ÅNGSTRÖM SYSTEM OF THE ^{12}C ^{18}O MOLECULE

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Photographs were made of the Ångström system in the emission spectrum of the ^{12}C ^{18}O molecule with dispersion between 0.6 and 1.1 Å/mm.

Rotational analysis was undertaken and points of perturbation found. For the $B^1\Sigma^+$ state the following constants were obtained: $G(1)-G(0) = (2033.56_4 \pm 0.02_4)$ cm^{-1}, $B_0 = (1.8553_3 \pm 0.0001_2)$ cm^{-1}, $D_0 = (6.1_1 \pm 0.1_2) \times 10^{-6}$ cm^{-1} and $B_0 - B_1 = (0.0244_8 \pm 0.0002_6)$ cm^{-1}. In addition, for the $A^1\pi$ state, some rotational constants and oscillation quanta from the less perturbed bands, were calculated.

The results obtained by the author for three isotope molecules of carbon oxide were used to obtain the vibrational and rotational constants for both electronic states. The perturbation shifts of the origins of the bands of all three molecules and isotopic electronic shifts, were also found.

Introduction

Continuing the research on the Ångström system (transition $B^1\Sigma^+ - A^1\pi$) in the carbon oxide isotope molecular spectra [1, 2] the system was obtained and investigated in the ^{12}C ^{18}O molecule. This was reported earlier in a brief note [3].

The spectrum of the ^{12}C ^{18}O molecule was not hitherto investigated, however, after having had sent the Letter to the Editor [3], the author was informed that this spectrum has been obtained independently with a medium dispersion, by Janjić, Pešić and Janković [4].

Experimental

The instrument, the way spectra were obtained, their measurement and the wavelength standards were described earlier [2]. The lamps used were of similar type as before and were filled with ^{12}C ^{18}O$_2$ where the content of the heavier oxygen isotope in oxygen was 18%.

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Results

Photographs of eight of the strongest bands of the Ångström system with dispersion between 0.6 and 1.1 Å/mm were made. Despite the concentration of the isotopic molecules being small, the spectrum lines were clear enough to perform measurements at least for some parts of the bands. The measurements however, were slightly less accurate than what could be expected from the value of dispersion. The accuracy of the wave number determination is estimated at 0.07 cm^{-1} (absolute position) and 0.03 cm^{-1} (relative position).

In Tables I–VIII the wave number of the rotational lines of the various bands and their interpretation, are given. The interpretation was made easier as, because of the small difference between the reduced masses, the bands were perturbed in practically the same places as in the ^{13}C ^{16}O molecule.

TABLE I

0–0 bands lines (in cm^{-1})

J	R branch	Q branch	P branch
1			
2		(22167.29)	
3		169.26	22158.45**
4		172.07	157.53**
5	22198.51**	(175.59)	157.53**
6	207.35**	(179.94)	159.11*
7	(205.96)	185.18**	150.55**
8	217.93*	(191.32)	154.84**
9	228.96*	22199.07	158.45*
10	240.06	208.69	(162.13)
11	251.62	201.35	(166.37)
12	264.02	210.83	171.37*
13	277.56	220.35	177.48*
14	281.18*	230.16	173.72**
15	297.49**	240.43	(182.60)
16	22313.09	251.27	190.86
17	(328.75)	262.66*	199.07
18	344.63	274.72	22207.68
19	361.13	287.42	216.79
20	377.95	22300.76	226.54
21	396.03	314.82	236.97
22	22414.66	329.72	(248.12)
23	perturbed	perturbed	perturbed
24		360.53	271.74
25		blended	285.47
26		397.26	22300.15
27		perturbed	perturbed
28		22428.38	324.97
29			342.85
30			(360.11)
31			perturbed

TABLE II

0–1 band lines (in cm^{-1})

J	R branch	Q branch	P branch
1			
2			
3		(20718.51)	20707.60**
4		721.53**	unmeasured
5		725.00*	706.51**
6	20755.23**	729.30	707.02**
7	763.91**	(734.43)	708.26*
8	773.24**	739.83	710.09*
9	783.26*	746.20	712.75*
10	(794.03)	(753.11)	(716.30)
11	20805.50*	761.22	720.16*
12	817.73*	772.08 767.66	725.00*
13	830.74	778.02	730.61*
14	845.44	788.01	737.92
15	(856.76)	798.58*	742.06*
16	872.35	20809.93	750.09
17	888.07	822.19	758.45
18	20904.44	833.55	767.45
19	921.48	847.32	777.15
20	939.17	861.43	(787.57)
21	957.57	876.20	798.58**
22	976.66	891.60	20810.23
23	996.46	20907.72	822.68
24	21016.93	924.57	835.88
25	(038.33)	(942.15)	849.71
26	060.12	960.42	864.37
27	21084.08	980.77	perturbed
28	21105.53	998.59	895.16
29	129.60	21019.00	20911.95
30	154.29	040.09	929.36
31	179.69	(061.86)	947.45
32	21205.80	084.37	966.27
33	(232.47)	21107.60	(985.67)
34	(260.10)	131.73	21005.99
35	288.17	158.59 150.08	026.91
36	317.07	180.21	unmeasured
37	346.66	206.56	070.97
38		233.40	094.07
39		260.86	21117.87
40			142.56

The wave number values not known for certain were marked in the Tables with asterisks.

In Table IX origins of the bands found by interpolation were listed together with estimated errors. Independently, using the least-square method, from the formulae of

TABLE III

0–2 band lines (in cm⁻¹)

J	R branch	Q branch	P branch
1	19309.75*		19298.64*
2	(315.05)	(19304.04)	296.41*
3	320.89*	306.07	294.92*
4	327.59*	309.04	294.16*
5	334.95**	312.76	294.16
6	343.20*	317.22	294.92
7	(351.88)	(322.34)	296.41
8	361.65*	328.14	298.64
9	372.03	334.95*	19301.58
10	383.16	342.33	305.31
11	395.02	350.49	309.75
12	19407.63	359.40	(315.05)
13	unmeasured	369.03	320.89
14	435.05	379.43	327.59
15	449.86	390.57	334.95*
16	465.45	19402.43	343.20
17	481.80*	415.06	352.15*
18	498.84	428.45	361.87
19	19516.68	442.57	372.28
20	535.24	457.44	383.51
21	554.60	473.08	395.52
22	574.75	489.48	19408.33
23	595.87	(19506.46)	422.05
24	19618.49	524.63	437.34
25	635.87	543.47	447.44
26	660.68	563.49	464.94
27	684.89	584.86	481.80
28	19709.64	19612.09	499.26
29	735.13	618.49	19517.47
30	761.56	645.18	536.60
31	(790.07)	668.67	557.67
32	19814.39	692.76	574.65*
33	perturbed	19718.72	perturbed
34	(871.61)	742.75	19617.32
35		769.16	640.16
36		796.95	664.30
37		19821.79	perturbed
38		851.22	

Jenkins and McKellar ([5], p. 188) for bands with unperturbed origins, the following values were found:

$$\sigma_{02} - \sigma_{05} = G(5) - G(2) = (4043.26_1 \pm 0.01_3) \text{ cm}^{-1};$$

$$\sigma_{03} - \sigma_{05} = G(5) - G(3) = (2662.117 \pm 0.006) \text{ cm}^{-1};$$

TABLE IV

0–3 band lines (in cm^{-1})

J	R branch	Q branch	P branch
1		17921.26**	
2		922.83	
3		925.19	17914.02
4		928.32	913.47
5	17954.52	932.27	913.73
6	962.93	936.98	(914.51)
7	972.16*	942.46	916.50
8	982.14	948.74	919.07
9	992.89	955.81	922.43
10	18004.41	963.65	926.57
11	016.75	972.28	931.51
12	029.90	981.70	(937.29)
13	043.80	991.92	943.73
14	058.49	18002.93	951.02
15	073.96	014.73	959.14
16	090.20	027.28	968.02
17	18107.30	040.68	977.69
18	125.15	054.90	988.17
19	143.78	070.06	999.48
20	163.33	18088.73	18011.61
21	183.80**	18101.35	024.69
22	18206.03	118.89	18039.57
23	18224.44	137.09	18050.62
24	247.74	156.14	066.62
25	271.26	176.56	082.76
26	(295.57)	195.29	099.68
27	18320.63*	216.29	(18117.18)
28	346.13	239.03	135.71
29	372.60	261.90	154.91
30	399.90	285.55	174.90
31	18427.91	18309.98	195.72
32	unmeasured	335.20	18217.29
33		361.21	239.65
34		387.84	262.67
35		unmeasured	286.69
36		unmeasured	unmeasured
37		unmeasured	unmeasured
38		18503.14	18363.47
39		unmeasured	390.63

and

$$B_2'' - B_5'' = (0.0653_9 \pm 0.0001_0) \text{ cm}^{-1};$$

$$B_3'' - B_5'' = (0.04340_7 \pm 0.00004_5) \text{ cm}^{-1}.$$

TABLE V

0–4 band lines (in cm^{-1})

J	R branch	Q branch	P branch
1			
2		16575.29	
3		577.75	
4		581.11**	16566.23
5	16607.42	585.20	566.65
6	(616.08)	590.16	567.94
7	625.62	595.96	570.06
8	635.94	16602.58	572.92
9	647.09	610.03	576.67
10	659.12	618.30	581.24**
11	671.87	627.41	586.62
12	685.43**	(637.36)	592.88
13	16700.03	648.12	(16600.03)
14	(715.19)	659.75*	607.83
15	731.44	672.15	616.55
16	748.43	685.43*	626.13
17	766.19	699.48	636.52
18	(784.55)	16714.42	647.77
19	16804.20	730.17	659.75**
20	824.46	746.77	672.73
21	845.53	764.19*	686.46
22	867.46	782.45	16701.01
23	890.22	16801.58	716.43
24	16913.79	821.34	732.70
25	938.24	842.09	749.80
26	963.48	863.68	767.73
27	989.55	886.12	786.45
28		16909.37	16806.06
29		933.48	826.57
30		958.42	847.84
31		984.18	870.00
32		17010.81	892.98
33		038.29	16917.09
34		066.62	(941.48)
35			unmeasured
36			992.30

The values of the rotational constants of the $A^1\pi$ state, using the $\Delta_2 F''(J)$ differences, were also found for three least perturbed bands:

$$B_2'' = (1.4844_8 \pm 0.0003_9)\ \text{cm}^{-1}; \quad D_2'' = 7_2 \times 10^{-6}\ \text{cm}^{-1};$$

$$B_4'' = (1.4402_6 \pm 0.0005_0)\ \text{cm}^{-1}; \quad D_4'' = 5_7 \times 10^{-6}\ \text{cm}^{-1};$$

$$B_5'' = (1.4202_6 \pm 0.0003_7)\ \text{cm}^{-1}; \quad D_5'' = 9_6 \times 10^{-6}\ \text{cm}^{-1}.$$

TABLE VI

0–5 band lines (in cm^{-1})

J	R branch	Q branch	P branch
1		15259.26	
2	15271.92**	260.98	
3	278.43**	263.59	15252.44
4	285.62	267.08	252.24
5	293.70**	271.46	252.88
6	15302.64	276.67	254.40
7	312.46	282.76	256.83**
8	323.14	289.74	260.05**
9	334.70	297.59	264.18
10	347.10	15306.31	269.22
11	360.39	315.91	275.12
12	374.53	326.37	281.88
13	389.56	337.72	289.51
14	(15405.58)	349.93	298.05
15	422.25	363.00	15307.45
16	429.91	376.95	317.74
17	458.44*	391.77	328.89
18	477.86	15407.50	340.92
19	(498.23)	424.10	353.82
20	15519.32	441.58	367.58
21	540.99*	459.96	382.00
22	564.26**	479.25	397.83
23	588.09	499.45	15414.30
24		15520.81	431.69
25		541.32	450.10
26			469.39
27			perturbed
28			15508.92
29			528.80
30			553.24
31			577.11

From six bands of $0-v''$ progression, average values of differences $\Delta_2 F'_0(J)$ were found for the state $B^1\Sigma^+$ and from them $B'_0 = (1.8553_3 \pm 0.0001_2)$ cm^{-1} and $D'_0 = (6.1_1 \pm 0.1_2) \times 10^{-6}$ cm^{-1}. Applying the formula of Jenkins and McKellar the value of the quantum $G'(1) - G'(0)$ $= (2033.56_4 \pm 0.02_4)$ cm^{-1} and the difference $B'_0 - B'_1 = (0.0244_8 \pm 0.0002_6)$ cm^{-1} were found. The knowledge of the difference $B'_0 - B'_1$ enabled to determine the constant B'_1 $= (1.8308_5 \pm 0.0002_8)$ cm^{-1} which could not be found for this isotopic molecule in any other way.

Predissociation in the ^{12}C ^{18}O molecule was found for the same J values as that for the ^{13}C ^{16}O molecule [6].

TABLE VII

1–0 band lines (in cm⁻¹)

J	R branch	Q branch	P branch
1		24199.16**	
2		200.47*	
3		202.42	24191.91**
4		205.03	190.67**
5		208.33	190.67*
6		212.42	191.91*
7		217.30	183.12
8		223.19	187.03
9		230.41	190.23
10		239.52	193.49
11		231.65	197.20
12		240.52	24201.62
13			207.20
14			perturbed

TABLE VIII

1–1 band lines (in cm⁻¹)

J	R branch	Q branch	P branch
1		22748.65*	
2		750.01*	
3		752.02*	
4		754.56*	
5		(758.07)	22739.60*
6		761.90*	
7		766.41*	
8		771.64*	742.34*
9	22814.21*	777.53*	744.59*
10		784.17*	747.46*
11		791.54*	751.14*
12		797.44*	755.34*
13		22807.12*	760.40*
14		(816.54)	(767.05)

The collective description of isotopic CO molecules

Investigations on the ^{12}C ^{16}O, ^{13}C ^{16}O and ^{12}C ^{18}O molecules have rendered sufficient data to perform the vibrational and rotational analysis of the spectra. Only revised and recently obtained results ([1], [2] and this paper) were used for this purpose.

The oscillation constants of the $A^1\pi$ state were known up to-date from the calculation of Reed [7] for the bands of the IV positive system in which perturbation shifts of the band

TABLE IX

Observed band origins of ^{12}C ^{18}O molecule (in cm^{-1})

Band	Band origins
0—0	22165.07 ± 0.05[a]
0—1	20714.43 ± 0.03
0—2	19301.63 ± 0.03
0—3	17920.49 ± 0.03
0—4	16572.80 ± 0.02
0—5	15258.36 ± 0.02
1—0	24198.51 ± 0.05[a]
1—1	22747.98 ± 0.05[a]

[a]from Q branch only.

TABLE X

Vibrational constants of ^{12}C ^{16}O molecule (in cm^{-1})

Constant	$A^1\pi$ state	$B^1\Sigma^+$ state
ω_e	$1518.42_1 \pm 0.06_6$	2153.92_9
$\omega_e x_e$	$17.67_8 \pm 0.02_6$	35.87_9
$\omega_e y_e$	$0.014_6 \pm 0.002_8$	0[a]

[a]assumed value.

TABLE XI

Rotational constants of ^{12}C ^{16}O molecule (in cm^{-1})

Constant	$A^1\pi$ state	$B^1\Sigma^+$ state
B_e	$1.6150_4 \pm 0.0005_7$	1.96127 ± 0.00003
α_e	$0.0224_4 \pm 0.0002_8$	0.02641 ± 0.00003
γ_e	$-0.00011_4 \pm 0.00003_2$	0[a]
D_e	—	$(6.51 \pm 0.02) \times 10^{-6}$

[a]assumed value.

TABLE XII

Perturbational shifts of band origins (in cm^{-1})

Band	Shift in molecule		
	^{12}C ^{16}O	^{13}C ^{16}O	^{12}C ^{18}O
$v'-0$	0	0.6_7	0.7_0
$v'-1$	-5.23	-1.7_1	-1.7_6
$v'-2$	0	0	0
$v'-3$	0	0	0
$v'-4$	-0.66	0	0
$v'-5$	$(0.11)?$	0	0

origins were not taken into account. The present calculation is based on the differences between the origins of the non-perturbed bands of three isotopic molecules ·(obtained generally from the Jenkins and McKellar formula). Taking into account isotopic relations between the constants, eleven equations were drawn from which, using the least-square method, 3 oscillation constants for the A state with their square standard deviations, were obtained (Table X).

Knowing the three oscillation quanta $\Delta G_{1/2}$ of the $B^1\Sigma^+$ state, the oscillation constants ω_e and $\omega_e x_e$ for the B state, were calculated (Table X). The latter constants have been earlier determined by McCulloh and Glockler [8] on the base of two, less accurately known, values of $\Delta G_{1/2}$ (the result does not differ much from the present one), and by Tilford and Vanderslice [9] whose result differs considerably from the present one.

The knowledge of the oscillation constants for both states enabled to determine the values of perturbation shifts of band origins (these are compared in Table XI) and also the values of the constants $\sigma_e = T'_e - T''_e$ for each isotopic molecule:

$$\sigma_e(^{12}C\ ^{16}O) = 21858.14\ cm^{-1}$$

$$\sigma_e(^{13}C\ ^{16}O) = 21858.67\ cm^{-1}$$

$$\sigma_e(^{12}C\ ^{18}O) = 21858.56\ cm^{-1}.$$

In order to calculate the rotational constants of the A state, B_v values of slightly perturbed bands calculated directly and differences ΔB calculated from the Jenkins and McKellar formula, were used. This made it possible to set 21 equations for which a weighted calculation using the method of least-squares was performed. In this way the constants B_e, α_e and γ_e were found (Table XII). These constants were also estimated earlier by Schmid and Gerö [11]. The obtained D_v values were not considered.

Rotational constants B_e and α_e of the B state were determined from the values of B_0 and $B_0 - B_1$ for the three molecules, with considerable accuracy (under the assumption that $\gamma_e = 0$). These values are found in Table XII, calculated for the $^{12}C\ ^{16}O$ molecule. In the same Table one may find the value od D_e calculated from the constants D_0 for the three molecules for the value $\beta_e = 0.38 \times 10^{-6}\ cm^{-1}$ determined from the equation relating β_e to other constants ([5], formula III, 125).

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