

## THE ANALYSIS OF THE HERZBERG SYSTEM IN THE $^{13}\text{C}^{16}\text{O}$ AND PARTLY IN THE $^{12}\text{C}^{16}\text{O}$ MOLECULES

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In the emission spectrum of the carbon monoxide isotopic molecules the Herzberg bands at a 0.6 Å/mm dispersion have been obtained. For the  $^{13}\text{C}^{16}\text{O}$  molecule all the seven bands of this system have been obtained and for the  $^{12}\text{C}^{16}\text{O}$  molecule the 0–2 and 0–3 bands only. A rotational analysis of these bands has been performed and the following constants were determined: the rotational constants of the  $C^1\Sigma^+$  and  $A''\Pi$  states, the band origins for the  $C^1\Sigma^+ - A''\Pi$  transition, and the new vibrational constants for the  $C^1\Sigma^+$  state.

### Introduction

The  $C^1\Sigma^+$  state was the subject of many studies in new systematic investigations of the electronic levels of the CO molecule, performed in recent years. Possibility for its explorations is given in the absorption as well as in the emission spectrum. In the absorption spectrum the  $C^1\Sigma^+$  state can be investigated from the Hopfield–Birge band system ( $C^1\Sigma^+ - X^1\Sigma^+$  transition) situated in the vacuum ultraviolet region. In emission,  $C$  state can be investigated from the Herzberg bands ( $C^1\Sigma^+ - A''\Pi$  transition) situated in the visible and near ultraviolet region. An intercombination  $C^1\Sigma^+ - a'^3\Sigma^+$  emission bands, only once mentioned [12], does not give any further possibility for studies, than the one derived from the above transitions.

Up to now most of the information about the  $C$  state has been derived from the high resolution studies of the  $C - X$  transition, reported by TILFORD and VANDERSLICE [22]. The 0–0 and 1–0 bands obtained in  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  molecules by these authors have made the calculation of the main molecular constants in this state possible. After detailed considerations, however, it seems that the constants obtained are doubtful. The same situation occurs for the constants of the  $B^1\Sigma^+$  state, derived in this paper from the analysis of the bands of the  $B - X$  system. Namely, in the calculations of the vibrational constants the authors have omitted the electronic isotope effect, what would not have been necessary, if both obtained vibrational quanta had been used.

Such an assumption has a significant effect upon the constant values (as can be seen from the detailed considerations) and consequently these values are very deformed. For example the  $\omega_e x_e$  constant values of both the

**Table I**  
0—0 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

<i>J</i>	<i>R</i>		<i>Q</i>		<i>P</i>	
1			27168.695**		27164.557*	
2	27181.209		169.910		162.529	
3	187.049		171.975		160.874*	
4	193.425		174.734*		159.931	
5	200.920		178.569		159.931	
6	209.800		182.542	27154.610	161.488	
7	220.305*	27208.190*	187.659	163.210	164.557	27152.493
8	234.040	220.305*	193.807	172.760	170.800	157.104
9		231.424	201.186	183.028		160.874*
10		242.590	210.461	192.720**		164.557*
11		254.099	222.102	203.435		168.695**
12		266.373	235.950**	213.032*		173.526
13	265.280	279.668		222.590	164.910	179.423
14	294.750	282.774		232.389	175.120	187.049
15	299.446	312.673*		242.590	184.383	197.611
16	315.138			253.374	192.720	
17	330.778			264.711	200.920	
18	346.693			276.665	209.437	
19	363.125			289.262	218.489	
20	380.149			302.509	228.140	
21	397.817			316.435*	239.433	
22	416.250*			331.138	249.490	
23			340.391*	347.374		262.086
24				361.591		272.630
25				378.823		286.183
26				397.308		301.028

*C* and *B* states obtained under this assumption are only about half of the real values.

Other papers published on the *C* state were concerned with the Herzberg bands, but as they were based upon either fragmentary or insufficiently accurate analyses they did not give any further information about this state [5, 9]. Therefore the author attempts to give complete studies of the *C* state by means of analyses of the Herzberg bands in isotopic molecules. In this way, due to the advantageous location of these bands and by the use of molecules

**Table II**  
0—1 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

<i>J</i>	<i>R</i>	<i>Q</i>	<i>P</i>	
1	25722.794**	25715.389	25711.659	
2	727.941	716.791	709.373	
3	733.753	718.877	707.743	
4	740.251	721.681*	706.814	
5	747.462	725.176	706.603	
6	755.367	729.363	707.065	
7	763.969	734.257	708.204*	
8	773.268	739.843	710.113	
9	783.271	746.126	712.690	
10	793.949	753.119	715.955	
11	805.347	760.832*	719.930	
12	817.436	769.324	724.615	
13	830.258	779.482	25774.940 730.009	
14	843.864		787.448 736.215	
15	858.620		798.100 743.573	
16	25871.180		809.325 25748.727	
17	887.450		821.241 757.632	
18	903.876		833.972 766.634	
19	920.858	845.671	850.365 776.205*	
20	938.497	860.486		786.493
21	956.826	875.227		797.439
22	975.827	890.604		809.100
23		906.630		821.419
24		923.375		834.471
25		940.822		848.243
26		959.053		862.785
27		976.313		876.398
28				893.364
29				910.004
30				927.294
31				945.290
32				963.953

**Table III**  
0—2 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

<i>J</i>	<i>R</i>	<i>Q</i>	<i>P</i>
1		24300.013	24296.035*
2	24312.659*	301.489	293.873*
3	318.563	303.690	292.446*
4	325.227	306.645	291.747*
5	332.618	310.344	291.747*
6	340.774	314.767	292.446*
7	349.615	320.029	293.873*
8	359.212	325.631	296.035*
9	369.553	332.348	298.967
10	380.628	339.730	302.629
11	392.442	347.847	307.029
12	404.984	356.690	312.163
13	418.287	366.274	318.041
14	432.300	376.594	324.662
15	447.068	387.651	332.029
16	462.569	399.459	340.136
17	478.824	412.012	348.990
18	495.817	425.300	358.599
19	513.566	439.343	368.952
20	532.057	454.131	380.074
21	551.335	469.679	391.976
22	571.418	485.984	404.681
23	592.392	503.052	418.287
24		520.946	433.381
25		539.660	455.138
26		559.385	24461.107
27		580.727	476.840
28		607.423	24592.392

more enriched with  $^{13}\text{C}$  isotope, the determination of the line wave numbers may be performed with greater accuracy than in vacuum ultraviolet studies.

The Herzberg bands in the  $^{12}\text{C}^{18}\text{O}$  molecule have been the subject of previous analyses [15]. In this paper the analysis of this system in  $^{13}\text{C}^{16}\text{O}$  and partly in  $^{12}\text{C}^{16}\text{O}$  molecules is presented.

**Table IV**  
0—3 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

<i>J</i>	<i>R</i>	<i>Q</i>	<i>P</i>
1	22923.907**	22916.454**	22912.754*
2	929.129**	918.040	910.606
3	935.244	920.377	909.236
4	942.072	923.493	908.644
5	949.684	927.403	908.809
6	958.088	932.043*	909.783
7	967.210*	937.546	911.532
8	977.216	943.786	914.060
9	987.948	950.806	917.373
10	999.458	958.605	921.464
11	23011.760	967.205	926.341
12	024.828	976.563	932.043*
13	038.677	986.715	938.434
14	053.313	997.646	945.670
15	068.740	23009.368	953.686
16	084.935	021.878	962.491
17	101.921	035.176	972.082
18	119.703	049.281	982.465
19	138.278	064.224	993.653
20	157.656	080.205	23005.654
21	177.876*	102.586	23094.658
22	199.091		112.861
23		23222.922	131.029
24			149.939
25			169.696
26			
			048.801
			032.358
			018.502
			23039.996
			059.954
			076.356
			093.218

### Experimental procedure

The emission spectrum of the Herzberg bands has been obtained from a hollow-cathode type lamp. This type of lamp, although many other discharge tubes were tried, provided the highest intensity of the Herzberg bands relative to other "blending" systems. To obtain the spectrum of the  $^{12}\text{C}^{16}\text{O}$  molecule, a lamp was filled with gaseous carbon dioxide of spectral purity. The spectrum of the  $^{13}\text{C}^{16}\text{O}$  molecule was obtained from a lamp filled with gaseous carbon

**Table V**  
0—4 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

<i>J</i>	<i>R</i>	<i>Q</i>	<i>P</i>
1		21566.514*	
2	21579.186*	568.173	21560.697
3	585.365*	570.643	559.462
4	592.361*	573.867*	559.065*
5	600.218*	578.039	559.462
6	608.933*	582.977	560.697
7	618.430*	588.739	562.744
8	628.699*	595.328	565.586
9	639.846*	602.742	569.310
10	651.816*	610.976	573.867*
11	664.563*	620.029	579.186*
12	678.229*	629.919	585.365*
13	692.620	640.630	592.361*
14	707.861	652.163	600.218*
15	723.924	664.563*	608.858*
16	740.819	677.717	618.354*
17	758.535	691.739	628.699*
18	777.079	706.593	639.846*
19	796.437	722.261	651.816*
20	816.628	738.779	664.563*
21	837.595*	756.112	678.229*
22	859.493	774.294	692.729*
23	882.163	793.366	708.044
24		813.031	724.213
25		833.732	741.062
26		855.250	758.993
27		877.804*	777.715

dioxide enriched in 95% isotope  $^{13}\text{C}$ . Pressure in both types of the lamps was 3 mmHg. The lamps were supplied by 600 V d.c. generator with current about 50 mA. Photographs were made in the 5th, 6th and 7th orders of the plane-grating PGS-2 spectrograph (VEB Carl Zeiss, Jena) with a reciprocal linear dispersion from 0.38 Å/mm to 0.83 Å/mm. Expositions were made on ORWO UV1-type plates for shorter wavelength bands and on Agfa-Gevaert 68A56 plates for the longer wavelength i.e. for the 0—4, 0—5 and 0—6 bands. The

**Table VI**  
0—5 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

<i>J</i>	<i>R</i>	<i>Q</i>	<i>P</i>
2	20262.840**	20251.664*	20244.219**
3	269.084*	254.292	243.098
4	276.308	257.753	242.870
5	284.364	262.063	243.495
6	293.284	267.273	244.976
7	303.062	273.353	247.341
8	313.729	280.257	250.560
9	325.252	288.122	254.654
10	337.640	296.767	259.632
11	350.897	306.331	265.465
12	365.004	316.747	272.170
13	380.023	328.020	279.762
14	395.871	340.188	288.167*
15	412.591	353.216	297.556
16	430.180	367.121	307.754
17	448.666	381.893	318.837
18	468.018	397.542	330.791
19	488.252	414.069	343.625
20	509.339*	431.482	357.344
21		449.764	371.919
22		468.900	387.427
23		489.034	

exposure time of bands ranged from 2.5 to 7 hours. For the wavelength calibration Fe and Kr standard lines from the hollow-cathode type lamp and ordinary Geissler lamp were employed. The measurements of the lines with an accuracy ( $1 \mu\text{m}$ ) were performed using Abbé-type comparator. As a result of the deviations analysis of the calibration spectrum lines, the accuracy of band lines was estimated. The absolute accuracy is about  $0.005\text{--}0.010 \text{ cm}^{-1}$  and  $0.003\text{--}0.005 \text{ cm}^{-1}$  is the internal one. The lines marked by one or two asterisks for various reasons, small intensity, blending, etc. are respectively less accurate. Calculated values of the wave numbers of the lines for the 0—0, 0—1 up to the 0—6 band in the  $^{13}\text{C}^{16}\text{O}$  molecule are listed in Tables I to VII. Wave numbers of lines for the 0—2 and 0—3 bands in the  $^{12}\text{C}^{16}\text{O}$  molecule are given in Tables VIII and IX.

**Table VII**  
0—6 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

<i>J</i>	<i>R</i>	<i>Q</i>	<i>P</i>
2		18964.676*	
3		967.852	
4		971.879	18957.460**
5	18999.051	976.768	958.200**
6	19008.390	982.517	960.207
7	018.881	989.149	963.132
8	030.105	996.656	966.937
9	042.209	19005.057	971.683*
10	055.192*	014.319*	977.199
11	069.067	024.498	983.646
12	083.844	035.550	990.995
13	099.503	047.514	999.245
14	116.007	060.370	19008.390
15	133.541	074.141	018.468
16	151.863	088.805	029.440
17	171.277	104.459	041.427
18	191.270*	120.817	054.056
19	212.382**	138.218	067.777
20		156.522*	082.423
21			097.939

### Results and discussion

The  $B_0$  and  $D_0$  rotational constants for the *C* state were determined from  $R(J)$  and  $P(J)$  branch lines, by means of  $\Delta_2 F'(J)$  term differences. For this purpose, average values of these differences were determined from all the seven bands in the  $^{13}\text{C}^{16}\text{O}$  molecule, and from both analysed bands in the  $^{12}\text{C}^{16}\text{O}$  molecule. Using the least-squares method, by means of the equation:

$$\Delta_2 F'(J) = (4B_0 - 6D_0)(J + 1/2) - 8D_0(J + 1/2)^3, \quad (1)$$

the following constants were calculated:

$$B_0^C = (1.85847 \pm 0.00015) \text{ cm}^{-1},$$

$$D_0^C = (5.67 \pm 0.19) \cdot 10^{-6} \text{ cm}^{-1}$$

for the  $^{13}\text{C}^{16}\text{O}$  molecule and



**Table VIII**  
0—2 band lines of  $^{12}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

$J$	$R$	$Q$	$P$
1		24244.041	24239.958
2	24257.236	245.593	237.768*
3	263.400**	247.900	236.170*
4	270.414	250.984	235.419
5	278.154	254.859	235.419
6	286.667	259.519	236.170*
7	295.955	265.128	237.664
8	306.011	270.912	239.958
9	316.843	277.918	243.021
10	328.435	285.657	246.860
11	340.798	294.158	251.473
12	353.936	303.430	256.863
13	367.865	313.475	263.029
14	382.537	324.287	269.973
15	398.000	335.877	277.695
16	414.234	438.231	286.194
17	431.250	361.381	295.479
18	449.033	375.306	305.546
19	467.610	390.007	316.402
20	486.973	405.496	328.045
21	507.117	421.773	340.490
22	528.079	438.840	353.755
23	549.916	456.701	367.865
24	572.897	475.386	383.080
25	24598.350*	494.919	400.948 24389.451
26		515.369	414.234
27		537.002	430.266
28		561.294 24544.412	448.465
29			467.357

$$B_0^C = (1.94345 \pm 0.00007) \text{ cm}^{-1},$$

$$D_0^C = (6.28 \pm 0.07) \cdot 10^{-6} \text{ cm}^{-1}$$

for the  $^{12}\text{C}^{16}\text{O}$  molecule. On the basis of these  $B_0^C$  constant values and the constant obtained in the  $^{12}\text{C}^{18}\text{O}$  molecule [15], including also the  $B_0$  and  $B_1$  constants determined from the analysis of the Hopfield—Birge bands [22],

**Table IX**  
0—3 band lines of  $^{12}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

<i>J</i>	<i>R</i>	<i>Q</i>	<i>P</i>
1	228 39.020**	22831.317	22827.426*
2	844.605	832.951	825.177
3	850.957	835.410	823.744
4	858.117	838.686	823.139
5	866.092	842.782	823.343
6	874.886	847.714**	824.369
7	884.522	853.423	826.216
8	894.930	859.972	828.883
9	22906.175	867.338	832.367
10	918.234	875.520	836.676
11	931.120	884.522	841.802
12	944.817	894.352	847.714**
13	959.334	22904.994	854.513
14	974.667	916.453	862.109
15	990.820	928.731	870.519
16	23007.789	941.843	879.761
17	025.583	955.767	889.816
18	044.167	970.491	22900.678
19	063.623	986.086	912.410
20	083.831**	23002.484	924.948
21	23104.973	019.708	938.318
22	126.812	037.708	952.473
23	149.527	056.631	067.532
24	173.103	076.340	983.390
25	197.478*	096.884	23000.072
26	23222.646*	23118.223	017.562
27		140.589	035.985

a set of seven equations for the constants  $B_e$  and  $\alpha_e$  in the *C* state was established.\* Its solution after using the Dunham isotope relations [1] gives the following constant for the  $^{12}\text{C}^{16}\text{O}$  molecule:

$$B_e^C = (1.95381 \pm 0.00036) \text{ cm}^{-1},$$

$$\alpha_e^C = (0.02005 \pm 0.00039) \text{ cm}^{-1}.$$

\* Taking primarily the constants  $B_e$ ,  $\alpha_e$  and  $\gamma_e$  for the fitting of this set of data, the constant value  $\gamma_e$  was found in limits of its standard error; therefore further the constant  $\gamma_e$  was omitted.

**Table X**  
Rotational constants of the  $C^1\Sigma^+$  state for the  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{16}\text{O}$  molecules (in  $\text{cm}^{-1}$ )

Molecule	$^{13}\text{C}^{16}\text{O}$		$^{12}\text{C}^{16}\text{O}$	
	Present results	After TILFORD and VANDERSLICE [22]	Present results	After SCHMID and GERG [18]
$B_0$	$1.85947 \pm 0.00015$	1.8590	$1.94345 \pm 0.00007$	1.9422
$B_1$	—	1.8389	—	—
$D_0$	$(5.67 \pm 0.19) \cdot 10^{-6}$	$7.6 \cdot 10^{-6}$	$(6.28 \pm 0.07) \cdot 10^{-6}$	$5.7 \cdot 10^{-6}$
$D_1$	—	$6.1 \cdot 10^{-6}$	—	—
$B_e$	—	—	$1.95381 \pm 0.00036^*$	—
$\alpha_e$	—	—	$0.02005 \pm 0.00039^*$	—

\* — calculated with the assumption  $\gamma_e = 0$ .

**Table XI**  
Rotational constants  $B_v$  of the  $A''I$  state in  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{16}\text{O}$  molecules (in  $\text{cm}^{-1}$ )

Molecule	$^{13}\text{C}^{16}\text{O}$			$^{12}\text{C}^{16}\text{O}$		
	Present results	After McCULLOCH and GLOCKLER [14]	After JANIĆ et al. [6]	Present results	After SCHMID and GERG [19]	After SIMMONS et al. [20]
$B_0$	—	—	—	—	1.6001	1.6001
$B_1$	$1.5092$ (4)	1.509	—	—	1.5775	1.5788
$B_2$	$1.4895$ (2)	1.489	—	—	1.5561	1.5576
$B_3$	$1.4679$ (6)	1.468	—	—	1.5329	1.5346
$B_4$	$1.4463$ (4)	1.446	1.4460 (6)	—	1.5089	1.5108
$B_5$	$1.4241$ (4)	1.424	1.4238 (6)	—	1.4861	1.4877
$B_6$	$1.3988$ (6)	—	—	—	1.4616	1.4630

The uncertainty given in parentheses corresponds to a standard deviation.

Present and earlier data for the values of the rotational constants are listed in Table X. Using the Kovács's functions  $f_Q(J)$ ,  $f_{PR}(J)$  and  $f_{\overline{PR}}(J)$  [2], the differences of the rotational constants for both combining states were determined. The average values computed from all the band lines are respectively:

$$\begin{aligned} B_0^C &= B_1^A = (0.3490 \pm 0.0006) \text{ cm}^{-1}, \\ B_0^C - B_2^A &= (0.3687 \pm 0.0002) \text{ cm}^{-1}, \\ B_0^C - B_3^A &= (0.3902 \pm 0.0004) \text{ cm}^{-1}, \\ B_0^C - B_4^A &= (0.4120 \pm 0.0004) \text{ cm}^{-1}, \\ B_0^C - B_5^A &= (0.4341 \pm 0.0004) \text{ cm}^{-1}, \\ B_0^C - B_6^A &= (0.4593 \pm 0.0006) \text{ cm}^{-1} \end{aligned}$$

for the  $^{13}\text{C}^{16}\text{O}$  molecule and

$$\begin{aligned} B_0^C - B_2^A &= (0.3863 \pm 0.0002) \text{ cm}^{-1}, \\ B_0^C - B_3^A &= (0.4094 \pm 0.0001) \text{ cm}^{-1} \end{aligned}$$

for the  $^{12}\text{C}^{16}\text{O}$  molecule. From these values and the constants  $B_0^C$  determined previously the rotational constants of the  $A^{1I}$  state have been calculated. The results are listed in Table XI. For the calculation of band origins two methods were applied; the first one for the regular bands and the second for the bands with perturbation in initial rotational levels.

For the perturbed i.e. the 0—0, 0—1 and 0—6 bands the band origins have been determined by extrapolation of  $Q(J)$  branch lines and by  $R(J-1) + P(J)$  lines combinations [1]. In the remaining bands, the band origins have been found by means of  $g_Q(J)$ ,  $g_{PR}(J)$  and  $g_{\overline{PR}}(J)$  functions [2]. The results obtained by use of both methods are listed in Table XII. Further, using the constants  $B_v$  listed in Table XI, it was possible to recalculate the  $\sigma_{ov}^{CA}$  band origins to the  $c_{ov}^{CA}$  values i.e. "reduced" band origins. These values simply contain the differences of the electronic and vibrational terms for both combining states. Using the  $c_{ov}^{CA}$  values determined in the  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{16}\text{O}$  molecules as well as in  $^{13}\text{C}^{18}\text{O}$  (on the basis of earlier data [15]), and including the vibrational quanta  $\Delta G_{1/2}^C$  of the  $C$  state in the  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{16}\text{O}$  molecules [22] one can obtain the following equations for the vibrational constants of the  $C$  state:

$$\begin{aligned} c_{ov}^{CA} + G^A(v) &= \sigma_e^{CA} + \frac{1}{2} \omega_e^C - \frac{1}{4} \omega_e x_e^C, \\ \Delta G_{\frac{1}{2}}^C &= \omega_e^C - 2\omega_e x_e^C \end{aligned}$$

for the  $^{12}\text{C}^{16}\text{O}$  molecule,

Table XII

Band origins of the  $C^1\Sigma^+ - A^1\Pi$  system in  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{18}\text{O}$  molecules (in  $\text{cm}^{-1}$ )

Molecule	$^{13}\text{C}^{16}\text{O}$		$^{12}\text{C}^{18}\text{O}$		
	Present results	After [9]	Present results	After JOHNSON and ASUNDI [7]	After [9]
0-0	27168.0 $\pm$ 0.2				
0-1	25714.691 $\pm$ 0.016			25686.1	
0-2	24299.217 $\pm$ 0.018	24299.4	24243.264 $\pm$ 0.019	24243.2	24243.3
0-3	22915.679 $\pm$ 0.021	22915.8	22830.499 $\pm$ 0.016	22830.5	22830.6
0-4	21565.641 $\pm$ 0.028	21565.7			
0-5	20249.066 $\pm$ 0.025	20249.1			
0-6	18962.32 $\pm$ 0.03				

$$c_{ov(1)}^{CA} + G_{(1)}^A(v) = \sigma_{e(1)}^{CA} + \frac{1}{2} \rho_1 \omega_e^C - \frac{1}{4} \rho_1^2 \omega_e x_e^C,$$

$$\Delta G_{\frac{1}{2}(1)}^C = \rho_1 \omega_e^C - 2\rho_1^2 \omega_e x_e^C$$

for the  $^{13}\text{C}^{16}\text{O}$  molecule and

$$c_{ov(2)}^{CA} + G_{(2)}^A(v) = \sigma_{e(2)}^{CA} + \frac{1}{2} \rho_2 \omega_e^C - \frac{1}{4} \rho_2^2 \omega_e x_e^C$$

for the  $^{13}\text{C}^{18}\text{O}$  molecule, where  $\rho_1^2$  and  $\rho_2^2$  are the ratios of the reduced masses of the  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{18}\text{O}$  molecules, relative to the  $^{12}\text{C}^{16}\text{O}$  molecule. The values of  $G^A(v)$  vibrational terms in the  $A^1\Pi$  state were found using Dunham isotopic relations and the following constants of this state:\*

$$\omega_e^A = 1518.398 \text{ cm}^{-1},$$

$$\omega_e x_e^A = 17.678 \text{ cm}^{-1},$$

$$\omega_e y_e^A = 0.0146 \text{ cm}^{-1}.$$

For the  $c_{ov}^{CA} + G^A(v)$  values on the left side of Eqs. (2) average values, determined from all regular bands have been used. In the solution of this set of equations, which permits avoiding the influence of the error of experimental data on the calculated constants (impossible in the direct method of solution), some simplifications can also be employed. Namely, the  $\sigma_e^{CA}$ ,  $\sigma_{e(1)}^{CA}$  and  $\sigma_{e(2)}^{CA}$  system origin values on the right side of equations may differ only by differences of the electronic isotope effects of  $C$  and  $A$  states.

\* The constants were determined from reduced band origins obtained from RYTEL data [11, 16, 17] and isotopic relations.

The fact that the  $C^1\Sigma^+$  and  $B^1\Sigma^+$  states are Rydberg states and belong to the same electronic configuration:  $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(m\sigma)$ , where  $m = 7$  for the  $B^1\Sigma^+$  states and  $m = 9$  for the  $C^1\Sigma^+$  [13, 21] was also taken into consideration. Therefore, it was assumed that the behaviour of both the  $B$  and  $C$  states is similar and they have the same electronic isotope effects. As the exact values of the differences of electronic isotope effects in  $B^1\Sigma^+$  and  $A^1\Pi$  states are known [16]\*\*

$$\sigma_e^{BA}(^{12}\text{C}^{16}\text{O}) - \sigma_{e(1)}^{BA}(^{13}\text{C}^{16}\text{O}) = -0.590 \text{ cm}^{-1},$$

and

$$\sigma_e^{BA}(^{12}\text{C}^{16}\text{O}) - \sigma_{e(2)}^{BA}(^{12}\text{C}^{18}\text{O}) = -0.489 \text{ cm}^{-1},$$

the same values, as differences of the electronic isotope effects in  $C^1\Sigma^+$  and  $A^1\Pi$  states were used. Under such assumption the set of equations (2) was solved yielding the following constant values:

$$\begin{aligned}\omega_e^C &= (2220.2 \pm 1.3) \text{ cm}^{-1}, \\ \omega_e x_e^C &= (37.09 \pm 0.84) \text{ cm}^{-1}, \\ \sigma_e^{CA} &= (26826.6 \pm 1.6) \text{ cm}^{-1}.\end{aligned}$$

The confrontation of these results with the vibrational constants of other Rydberg states is presented in Table XIII. The fact that the constant values are quite similar proves the earlier hypothesis that the constants of all Rydberg states may be very similar [13], as well as the correctness of our assumptions.

Table XIII

Vibrational constants  $\omega_e, i, \omega_e X_e$  of the known Rydberg states in the  $^{12}\text{C}^{16}\text{O}$  molecule (in  $\text{cm}^{-1}$ )

Constant State		$\omega_e$	$\omega_e x_e$
$C^1\Sigma^+$	Present results	$2220.2 \pm 1.3$ (2175.92)*	$37.09 \pm 0.84$ (14.76)*
	After RYTEL [16]	2153.929	35.879
$B^1\Sigma^+$	After McCULLOH and GLOCKLER [14]	2160.7 (2112.70)*	39.3 (15.22)*
	After KÉPA et al. [10]	2246.85	46.53
$c^3\Pi$	After DANIELAK et al. [8]	2246	—
$j^3\Sigma^+$	After TILFORD and VANDERSLICE [22]	(2196)*	(15.0)*

( ) \* TILFORD and VANDERSLICE results [22].

\*\* The values were recalculated using the reduced band origins and new vibrational constants of the  $A^1\Pi$  state, presented earlier.

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