

THE ÅNGSTRÖM SYSTEM OF THE $^{13}\text{C}^{16}\text{O}$ MOLECULE

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Photographs of the Ångström system in the spectrum of the $^{13}\text{C}^{16}\text{O}$ molecule have been taken with a dispersion ranging from 0.6 to 1.15 Å/mm. The wave numbers of the spectral lines and the band origins of all eight strongest bands were found. The lines were interpreted and the places exhibiting perturbation indicated. The first quantum and the rotational constants of the $B^1\Sigma^+$ state were calculated, and the obtained values are $G(1)-G(0) = (2037.320 \pm 0.009) \text{ cm}^{-1}$, $B_0 = (1.8625 \pm 0.0001) \text{ cm}^{-1}$, $B_1 = (1.8373 \pm 0.0006) \text{ cm}^{-1}$, $D_0 = (6.20 \pm 0.07) \times 10^{-6} \text{ cm}^{-1}$, $D_1 = (5.8 \pm 1.2) \times 10^{-6} \text{ cm}^{-1}$, $B_0 - B_1 = (0.02467 \pm 0.00005) \text{ cm}^{-1}$. Also, the values of $B_e = (1.96127 \pm 0.00003) \text{ cm}^{-1}$ and $\alpha_e = (0.02641 \pm 0.00003) \text{ cm}^{-1}$ (calculated per $^{12}\text{C}^{16}\text{O}$ molecule) were obtained.

Introduction

An investigation of the isotopic spectra of CO molecules can yield ample information concerning this very important molecule.

The Ångström system in the spectrum of the $^{13}\text{C}^{16}\text{O}$ molecule has already been the subject of research by McCulloh and Glockler [1] and Douglas and Møller [2]. In the work of the former authors the dispersion was 5.6 Å/mm and they gave preliminary values of the rotational and vibrational constants. The photographs of Douglas and Møller were taken already with a slightly better dispersion (2.5 Å/mm), but as they were primarily interested in the predissociation phenomenon only the 0-2 and 1-1 bands, and a part of the 0-1 band, had been studied.

This author has attempted to obtain all the stronger bands of the Ångström system with better dispersion and to assign them a proper interpretation.

Experimental conditions

The emission spectrum was obtained under conditions of high rotational temperature in an ordinary discharge tube. The tube was filled with carbon oxide containing 70% of ^{13}C , and the pressure inside ranged from 5 to 10 mm Hg. The Ångström bands were photographed

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in the spectra of the 4th, 5th and 6th order obtained in a 2 m plane grating PGS spectrograph (VEB Carl Zeiss, Jena). The dispersion ranged from 0.6 to 1.15 Å/mm, the iron spectrum being used as a reference. The temperature in the spectrograph chamber was well stabilized. The measurements were performed with an Abbé-type comparator. The wave numbers were calculated from the wavelengths with the help of the Kayser tables [3] with account taken of the Edlén corrections [4]. Exposures of ORWO-NP-27 films ranged from 5 to 15 min.

Results

The rotational lines of all the stronger bands of the Ångström system, *i.e.* 0–0, 0–1, 0–2, 0–3, 0–4, 0–5, 1–0 and 1–1, have been obtained and measured, in general, up to the predissociation limit. An interpretation of the lines was made, rendered difficult because of perturbations present in the lower $A^1\pi$ state. The analysis of the 0–0 band, being the most perturbed one, was especially difficult. The interpretation of the rotational lines and their wave numbers are given in Tables I to VIII. The places where perturbations appear are apparent in the tables. The lines blended with those of the $^{12}\text{C}^{16}\text{O}$ molecules are written in parenthesis, whereas figures marked by one or two asterisks are the less reliable or unreliable wave number values, respectively. Relative errors for the remaining lines do not, according to the author's assessment, exceed 0.02 cm^{-1} , and absolute errors 0.05 cm^{-1} .

The wave numbers of the 0–1, 0–2 and 1–1 bands are in a good agreement with those given by Douglas and Møller [2]. In a number of bands predissociation is observed in the same places as indicated by the mentioned authors. Band origins have been calculated by interpolating the *P* and *R* branches and extrapolating the *Q* branch; also their errors have been estimated. In Table IX the obtained wave numbers of the band origins are given and compared with corresponding values taken from other papers.

On the basis of an analysis of the plot of $\Delta_2 F''(J)/J+1/2$ against $(J+1/2)^2$ it was first seen that the origins of the 0–0, 0–1, 1–0 and 1–1 bands are displaced due to rotational perturbations, whereas the remaining bands have unperturbed origins. Moreover, it was clear that the displacement of the 0–1 and 1–1 bands was much smaller than that for an ordinary molecule [5].

Making use of the calculated differences $\Delta_2 F'_0(J)$ and $\Delta_2 F'_1(J)$ the rotational constants of the $B^1\Sigma^+$ state were found by then method of least squares. The following values were obtained:

$$B_0 = (1.8625 \pm 0.0001)\text{ cm}^{-1}, D_0 = (6.20 \pm 0.07) \times 10^{-6}\text{ cm}^{-1},$$

$$B_1 = (1.8373 \pm 0.0006)\text{ cm}^{-1}, D_1 = (5.8 \pm 1.2) \times 10^{-6}\text{ cm}^{-1}.$$

In addition, the mean values of the differences between the corresponding wave numbers of the 1–0 and 0–0 bands, and also the 1–1 and 0–1 bands, have been calculated. According to Jenkins and McKellar [6] these values give the expression $G(1) - G(0) = (B_0 - B_1)J(J+1)$. By means of the method of least squares the values of the first vibrational quantum of the *B* state and the difference $B_0 - B_1$, together with their mean square errors,

TABLE I

0—0 band

<i>J</i>	<i>R</i> branch	<i>Q</i> branch	<i>P</i> branch
1	22173.63**	(22166.37)	22162.61**
2	178.93	167.72	160.31*
3	184.82	169.81	158.84**
4	191.61	172.60	158.01*
5	199.04	176.13	158.01*
6	22207.78	180.45	22159.36
7	22206.26	185.62	22150.42
8	218.41	191.83*	155.09
9	229.63	199.34	158.84*
10	240.85	22208.66	162.61*
11	252.49	220.37	166.88
12	264.90	234.47	171.81*
13	278.26	221.09	177.80
14	22281.48	293.46	22173.63*
15	298.28	22311.53	182.95
16	22314.12**	241.32	22196.21
17	329.86	252.20	(191.32)
18	345.93	263.69	199.73
19	362.49	275.76	22208.40
20	379.68*	288.51	217.59
21	397.51*	(22301.82)	227.37
22	22416.03	315.97	237.81
23	436.20	330.83	249.02
24	22429.31**	22340.17	22261.82**
25	454.32	22347.20	unmeasured
26	475.34	361.60	22272.44
27	497.70	379.02	286.20
28	22509.55	397.69	301.23
29	536.67	22421.06	22320.95
30	561.36	22405.84	22305.73
31	587.13	429.31	325.53
32	22618.02	(450.41)	342.89
33	(22599.50)	472.42	361.29
34	629.17	22481.12	22384.91
35	656.11	22499.70	22366.34
36	682.90	507.20	388.77
37	unmeasured	530.54	22408.44
38	22738.03	553.54	427.83
39	765.96	577.14	447.83
40		22601.18	468.43
		625.86	489.14
		651.14	22510.83
		677.12	(533.12)
		22710.09	556.09

TABLE II

0—1 band

<i>J</i>	<i>R</i> branch	<i>Q</i> branch	<i>P</i> branch
1		20713.17	20709.45*
2	20725.79	714.58	707.14
3	731.63	716.72	(705.51)
4	738.16*	719.56	704.63**
5	745.46	722.99**	704.46
6	753.41*	(727.29)	704.98
7	762.07	732.27	706.20
8	771.45	737.94	708.12
9	781.49	744.30	710.73
10	792.29	751.37	714.09
11	20803.79	759.16	718.16
12	816.02	767.75	722.99**
13	828.91	20778.04	20773.52
14	842.64		786.08
15	857.52		796.85**
16		20870.20	20808.20
17	unmeasured		320.25
18	20903.18		833.12
19	920.31	20844.97	20849.66
20	938.11	859.80	
21	956.58	874.82	
22	975.74	890.29	20808.66
23	995.62	20906.52	821.18
24	21016.20	923.45	834.36
25	037.49	941.10	848.32
26	059.55	959.50	863.05
27	21080.61	21084.79	981.05
28	105.11		20976.93
29	129.27		997.78
30	154.09		21018.28
31	179.57		039.43
32	21205.75		061.29
33	(232.47)		083.84
34	(260.13)		21107.20
35	288.52		131.44
36	21317.55	21150.40	21005.25
37	347.27**	180.11	026.26
38	377.74**	206.58	047.98
39		233.47	070.44
40		(261.21)	093.63
		289.40*	21117.54
			142.32

TABLE III

0-2 band

<i>J</i>	<i>R</i> branch	<i>Q</i> branch	<i>P</i> branch
1	19305.21**	19297.79	19294.04*
2	310.44**	299.25	(291.88)
3	316.40**	301.49	290.31
4	323.14**	304.47	289.57
5	330.51**	308.20	289.57
6	(338.64)	312.68	290.31
7	347.81**	317.99	(291.88)
8	357.33	323.66	294.04
9	367.74	330.51*	297.01
10	378.91	337.92	19300.74
11	390.81	346.11	305.21
12	19403.50	355.05	310.44
13	416.85	364.77	316.40
14	431.00	375.16	323.14
15	445.88	386.35	330.51**
16	461.52	398.28	(338.64)
17	477.96*	410.96	347.81*
18	unmeasured	424.38	357.54
19	19512.94	438.20	368.03
20	531.58	453.50	379.29
21	551.01	469.20	391.34
22	571.22	485.67	19404.20
23	592.38*	502.87	417.97
24	19615.04	520.94	433.19
25	19632.42	539.85	455.44
26	657.55	559.75	19443.22
27	681.87	581.27	461.02
28	706.69	19608.14	477.96*
29	732.27	19592.86	495.51
30	758.77	618.55	513.76
31	19787.08	642.01	532.94
32	19809.96	665.59	19553.95
33	(840.01)	689.79	19569.54
34	869.02	19714.92	592.38*
35	899.19	739.94	19614.02
36		766.41	636.96
37		793.97	660.91
38		(19820.29)	19682.96
39		848.75	19708.88
		878.45	

TABLE IV

0-3 band

<i>J</i>	<i>R</i> branch	<i>Q</i> branch	<i>P</i> branch
1		17914.29*	17910.52*
2		915.83*	908.37
3	17933.09	918.18	907.01
4	939.99	921.34	906.44
5	947.62	925.28	906.65
6	956.07	930.01	907.65
7	965.34*	935.53	909.45
8	975.34	941.83	912.04
9	986.15	948.93	915.41
10	997.75	956.82	919.58
11	18010.13	965.49	924.53
12	023.34	974.94	930.28
13	037.26*	985.23	936.82
14	052.03	996.23	944.19
15	067.56	18008.08	952.27
16	083.88	020.71	961.19
17	18101.00	034.14	970.90
18	118.91	048.42	981.42
19	137.63	063.46	992.75
20	157.17	079.57	18004.88
21	177.56	18102.10	unmeasured
22	198.91		18031.88
23	18214.09		18039.68
24	241.61		059.77
25	unmeasured		076.36
26	289.94	18185.69	093.40
27	18315.02	210.88	18111.12
28	340.83	233.28	129.62
29	367.43	256.28	148.90
30	394.81	280.05	168.97
31	18423.00	(18304.46)	189.83
32	451.97	329.90	18211.51
33	481.74	356.03	234.00
34	18512.17	382.84	257.18
35	543.53	(18410.48)	281.29
36	575.69	439.12	18306.19
37	18608.62	468.44	331.86
38	642.38	498.56	358.36
39		18529.49	385.67
40		561.30	

TABLE V

0-4 band

<i>J</i>	<i>R</i> branch	<i>Q</i> branch	<i>P</i> branch
1		16564.29	16560.62**
2		565.94	558.55**
3		568.43**	557.30**
4	16590.41*	571.78**	556.87
5	598.28	575.90	557.30
6	16607.00	580.90	558.55
7	616.52	586.72	560.62
8	626.90	593.39	563.60
9	638.10	16600.86	567.37
10	650.13	609.18	571.95*
11	663.03**	618.32	577.36
12	676.57**	628.30	(583.68)
13	691.20*	639.16	590.76
14	16706.58	650.75*	598.72
15	722.75	663.25*	16607.44
16	739.78	676.73**	617.04
17	757.64	690.71	627.52
18	776.29	16705.69	638.78
19	795.82	721.51	650.90*
20	16816.16	738.16	663.86
21	837.34	755.66	677.66
22	859.32	773.97	692.28
23	882.18	793.18	16707.77
24	16905.87	16813.04	724.04
25	930.39	833.92	741.22
26	955.72	855.61	759.25
27	981.91	878.12	778.09
28	17008.93	16901.48	797.77
29	036.80	925.68	16818.31
30	065.51	950.71	839.69
31	095.07	976.62	861.95*
32	17125.51	17003.35	885.08
33	156.97	030.97	16909.24
34	17187.55	unmeasured	16932.53
35	221.28	088.77	958.97
36	255.14	17119.27	985.57
37		147.34	17012.94
38		180.91	041.21
39		214.01	070.37?

TABLE VI

0-5 band

<i>J</i>	<i>R</i> branch	<i>Q</i> branch	<i>P</i> branch	
1	(15255.04)	15247.71	15243.98	
2	260.65	249.48	242.01	
3	267.01	252.10	240.91	
4	274.23	255.60	240.69	
5	(282.27)	259.97	241.34	
6	291.31	265.22	242.87	
7	15301.16	271.36	245.27	
8	311.87	278.37	248.57	
9	323.43	286.24	252.72	
10	335.88	294.99	257.77	
11	349.26	15304.62	263.69	
12	363.56	315.11	270.50	
13	378.61	326.53	278.17	
14	394.60	(338.61)	286.76	
15	15411.44	351.94	296.16	
16	429.16	365.97	15306.47	
17	447.77	380.88	317.66	
18	467.24	396.65	329.72	
19	487.60	15413.32	342.70	
20	15508.85	(430.99)	356.59	
21	530.98	449.30	371.31	
22	(553.97)	468.63	386.98	
23	577.88	488.84	15403.50	
24	15602.71	15510.09	420.91	
25	628.46	532.98	439.33	
26	654.89*		458.44	
27	683.13		479.33	
28		15708.52		15497.36
29		740.08	603.02	521.60
30		768.65	629.60	542.82
31		15800.02	654.89*	566.88
32		832.27	681.07	591.83
33			15710.07	
34		15736.04	743.63	
35	15897.42	768.06		15642.44
36		799.18		669.87
37		15831.02		698.10
38		863.76		15727.21
39		896.94		756.77
40		15932.18		
				15817.08

TABLE VII

1-0 band

<i>J</i>	<i>R</i> branch	<i>Q</i> branch	<i>P</i> branch
1	24211.31	24203.64	24199.95**
2	216.31**	204.89	197.80**
3	221.57**	206.82	195.96**
4	228.06	209.45	194.95*
5	235.38*	212.75	194.95*
6	24243.66	216.75	24195.96*
7	24241.83	221.57	24186.69
8	253.51	227.40	191.01
9	264.23	234.45	194.49
10	274.90	243.32	197.80
11	285.97	254.44	24201.54
12	297.68	24267.96	205.92
13	24310.39	253.91	211.31
14	24312.88	263.12	24206.47
15	328.85	272.75	215.17
16	343.90	282.83	222.86
17	358.82*	293.44	230.40
18	373.88	24304.67*	238.21
19		316.42	246.49
20			24255.39**

TABLE VIII

1-1 band

<i>J</i>	<i>R</i> branch	<i>Q</i> branch	<i>P</i> branch
1		22750.41	
2		751.74	22744.40*
3		753.71	
4		756.36	741.60**
5		759.66	741.26
6	22789.28	763.57	741.60*
7	797.64	768.15	742.46
8	22806.53	773.47	744.04
9	unmeasured	779.38	746.33
10	826.33	(786.21)	749.22
11	837.21	793.21	752.78
12	848.78	22801.22	757.03
13	861.04	810.84	22806.30
14	873.99		818.24
15	22888.10		828.24
16		22899.93	838.79
17		915.46	850.01
18		931.08	22861.99
19		22872.87	22774.37
20			22778.91
			787.09
			795.40
			22804.25
			813.69

Band origins (in cm^{-1})

Band	After Mc Culloh and Glockler [1]	After Douglas and Møller [2]	This work
0-0	—	—	$22165.63 \pm 0.05^*$
0-1	20712.5	20712.50	20712.48 ± 0.02
0-2	19297.1	19297.00	19297.02 ± 0.02
0-3	17913.5	—	17913.46 ± 0.01
0-4	16563.6	—	16563.44 ± 0.02
0-5	15246.8	—	15246.84 ± 0.01
1-0	—	—	$24203.01 \pm 0.05^*$
1-1	22749.9	22749.76	22749.75 ± 0.03

* From Q branch only.

have been calculated from these differences. The values $G(1) - G(0) = (2037.320 \pm 0.009) \text{ cm}^{-1}$ and $B_0 - B_1 = (0.02467 \pm 0.00005) \text{ cm}^{-1}$ were obtained and it is noteworthy that the difference $B_0 - B_1$ is evaluated with an error smaller than those of B_0 and B_1 themselves.

By taking the differences $B_0 - B_1$ corresponding to the $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ molecules [5] it was possible to calculate the constant α_e of the B state with considerable accuracy (assuming that the γ_e constant equals 0, what is relatively reasonable). The value of $\alpha_e = (0.02641 \pm 0.00003) \text{ cm}^{-1}$, calculated per $^{12}\text{C}^{16}\text{O}$ molecule, was obtained. Accepting this value of α_e and taking the value of B_0 (being evaluated more exactly than B_1) for both of the isotopic molecules, the value of $B_e = (1.96127 \pm 0.00003) \text{ cm}^{-1}$ was obtained for the B state of the $^{12}\text{C}^{16}\text{O}$ molecule.

Evaluation of the rotational constants of the $A'\pi$ state and a full vibrational analysis has been postponed until the data corresponding to the isotopic $^{12}\text{C}^{18}\text{O}$ molecule [7] is completely elaborated. For then it will be possible to work with a greater number of bands of unperturbed origins. It will also be possible then to calculate the vibrational constants of the $B^1\Sigma^+$ state more accurately [1].

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