	33.8	34.2				33.2
5	43.0	42.4		42.0	41.7	41.6				40.2
6	50.7	50.3		49.7	49.2	49.6				48.2
7	58.4	57.6			56.6					
8	66.1				64.2					
—										
13			104.1					100.8		
14			111.9			109.4	108.4	108.2	107.5	106.4
15	120.8		119.3			117.0	115.9	116.1	114.6	113.7
16	128.5		127.1	125.6		124.5	123.2	123.2	121.9	120.8
17	136.3		134.7	133.4		131.9	130.7	130.9	129.1	128.0
18	144.1	142.7	142.5	141.3	139.3	139.2	138.1	138.3	136.6	135.3
19	151.7	150.3	150.1	149.0	146.9	147.3	145.6	145.7	144.1	142.6
20	159.2	157.8	157.8	156.5	154.5	154.7	153.0	153.1	151.5	149.8
21	167.2	165.7	165.6	163.7	161.9	162.1	160.4	160.4	158.6	157.2
22	175.0	173.1	173.5	171.5	169.3	169.9	168.1		166.4	164.2
23	182.7	180.8	181.2	179.0	176.6	177.2	175.2		173.6	171.3
24	190.5	188.4	188.3	186.2	185.6	185.0	182.7		180.5	179.0
25	198.0	196.2	195.9	194.0	191.8	192.1	190.0		188.5	185.9
26	205.6	203.9	203.2	201.7	198.9	199.7	197.2		195.5	192.8
27	213.3	211.1	211.2	209.4	206.1	207.0	204.9		202.5	200.3
28	221.1	218.8	218.7	216.2	213.8	214.3	212.4		210.1	207.6
29	228.6	226.8	225.9	223.3	221.0	221.9	219.6		217.3	214.8
30	236.6	234.0			228.3	229.2	227.0		224.7	221.8
31	243.9	241.7			236.1		234.3		231.8	
32	251.3	249.2			243.3		241.4			
33	259.2	256.5			250.7		248.9			
34					257.8		256.3			
35					265.1		263.4			
36					272.8		270.8			
37					280.4		277.8			
38					288.2		285.3			
39					294.2					
40					301.9					
41					309.2					

The Tables I to X contain the measurements. The accuracy is ± 0.1 cm^{-1}. Most of the band lines appear single (the bands are composed of P and R branches as is usual for the case $^2\Sigma \rightarrow {}^2\Sigma$). Only lines with high rotational quantum numbers show an increasing broadening and in some cases also splittings could be observed. Unfortunately (but naturally) the broadening or splitting causes a more rapid decrease of the intensity and so only a few doublets could be measured. Besides that, the dispersion and resolution of the grating used in the region of these bands allows one to observe doublets only when the separation is larger than 0.5 cm^{-1} (in the third order) or 1 cm^{-1} (in the second order). Considering these facts, not much can be said about the magnitude of the ρ-type doubling of the $^2\Sigma$ terms. It may be pointed out that while in most of the bands the doubling starts with rotational quantum numbers about 30 to 34, in the $1 \rightarrow 4$ band ($\lambda = 2577.7$A) no doublings were observed until rotational quantum numbers 40 to 42, while on the other hand in the 3→5 band ($\lambda = 2504.5$A) the lines $P(23)$ and $R(24)$ already show relatively large doublings (1.3 cm^{-1} width). Within the above stated and not very high observational accuracy no definite perturbations in the doublets could be observed, although the doublet widths increase not very regularly with the rotational quantum numbers.

The K numbering of the lines is given by the combination-differences listed in Tables XI and XII on the basis of the formula:

$$\Delta_2 T'(K) = R(K) - P(K) = 4B'(K + \tfrac{1}{2})$$

and

$$\Delta_2 T''(K) = R(K-1) - P(K+1) = 4B''(K + \tfrac{1}{2}).$$

For calculating the B' and B'' values only lines without observable splittings were used. The B' and B'' constants vary in the usual way with the vibrational quantum numbers v' and v''. We find:

$v'=$	0	1	2	3	4		
$B'=$	1.77	1.73	1.70	1.66	1.63		and
$v''=$	1	2	3	4	5	6	7
$B''=$	1.92	1.91	1.88	1.86	1.84	1.83	1.81

In using these values, on the basis of the well-known formula $B_v = B_e - \alpha(v + \tfrac{1}{2})$, and with the reduced mass 11.4×10^{-24} grams for the CO molecule the following constants were obtained:

	upper $^{*2}\Sigma$	lower $^{2}\Sigma$	state
B_0	1.77	1.94	$\times cm^{-1}$
B_e	1.778	1.954	$\times cm^{-1}$
α	0.032	0.019	$\times cm^{-1}$
I_e	15.56	14.16	$\times 10^{-40}$ g cm^2
r_e	1.168	1.114	$\times 10^{-8}$ cm.

The writer wishes to express his thanks to Professor Robert S. Mulliken, who suggested the work above.