Journal of Molecular Spectroscopy **197,** 199–211 (1999)
Article ID jmsp.1999.7916, available online at http://www.idealibrary.com on IDEAL®

The 3*A* Band System in the Spectrum of the $^{13}C^{16}O$ Molecule

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Received February 17, 1999; in revised form May 20, 1999

In the emission spectrum of the carbon monoxide $^{13}C^{16}O$ isotopic molecule three bands comprising about 1820 lines of the 3*A* band system ($c^3\Pi$–$a^3\Pi$) were recorded and analyzed. The 0–0 and 0–1 bands of this system were photographed for the first time and the 0–2 band was rephotographed by using methods of conventional high-resolution spectroscopy. The result of the rotational band analysis includes expanding of the spectrum interpretation up to $J = 25$ as well as the identification of four previously unobserved branches P_{13}, R_{13}, P_{31}, and R_{31}. Because of strong perturbations in the $c^3\Pi$ ($v = 0$) state, the calculation of the rovibronic structure constants was performed only for the lower $a^3\Pi$ state. By using a calculation based on a nonlinear least-squares method, an effective Hamiltonian of Brown [J. M. Brown, E. A. Colbourn, J. K. G. Watson, and F. D. Wayne, *J. Mol. Spectrosc.* **74,** 294–318 (1979)] and a separative procedure proposed by Curl–Dane–Watson [R. F. Curl and C. B. Dane, *J. Mol. Spectrosc.* **128,** 406–412 (1988); J. K. G. Watson, *J. Mol. Spectrosc.* **138,** 302–308 (1989)], it was possible to derive the rotational structure constants for the $v = 0$, 1, and 2 levels for the $a^3\Pi$ state in the $^{13}C^{16}O$ isotopic molecule. Term values for the $c^3\Pi$ ($v = 0$) level and the equilibrium molecular constants for the $a^3\Pi$ state also are reported. © 1999 Academic Press

INTRODUCTION

The 3*A* band system appearing in the emission spectrum of the CO molecule is a result of the $c^3\Pi$–$a^3\Pi$ transition and belongs to the group of many triplet transitions in the CO molecule. So far this band system was observed as an exclusively one 0–v'' progression and is located in the ultraviolet (2200–2800 Å) region of the spectrum. The identification of the upper state of this system as the $c^3\Pi$ state was performed by Tilford (*1*). Danielak *et al.* (*2*), on the basis of the analysis of the isotopic head shifts of the bands of this system, confirmed that the upper level of the observed progression was the $v' = 0$.

The 3*A* band system spectrum was obtained under high resolution in the $^{12}C^{16}O$ molecule by Schmid and Gerö (*3*), Gerö (*4*), Ginter and Tilford (*5*), and Rytel and Rytel (*6*). The result of the spectrum analyses was both the identification of lines of this complex spectrum region and partial quantitative characteristics of both states involved in this transition. It was particularly interesting to observe the existence of a strong and complex multistate perturbation of the $c^3\Pi$ ($v = 0$) level (*7*) located above the first dissociation energy level, i.e., above 11.01 eV.

The 3*A* band system investigations performed so far in isotopic molecules included the $^{13}C^{16}O$ (*8*) and $^{14}C^{16}O$ (*9*) molecules and were fragmentary and preliminary. The application of different methods of spectrum fitting made the comparison and analysis of the derived rovibronic structure constants for different isotopic molecules very difficult. Therefore, the authors have decided to record and analyze the 3*A* band system spectrum in the $^{13}C^{16}O$ molecule in the regular structure region of the $a^3\Pi$ state comprising the unobserved so far 0–0 and 0–1 bands, as well as to rerecord and reanalyze the 0–2 band. The objective of the present work was both to identify this spectrum region and perform a unified treatment based on the Hamiltonian model proposed by Brown *et al.* (*10*) of the $a^3\Pi$ state in $^{13}C^{16}O$ for $v = 0$, 1, and 2.

EXPERIMENTAL DETAILS

The emission spectrum of the $c^3\Pi$–$a^3\Pi$ system of the $^{13}C^{16}O$ was obtained from a Geissler-type water-cooled tube filled with $^{13}C^{16}O$ gas (92%) at a total pressure of about 10 Torr. The discharge cell was made of a 22-cm long (0.5-cm inner diameter) Pyrex tube with a water-cooled jacket. The electrodes were made of 4-cm long stainless steel sheets 0.5-mm thick and mounted inside a water-cooled glass tube of 3-cm inner diameter. The tube was operated at about 6 kV and 120 mA ac. Spectra were obtained by using a 2-m Ebert plane-grating PGS-2 spectrograph equipped with a 651 grooves/mm grating with a total number of grooves of 45 600, blazed at 1.0 μm. The observations were made in the eleventh order, which permitted obtaining a spectrum with a reciprocal linear dispersion in the range of 0.029–0.039 nm/mm and with a theoretical resolving power of about 500 000. The exposure time on the ORWO UV-1 plates varied from 4 to 25 h. As a calibration spectrum the Th standard lines (*11*) obtained from several overlapped orders of spectrum from a water-cooled hollow-cathode tube were used.

The measurements were carried out carefully by using an

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TABLE 1
Observed Wavenumbers (in cm^{-1}) and Rotational Assignments for the 0–0 Band of the $c^3\Pi$–$a^3\Pi$ System of the $^{13}C^{16}O$ Molecule[a]

J	R_{11ee}	R_{11ff}	P_{11ee}	P_{11ff}	R_{12ee}	R_{12ff}
1	43639.719(-2)	43638.035(19)			43596.893*	43596.928*
2	43641.032(-16)	43639.469(-13)	43630.653(8)	43628.922(24)	43597.935(-7)	43598.057(7)
3	43643.301(14)	43641.522*	43624.826(-14)	43623.174(-19)	43599.613(-4)	43599.724*
4	43646.371*	43644.854(25)	43620.218(29)	43618.715(14)	43601.786(-21)	43601.952(30)
5	43650.077*	43648.719(-2)	43616.482(51)	43615.024*	43604.584(-23)	43604.797(22)
6	43654.522(62)	43653.432(44)	43613.350(0)	43612.020(-32)	43607.961(-9)	43608.100*
7	43659.758(34)	43658.710(-48)	43610.969*	43609.905(6)	43611.920(-13)	43612.218(46)
8	43665.497(-11)	43664.836(23)	43609.384*	43608.454(-34)	43616.242(-6)	43616.617(-32)
9	43672.131(-11)	43671.634(7)	43608.579(-21)	43607.746(-3)	43621.251(-6)	43621.758(28)
10	43679.313(-24)	43679.098(-8)	43608.325*	43607.665(3)	43626.680(-1)	43627.345(7)
11	43687.346*	43687.184(-7)	43608.708(-7)	43608.386*	43632.339*	43633.443(17)
12	43695.846(26)	43696.091*	43609.739(19)	43609.565(-25)	43639.245(5)	43640.104(18)
13	43704.972(8)	43705.480(4)	43611.367(-13)	43611.468(10)	43645.975*	43647.468*
14	43714.731*	43715.579(-1)	43613.833*	43613.991(-2)	43653.863(-3)	43655.192(2)
15	43725.179(-18)	43726.400(26)	43616.666(6)	43617.245(-7)	43661.997*	43663.568(-33)
16	43736.226(0)	43737.662(0)	43620.079*	43621.067(-22)		
17	43747.891(0)	43749.700(-26)	43624.349(-9)	43625.630(27)		
18	43760.177(-13)	43762.275*	43629.173*	43630.686*		
19	43773.019*	43775.733(15)	43634.611*	43636.395(26)		
20	43786.617(0)	43789.597(15)	43640.495(13)	43642.879*		
21	43800.856(0)	43804.016*	43647.121*	43649.736(-15)		
22	43815.567(-12)	43819.315*	43654.356*	43657.290(-15)		
23	43830.917*	43835.152(-11)	43662.177*	43665.621*		
24	43847.006(0)	43851.615(0)	43670.663(12)	43674.495(0)		
25	43863.593(0)	43868.713(0)	43679.778*	43683.964(11)		

J	P_{12ee}	P_{12ff}	R_{13ee}	R_{13ff}	P_{13ee}	P_{13ff}
2	43587.521(-18)	43587.434(-31)	43562.398(-1)	43562.463*	43552.006(10)	43551.967(6)
3	43581.179(9)	43581.057*	43563.051(-15)	43563.168(2)	43544.627(8)	43544.702*
4	43575.837*	43575.701*	43563.969(6)	43564.214(22)	43537.918(-5)	43538.058(-8)
5	43571.027(-40)	43570.973(-28)	43565.308*	43565.522(-25)	43531.673(-7)	43531.798(25)
6	43566.862(1)	43566.860(-16)	43566.776(-49)	43567.258(-13)	43525.730(14)	43525.905(-30)
7	43563.273(23)	43563.379*	43568.728*	43569.344(11)		
8	43560.184(-3)	43560.327(3)	43571.169*	43571.768(14)		
9	43557.609*	43557.847(-6)	43573.842(0)	43574.618(-27)		
10	43555.607(17)	43555.886(-8)	43576.919(-10)	43577.943(-4)		
11	43554.180(23)	43554.533(-8)	43580.482(13)	43581.605(-29)		
12	43553.155(16)	43553.745(31)	43584.512(-42)	43585.794(-16)		
13	43552.666(0)	43553.377(8)	43588.981(-14)	43590.577(22)		
14	43552.833(11)	43553.669*	43593.986(3)	43595.763(21)		
15	43553.488*	43554.460(-20)	43599.408(26)	43601.465(-20)		

[a] Figures in parentheses denote observed minus calculated values in units of 10^{-3} cm^{-1}.
* The lines marked by asterisk are less accurate and not used in the evaluation of molecular constants.

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TABLE 1—*Continued*

J	R_{21ee}	R_{21ff}	P_{21ee}	P_{21ff}	R_{22ee}	R_{22ff}
1	43646.579(-20)	43644.984*			43603.885(16)	43603.778*
2	43652.004(-38)	43650.259(23)	43632.540*	43631.028(-27)	43608.951(14)	43608.833(30)
3	43658.125(-22)	43656.361(28)	43631.714(-4)	43630.062(0)	43614.458(-20)	43614.108*
4	43665.008(3)	43663.172(16)	43631.179(-5)	43629.448(-6)	43620.648*	43620.282(33)
5	43672.633(8)	43670.764(18)	43631.329(37)	43629.643*	43627.263(2)	43626.759(-41)
6	43680.998(21)	43678.998(-40)	43632.090(-35)	43630.356(-23)	43634.481(-7)	43633.905(43)
7	43690.120(-2)	43688.088*	43633.685(-8)	43631.919(-6)	43642.276(-55)	43641.487*
8	43699.846(-17)	43697.694(-7)	43635.893*	43634.071*	43650.606(2)	43649.540(3)
9	43710.409(-10)	43708.121(7)	43638.993(-6)	43636.943*	43659.530(-4)	43658.252(34)
10	43721.526(-20)	43719.129(-21)	43642.591(-10)	43640.567(17)	43668.806*	43667.369(-13)
11	43733.372*	43730.845(21)	43646.979(-13)	43644.726*	43678.874(-4)	43677.028(-31)
12	43745.912(-35)	43743.145*	43651.912(-18)	43649.709*	43689.298*	43687.507*
13	43759.103(-23)	43756.162(15)	43657.670*	43655.074(-17)	43700.446(32)	43698.043(-15)
14	43772.950(-7)	43769.821*	43663.898(9)	43661.249(13)	43712.070*	43709.381(10)
15	43787.442(-2)	43784.060(21)	43670.938*	43667.788*	43724.164(-24)	43721.162*
16					43736.953(-3)	43733.630(-12)
17					43750.330(5)	43746.566*
18					43764.265*	43760.050*
19					43778.576*	43774.334(21)
20					43793.718(-21)	43788.870(-2)
21					43809.363(11)	43804.222*
22					43825.601*	43820.002(-16)
23					43842.518*	43836.418(19)
24					43859.978(0)	43853.470(0)
25					43878.124(0)	43871.123(0)

J	P_{22ee}	P_{22ff}	R_{23ee}	R_{23ff}	P_{23ee}	P_{23ff}
2	43589.548(9)	43589.641(19)	43573.410(16)	43573.281(-17)	43553.988(-9)	43554.125(8)
3	43588.073(25)	43587.908*	43578.096*	43577.808(19)	43551.479(-18)	43551.623*
4	43586.793(32)	43586.538(-11)	43582.732(-6)	43582.518(-2)	43548.900(-18)	43548.799(-20)
5	43585.946(19)	43585.592(-32)	43587.799*	43587.639*	43546.527(-13)	43546.381(-16)
6	43585.456*	43585.228(25)	43593.323(-19)	43592.853*	43544.527(38)	43544.213(-49)
7	43585.915(12)	43585.368(30)	43599.290(47)	43598.562(-21)	43542.800(-14)	43542.497(-2)
8	43586.714(9)	43586.070*	43605.426(9)	43604.656(15)	43541.514(-4)	43541.075(-3)
9	43588.130(16)	43587.112(9)	43612.111(-8)	43611.118(-14)	43540.587*	43540.029(12)
10	43590.007*	43588.846*	43619.179(39)	43617.993(1)	43540.210(16)	43539.365(-27)
11	43592.427(-7)	43591.035(8)	43626.749(50)	43625.279(12)	43540.296(42)	43539.200(-35)
12	43595.348(-1)	43593.816*	43634.750*	43633.120*	43540.739*	43539.515(34)
13	43598.851(-45)	43597.052(50)	43643.095*	43641.296*	43541.639(0)	43540.137(-35)
14	43602.940(-8)	43600.841(-4)	43652.271*	43649.906(-17)	43543.097(33)	43541.389(-8)
15	43607.554(-11)	43605.227*	43661.652(22)	43659.152(3)	43545.008(1)	43543.176*
16	43612.748(7)	43610.053(7)				
17	43618.499(4)	43615.505(-24)				
18	43624.852(3)	43621.510(12)				
19	43631.806(-5)	43628.121*				
20	43639.193*	43635.233(0)				
21	43647.385*	43642.967(-21)				
22	43656.067(21)	43651.170(3)				
23	43665.270(-11)	43660.055*				
24	43675.289*	43669.586(16)				
25	43685.675*	43679.571(-19)				

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TABLE 1—*Continued*

J	R_{31ee}	R_{31ff}	P_{31ee}	P_{31ff}	R_{32ee}	R_{32ff}
1	43657.496(-14)	43655.929*			43614.770(-10)	43614.960(-18)
2	43666.661(-1)	43665.189(8)			43623.539(-18)	43623.716(-34)
3	43676.387*	43675.041(-23)	43642.718*	43641.159(-3)	43632.755(-9)	43633.023(25)
4	43686.949(-21)	43685.825(17)	43645.837(33)	43644.395(-7)	43642.467*	43642.814*
5	43698.277(10)	43697.203(2)	43649.665*	43648.269(-31)	43652.865(-37)	43653.219(-36)
6	43710.258(38)	43709.506*	43654.089(0)	43653.048(18)	43663.758(27)	43664.239( )
7	43722.977(26)	43722.388(45)	43659.317(-19)	43658.392(12)	43675.161(0)	43675.745(-12)
8	43736.608*	43735.947(-14)	43665.404*	43664.470(-43)	43687.079*	43687.822(26)
9	43750.511*	43750.200(-15)	43671.826(-2)	43671.341(8)	43699.565(11)	43700.312(-7)
10	43765.177(10)	43765.310(-10)	43679.169*	43678.730*	43713.433*	43713.575(23)
11	43780.524(1)	43780.969(-52)	43686.940*	43686.568*	43725.955(-10)	43727.546*
12	43796.597(-6)		43695.404*	43695.807(2)	43740.002(-20)	43741.496(-17)
13			43704.723(28)	43705.302(13)	43754.594(7)	43756.300(13)
14			43714.573(28)	43715.431(10)	43769.667(-8)	43771.611(5)
15			43724.982(-13)	43726.154(1)	43785.307(29)	43787.623(0)

J	P_{32ee}	P_{32ff}	R_{33ee}	R_{33ff}	P_{33ee}	P_{33ff}
2			43587.998(-16)	43588.254(10)		
3	43598.982(24)	43599.085(-11)	43596.236(22)	43596.612*	43562.489*	43562.649(32)
4	43601.366(-14)	43601.519(24)	43604.724(21)	43605.162(-9)	43563.554(17)	43563.764(-1)
5	43604.201(-12)	43604.362(7)	43613.551(36)	43614.111*	43564.825(-2)	43565.148(22)
6	43607.592(-8)	43607.843(-12)	43622.583(-2)	43623.346(51)	43566.462(8)	43566.898(-15)
7	43611.577(32)	43611.803(11)	43632.042(-30)	43632.907(-10)	43568.434(-22)	43568.964(11)
8	43615.908(-40)	43616.359(10)	43641.822(-15)	43642.893(-7)	43570.738(-23)	43571.432(-21)
9	43620.878*	43621.387(-50)	43652.142(2)	43653.311*	43573.535(6)	43574.369(18)
10	43626.385(19)	43626.826*	43662.770(10)	43664.066*	43576.610(-4)	43577.647(-5)
11	43632.435(-18)	43633.273*	43673.763(-22)	43675.429(-34)	43580.279(5)	43581.359(22)
12	43638.869*	43639.902(-26)	43685.342(5)	43687.260(22)	43584.264(-20)	43585.662(10)
13	43646.138*	43647.247(48)	43697.340(10)	43699.451(-6)	43588.727(2)	43590.392(24)
14	43653.611(7)	43654.940*	43709.799(8)	43712.230*	43593.706(-15)	43595.567(-15)
15	43661.837*	43663.261*	43722.690(-29)	43725.408*	43599.176(-4)	43601.257(-8)
16			43736.162*	43739.341(12)	43605.043*	43607.445(-5)
17			43750.077*	43753.687*	43611.733*	43614.300(0)
18			43764.779(-7)	43768.566(17)	43618.612(0)	43621.630(-12)
19			43779.951*	43783.903(-3)	43626.172*	43629.498*
20			43795.557(23)	43800.097*	43634.239(7)	43637.928(-17)
21			43811.557(-23)	43816.495*	43642.734*	43646.866(3)
22			43828.391(0)	43833.692*	43652.097(-23)	43656.530*
23			43845.788(6)	43851.417*	43661.774(22)	43666.833*
24			43863.713(0)	43869.901(0)	43672.229*	43677.510*
25			43882.297(0)	43888.941(0)	43683.159(-6)	43688.876(0)

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TABLE 2
Observed Wavenumbers (in cm^{-1}) and Rotational Assignments for the 0–1 Band of the $c^3\Pi$–$a^3\Pi$ System of the $^{13}C^{16}O$ Molecule[a]

J	R_{11ee}	R_{11ff}	P_{11ee}	P_{11ff}	R_{12ee}	R_{12ff}
1		41961.108*			41920.005(-40)	41920.215*
2	41964.037(-6)	41962.465(-3)	41953.505*	41951.741*	41921.122(12)	41921.149(-34)
3	41966.406(23)	41964.813(-23)	41947.702*	41946.231*	41922.786*	41922.946(16)
4	41969.415(-23)	41968.098(9)	41943.406(3)	41941.931(29)	41925.229(20)	41925.350(-10)
5	41973.348(38)	41972.081(-12)	41939.783(-25)	41938.391(40)	41928.151(-4)	41928.371(25)
6	41978.011(24)	41976.942(26)	41936.740*	41935.581*	41931.746(20)	41931.901*
7	41983.603*	41982.473(-22)	41934.754(-35)	41933.661(-18)	41935.843(-23)	41936.187(31)
8	41989.589*	41988.800(9)	41933.444(-7)	41932.670*	41940.476(-7)	41941.292*
9	41996.391(-16)	41995.866(-24)	41932.834(7)	41932.034(7)	41946.085*	41946.389*
10	42003.670*	42003.751(29)	41933.109*	41932.239(-11)	41951.717*	41952.283(-11)
11	42012.235(12)	42012.212(-22)	41933.678(18)	41933.243(-7)	41957.913*	41958.852(13)
12	42021.130(-35)	42021.397(2)	41935.056(-9)	41934.985(27)	41964.982(-5)	41965.918(-3)
13	42030.766(-18)	42031.290(-13)	41937.152*	41937.313(-9)	41972.435*	41973.672(20)
14	42041.031(-5)	42041.888(6)	41939.981(-16)	41940.303(-16)	41980.645*	41981.948(-15)
15	42051.955(28)	42053.139(1)	41943.446(6)	41944.152*	41989.167(-22)	41990.884(12)
16	42063.554*	42065.041(23)	41947.487(-15)	41948.447(17)	41998.579(31)	42000.317(-16)
17	42075.785(21)	42077.614(-12)	41952.199(7)	41953.394*	42008.378*	42010.589*
18	42088.700*	42090.819(-24)	41957.667(-26)	41959.056*	42018.966*	42021.168(24)
19	42102.145*	42104.780*	41963.594(-7)	41965.548(19)	42029.732(-9)	42032.581(0)
20	42116.387*	42119.425(0)	41970.416(-16)	41972.753*		42044.496(-18)
21			41977.659(9)	41980.109*		
22			41985.598(0)	41988.659(23)		
23			41994.887(0)	41997.682(0)		
24			42003.562(0)	42007.354(0)		
25			42013.463(0)	42017.750(0)		

J	P_{12ee}	P_{12ff}	R_{13ee}	R_{13ff}	P_{13ee}	P_{13ff}
2	41910.856(-17)	41910.517(0)	41885.528*	41885.815(29)	41875.457(17)	41875.418*
3	41904.433(40)	41904.331*	41886.051*	41886.585(6)	41867.975(0)	41867.770*
4	41899.154(-19)	41899.029*	41887.443*	41887.810(31)	41861.496(9)	41861.571(-21)
5	41894.655(2)	41894.575(-28)	41889.043*	41889.287(-7)	41855.361*	41855.540(-12)
6	41890.677(34)	41890.703(4)	41890.817(17)	41891.185(-42)	41849.685(-32)	41849.931(-34)
7	41887.234(-15)	41887.353(12)	41893.024(-7)	41893.489*	41844.430(17)	
8	41884.448(-18)	41884.617(15)	41895.589(5)	41896.280(-2)	41839.532(-36)	
9	41882.245(-1)	41882.421(-17)	41898.663*	41899.571(44)	41835.178(24)	
10	41880.582*	41880.826(5)	41902.243(25)	41903.208(-45)	41831.103(1)	
11	41879.451(-19)	41879.843(-12)	41906.237(-8)	41907.454(18)	41827.701(18)	
12	41878.871(-16)	41879.352*	41910.744(14)	41911.875*		
13	41878.937(-4)	41879.833*	41915.712(-6)	41917.118*		
14	41879.576(42)	41880.416(17)	41921.406*	41923.043(13)		
15	41880.722(19)	41881.771(-7)	41927.148(-14)	41929.223*		
16	41882.433(20)	41883.724(-21)	41933.835(-5)	41936.190*		
17	41884.744*	41886.303(-12)	41940.899*	41943.639*		
18	41887.612*	41889.438(-6)	41948.671(16)	41951.568*		
19	41891.066(-14)	41893.238(-7)	41956.851*	41960.213*		
20	41895.249*	41896.679*	41965.711*	41969.255(-4)		

[a] Figures in parentheses denote observed minus calculated values in units of 10^{-3} cm^{-1}.
* The lines marked by asterisk are less accurate and not used in the evaluation of molecular constants.

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TABLE 2—*Continued*

J	R_{21ee}	R_{21ff}	P_{21ee}	P_{21ff}	R_{22ee}	R_{22ff}
1	41969.552(8)	41967.827(-4)			41926.969(-12)	41926.758*
2	41974.975(-1)	41973.244(0)	41955.589(-35)	41954.124(-21)	41932.132*	41931.963(3)
3	41981.221(16)	41979.477*	41954.860(43)	41953.038*	41937.624*	41937.608*
4	41988.277*	41986.382(-13)	41954.322(-14)	41952.736(57)	41943.950(-16)	41943.808*
5	41995.989(16)	41994.146*	41954.639(9)	41952.809(-38)	41950.829(11)	41950.457*
6	42004.497(-11)	42002.508(-49)	41955.737*	41953.844*	41958.448*	41957.576(-26)
7	42013.791(-33)	42011.817(24)	41957.455(3)	41955.636(-21)	41966.291(8)	41965.469(13)
8	42023.822(-31)	42021.766(15)	41959.992(20)	41958.166(35)	41974.893(24)	41973.912(49)
9	42034.623(-41)	42032.399(-8)	41963.251(7)	41961.392*	41984.123(40)	41982.796(-22)
10	42046.153(-8)	42043.793(11)	41967.198(-4)	41965.103*	41993.850(9)	41992.352(0)
11	42060.022*	42055.834(1)	41971.952(36)	41969.694*	42004.197(11)	42002.390(-49)
12	42071.274*	42068.591(12)	41977.289(-5)	41975.089*	42015.145(-13)	42013.086(-20)
13	42085.024*	42081.994(3)	41983.382(14)	41980.965(43)	42026.683(2)	42024.259*
14	42099.264(23)	42095.821*	41990.195(28)	41987.483(-20)	42038.762(-16)	42036.144(-12)
15	42114.212(-21)	42110.813(5)	41997.629(20)	41994.749(16)	42051.467(-29)	42048.517(-23)
16			42005.732(25)	42002.611(-11)	42064.766(-28)	42061.471(6)
17			42014.489(-9)	42011.088(-60)	42078.687(-3)	42075.147(-10)
18			42023.956(18)	42020.263(-12)	42093.398*	42089.203(-35)
19			42034.157*	42030.139*	42108.327(-15)	42104.059(24)
20						42119.425(0)
21						
22						
23						
24						
25						

J	P_{22ee}	P_{22ff}	R_{23ee}	R_{23ff}	P_{23ee}	P_{23ff}
2	41912.728(35)	41912.881(21)	41896.593(-19)	41896.506(-57)	41877.260(0)	41877.374*
3	41911.320(-9)	41911.096*	41901.300(2)	41901.100(25)	41874.880(-30)	41874.906(4)
4	41909.923*	41910.115*	41906.314(33)	41906.090(4)	41872.456(35)	41872.367(-3)
5	41909.476(1)	41909.113(14)	41911.470*	41911.290(18)	41870.248(-28)	41870.142*
6	41909.381(-20)	41909.014(8)	41917.318(-3)	41916.918(50)	41868.478(3)	41868.160*
7	41909.880(-31)	41909.306(-12)	41923.465(17)	41922.850(-5)	41867.077(1)	41866.735(16)
8	41910.958(-30)	41910.224(-19)	41930.181*	41929.219(-23)	41866.112(23)	41865.633(10)
9	41912.670(7)	41911.611*	41936.976(-15)	41936.065(22)	41865.565(-6)	41864.930(-32)
10	41914.896(15)	41913.761(-20)	41944.451(3)	41943.174*	41865.483(-5)	41864.720(-21)
11	41917.690(-36)	41916.361(-10)	41952.520*	41951.064(28)	41865.956(17)	41864.987(18)
12	41921.254*	41919.526(-18)	41960.892(-9)	41959.261(1)	41866.859(1)	41865.705(7)
13	41925.084(-12)	41923.275(3)	41969.974*	41967.906*	41868.289(-13)	41866.885(-26)
14	41929.674(-31)	41927.611(28)	41979.384(-8)	41977.245(23)	41870.344(25)	41868.765*
15	41934.864(-7)	41932.448(-19)	41989.468(-1)	41986.969(-13)	41872.830(-15)	41870.831*
16	41940.607(-11)	41937.964(26)	42000.073(-13)	41997.216(-20)	41875.896(-13)	41873.682(-26)
17	41947.031(41)	41944.018(34)	42011.267(3)	42008.255(37)	41879.581(17)	41877.102(57)
18	41953.969(18)	41950.640*	42023.139*	42019.563(8)	41883.780(5)	41880.919(26)
19	41961.419*	41957.980(39)	42035.405(15)	42031.569(-10)	41888.647*	41885.420(-66)
20	41969.729(7)	41965.610*	42048.531*		41893.963(-7)	41890.474(27)
21	41978.734*	41974.173(-14)				
22	41988.101*	41983.179*				
23	41998.130(0)	41992.940(0)				
24	42008.972(0)	42003.303(0)				
25	42020.207(0)	42014.261(0)				

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TABLE 2—*Continued*

J	R_{31ee}	R_{31ff}	P_{31ee}	P_{31ff}	R_{32ee}	R_{32ff}
1	41980.462(7)	41979.044(-27)			41937.892(-1)	41938.229(27)
2	41989.778*	41988.185(12)			41946.735(37)	41946.779*
3	41999.487(-13)	41998.163(-31)	41965.740(12)	41964.209*	41956.009(-3)	41956.281(-7)
4	42010.197(13)	42009.056(20)	41968.908*	41967.702*	41965.969(15)	41966.115*
5	42021.593(-4)	42020.504(-28)	41972.915(-10)	41971.722(14)	41976.428(-14)	41976.780(-4)
6	42033.799(35)	42032.943(19)	41977.579*	41976.637(34)	41987.494(-9)	41987.947(-22)
7	42046.719(-21)	42046.094(0)	41983.073(-3)	41982.208*	41999.126*	41999.726(-30)
8	42060.363(22)	42060.022(38)	41989.182(-46)	41988.471(-26)	42011.371(14)	42012.113(17)
9	42074.724(16)	42074.598(-13)	41996.186(26)	41995.651(26)	42024.129(2)	42025.029(7)
10	42089.740(-10)	42089.951(6)	42003.656(-34)	42003.403(-40)	42037.459(30)	42038.523(7)
11			42011.861*	42011.883*	42051.355*	42052.600(-16)
12			42020.757*	42021.187(7)	42065.786(-9)	42067.262(21)
13			42031.975(0)	42030.893*	42080.843(13)	42082.510(-22)
14			42040.814(10)	42041.632(-6)	42096.448(10)	42098.425(30)
15					42112.583(20)	42115.840*
16						42131.480*
17						
18						
19						
20						

J	P_{32ee}	P_{32ff}	R_{33ee}	R_{33ff}	P_{33ee}	P_{33ff}
2			41911.007*	41911.470(-21)		
3	41922.223(-18)	41922.341*	41919.582(-11)	41919.933(-3)	41885.960*	41886.216*
4	41924.741(-20)	41924.908(30)	41928.269(0)	41928.699(-28)	41887.057(-18)	41887.275(-22)
5	41927.817(47)	41927.961(1)	41937.229(-13)	41937.778(46)	41888.560(-11)	41888.934(25)
6	41931.361(-28)	41931.630(-17)	41946.565(-11)	41947.238(3)	41890.386*	41890.905(-8)
7	41935.294*	41935.765(-14)	41956.346(-19)	41957.143(-13)	41892.735(35)	41893.319*
8	41939.991*	41940.745*	41966.492(34)	41967.473(-3)	41895.377(32)	41896.014(25)
9	41945.594(14)	41945.972*	41977.190*	41978.249(1)	41898.396*	41899.279(17)
10	41951.339(-30)	41952.001(-13)	41988.029(-7)	41989.457(-19)	41901.969(-6)	41902.975(1)
11	41957.797(26)	41958.580(4)	41999.542*	42001.220(6)	41905.942(-43)	41907.173(0)
12	41964.675(-30)	41965.588*	42011.528(-10)	42013.407(12)	41910.465(17)	41911.734*
13	41972.296*	41973.471(22)	42024.031(-6)	42026.167(-5)	41915.457*	41917.078(-12)
14	41980.334(-9)	41981.676(-42)	42036.976*	42039.442(-20)	41920.974(18)	41922.801(16)
15	41989.005(-16)	41990.703(44)	42050.505(-31)	42053.221*	41927.002(9)	41929.083(-17)
16	41998.290(13)	42000.169(-7)	42064.610(-5)	42067.623(-6)	41933.546(-23)	41935.945(-3)
17	42008.069(12)	42010.392*	42079.411*	42082.732*	41940.691*	41943.281*
18	42018.479(-1)	42020.976(7)	42094.499*	42098.304*	41948.311(6)	41951.286(0)
19		42032.353(-3)	42110.369*	42114.448(3)	41956.605*	41959.903(3)
20			42126.757(29)	42131.162(18)	41965.345*	41969.045*
21					41974.704*	41978.971(-3)
22					41984.915(-29)	41989.308(-18)
23					41995.312(0)	42000.397(0)
24					42007.354(0)	42012.010*
25					42018.643(0)	42024.419(0)

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TABLE 3
Observed Wavenumbers (in cm^{-1}) and Rotational Assignments for the 0–2 Band of the $c^3\Pi$–$a^3\Pi$ System of the $^{13}C^{16}O$ Molecule[a]

J	R_{11ee}	R_{11ff}	P_{11ee}	P_{11ff}	R_{12ee}	R_{12ff}
1	40313.434(6)	40311.801(-23)			40271.076(14)	40271.114(12)
2	40314.952(13)	40313.349(-29)	40304.457*	40302.885(3)	40272.191(-18)	40272.265(16)
3	40317.373(38)	40315.863(-21)	40298.835(-22)	40297.234*	40274.053(-5)	40274.165(19)
4	40320.591(22)	40319.174(-14)	40294.496(-22)	40293.063(37)	40276.553(-9)	40276.661(19)
5	40324.619(-11)	40323.369(-8)	40291.025(-17)	40289.664(-11)	40279.703(-8)	40279.849(17)
6	40329.455(-28)	40328.441(43)	40288.363(-19)	40287.102(8)	40283.488(13)	40283.661(-8)
7	40335.094(12)	40334.242*	40286.506(-15)	40285.358(-11)	40287.804(-11)	40288.102(10)
8	40341.459*	40340.850*	40285.432(6)	40284.437(-7)	40292.759*	40293.149(-19)
9	40348.621(4)	40348.137(-3)	40285.071(23)	40284.256(6)	40298.378(20)	40298.897(35)
10	40356.479(-36)	40356.283(2)	40285.477(-5)	40284.835(-8)	40304.540(-2)	40305.199(2)
11	40365.118(7)	40365.098(-34)	40286.557(2)	40286.168(-9)	40311.314(16)	40312.096(-20)
12	40374.425(-25)	40374.728(2)	40288.437(34)	40288.264(-2)	40318.700(20)	40319.650(-18)
13	40384.540(14)	40385.086*	40290.914(-15)	40291.080(39)	40326.690(-3)	40327.841(21)
14	40395.256(11)	40396.094(-5)	40294.172(-9)	40294.544(2)	40335.231(-23)	40336.673(3)
15	40406.671(-6)	40407.891*	40298.165(10)	40298.733(5)	40344.462(17)	40346.109(32)
16	40418.815(-11)	40420.350(27)	40302.772(14)	40303.662(-25)		
17	40431.670*	40433.462(6)	40308.065(0)	40309.268(-3)		
18	40445.205(1)	40447.291(-7)	40314.092(12)	40315.613(-27)		
19	40459.356(-16)	40461.929(-16)	40320.853*	40322.624(-5)		
20	40474.253*	40477.174*	40328.171(-1)	40330.327(7)		
21			40336.208(16)	40338.830(16)		
22			40345.007*	40347.967*		
23			40354.447(0)	40357.804(0)		
24						
25						

J	P_{12ee}	P_{12ff}	R_{13ee}	R_{13ff}	P_{13ee}	P_{13ff}
2	40261.801(-10)	40261.691*	40236.902(-4)	40237.003(26)	40226.518(11)	40226.479(-3)
3	40255.632*	40255.556(-12)	40237.742(-44)	40237.946(8)	40219.310(1)	40219.382(23)
4	40250.541(31)	40250.444(-37)	40239.080(33)	40239.218(-10)	40212.865*	40213.053(-13)
5	40246.156(32)	40246.075*	40240.738(28)	40241.006(35)	40207.118(-5)	40207.274(4)
6	40242.365(-10)	40242.376(11)	40242.787(9)	40243.138(-17)	40201.662(-16)	40201.834(-16)
7	40239.254(-1)	40239.335*	40245.252(10)	40245.826*	40196.688(7)	40196.899(-33)
8	40236.719(-19)	40236.817(-20)	40248.248(21)	40248.866(37)	40192.155(19)	40192.507(8)
9	40234.755(-34)	40234.965(-7)	40251.656*	40252.393(-10)	40185.099*	40188.502(-10)
10	40233.486(-23)	40233.748(-11)	40255.542(24)	40256.493(-12)	40184.492(7)	40184.489*
11	40232.708(-34)	40233.149(-12)	40259.925(7)	40261.105(7)	40181.370(8)	40182.214*
12	40232.622(-11)	40233.214(6)	40264.894(27)	40266.173*	40178.811(-8)	40179.786(4)
13	40233.079(-16)	40233.864(22)	40270.355(-27)	40271.891(-26)		40177.924(-14)
14	40234.180(-11)	40235.128(15)	40276.388(-2)	40278.258(28)		
15	40235.929(6)	40237.078*	40282.969(-10)	40285.019(-29)		

[a] Figures in parentheses denote observed minus calculated values in units of 10^{-3} cm^{-1}.
* The lines marked by asterisk are less accurate and not used in the evaluation of molecular constants.

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TABLE 3—*Continued*

J	R_{21ee}	R_{21ff}	P_{21ee}	P_{21ff}	R_{22ee}	R_{22ff}
1	40320.342(-13)	40318.720(33)			40278.004(14)	40277.975(10)
2	40325.877(-31)	40324.166(-14)	40306.557(10)	40304.983(15)	40283.206(28)	40283.044(-7)
3	40332.209(19)	40330.492(13)	40305.790(5)	40304.143(-25)	40288.889(-24)	40288.723(-18)
4	40339.322(19)	40337.522(-21)	40305.517(30)	40303.872(44)	40295.282(-15)	40294.999(2)
5	40347.214(-1)	40345.408(-6)	40305.907(9)	40304.260(-11)	40302.390*	40301.857(-12)
6	40355.950(-23)	40354.066(-2)	40307.083(-33)	40305.443(-7)	40309.991(25)	40309.339(-1)
7	40365.482(-34)	40363.502(10)	40309.170*	40307.439(33)	40318.266(17)	40317.385(-21)
8	40375.753*	40373.715(24)	40311.931(15)	40310.093(-21)	40327.123(-31)	40326.083(0)
9	40386.855(-41)	40384.689(31)	40315.489(7)	40313.563(0)	40336.679(43)	40335.371(-9)
10	40398.703(-34)	40396.334(-4)	40319.832(26)	40317.723(-36)	40346.763(-2)	40345.251(-3)
11	40411.322(-19)	40408.812(24)	40324.853(21)	40322.688(-7)	40357.539(11)	40355.777(5)
12	40424.597(-22)	40421.906(-8)	40330.646(20)	40328.321(-1)	40368.862(14)	40366.859(3)
13	40438.672(-22)	40435.728(-20)	40337.140(-20)	40334.695(-2)	40380.872(11)	40378.574(26)
14	40453.457(-12)	40450.209*	40344.362(12)	40341.711(-20)	40393.497(19)	40390.844(-2)
15	40468.990(21)	40465.558(32)	40352.595*	40349.451(-5)	40406.726(-11)	40403.755(-33)
16					40420.609(1)	40417.293*
17					40435.157(26)	40431.538(-5)
18					40450.386*	40446.314(-25)
19					40466.215(7)	40461.952*
20					40482.682(-19)	40477.987(-10)
21						40494.790(11)
22						
23						
24						
25						

J	P_{22ee}	P_{22ff}	R_{23ee}	R_{23ff}	P_{23ee}	P_{23ff}
2	40263.823(6)	40263.899*	40247.854(-20)	40247.739(-41)	40228.497(-17)	40228.553(-15)
3	40262.523(16)	40262.408(-22)	40252.639(-2)	40252.558(26)	40226.213(-23)	40226.226(4)
4	40261.469(-11)	40261.283(0)	40257.764(-18)	40257.593(10)	40223.970(5)	40223.886(18)
5	40260.989(10)	40260.739(13)	40263.302(6)	40262.973(-35)	40221.965(-13)	40221.842(-23)
6	40261.150(40)	40260.737(17)	40269.272(3)	40268.823(-1)	40220.419(7)	40220.205(0)
7	40261.904*	40261.353(33)	40275.669(-6)	40275.032(-24)	40219.262(-5)	40218.956(-13)
8	40263.212(-17)	40262.567*	40282.560(9)	40281.758(14)	40218.623(-3)	40218.193(25)
9	40265.221(-2)	40264.285(-1)	40289.885(9)	40288.924(3)	40218.481(18)	40217.864(37)
10	40267.833(-1)	40266.664(-10)	40297.759(18)	40296.579(17)	40218.807(-2)	40217.990(8)
11	40271.001(-19)	40269.662(-18)	40306.181(34)	40304.665*	40219.626(-13)	40218.721*
12	40274.845(-9)	40273.255(-10)	40315.096*	40313.440(10)	40221.050(8)	40219.839(0)
13	40279.363(37)	40277.497(-2)	40324.534(-17)	40322.644(-1)	40222.972(-43)	40221.570(-25)
14	40284.355(-5)	40282.316(15)	40334.606(-8)	40332.431(25)	40225.569*	40223.806*
15	40290.106(15)	40287.713(-6)	40345.288(17)	40342.762(2)	40228.638(12)	40226.697(6)
16	40296.434(1)	40293.726(-22)				
17	40303.395(-28)	40300.427(-1)				
18	40311.033(-1)	40307.781*				
19	40319.277(-26)	40315.685(5)				
20	40328.245*	40324.259(25)				
21	40337.891(-7)	40333.544*				
22	40348.183(19)	40343.445(10)				
23	40359.157(0)	40353.990(-11)				
24	40370.825(0)	40365.232(0)				
25	40383.208(0)	40377.110(0)				

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TABLE 3—*Continued*

J	R_{31ee}	R_{31ff}	P_{31ee}	P_{31ff}	R_{32ee}	R_{32ff}
1	40331.317(15)	40329.801(-11)			40288.946(9)	40289.091(0)
2	40340.493(-25)	40339.100(-14)			40297.823(35)	40297.967(-18)
3	40350.488(-4)	40349.045*	40316.695(-36)	40315.281(-13)	40307.231(16)	40307.492(9)
4	40361.285(-8)	40360.142(0)	40320.124(27)	40318.758(-4)	40317.248(-38)	40317.556(-41)
5	40372.902(20)	40371.910(14)	40324.221(22)	40322.997(-16)	40327.960(-3)	40328.352(2)
6	40385.275*	40384.468(-2)	40329.144(38)	40328.067(18)	40339.218(14)	40339.725(-16)
7	40398.414(40)	40397.838(24)	40334.811(37)	40333.909(22)	40351.089(-18)	40351.690(-36)
8	40412.293(11)	40411.910(-24)	40341.125(-29)	40340.414*	40363.593(-2)	40364.339(13)
9	40426.954(44)	40426.814(-23)	40348.409*	40347.840*	40376.652(2)	40377.564(5)
10	40442.351(24)	40442.537(9)	40356.224(-22)	40356.028(27)	40390.326(-28)	40391.444(0)
11	40458.418(-11)	40458.894(-26)	40364.826(-21)	40364.954*	40404.603(-13)	40405.919(14)
12	40475.242(-40)	40476.081(14)	40373.230*	40374.514(1)	40419.513(2)	40421.001(-8)
13		40493.943(10)	40383.187*		40435.038(0)	40436.738(4)
14		40512.518(14)	40395.037(24)		40451.118(13)	40453.380*
15					40467.839(3)	40470.157*

J	P_{32ee}	P_{32ff}	R_{33ee}	R_{33ff}	P_{33ee}	P_{33ff}
2			40262.458(-26)	40262.737(23)		
3	40273.449(-5)	40273.554(-2)	40270.924(-19)	40271.296(20)	40237.198(16)	40237.374(26)
4	40276.077(-12)	40276.230(13)	40279.780(9)	40280.183(1)	40238.802*	40238.728*
5	40279.251(-30)	40279.482(14)	40289.002*	40289.488(-2)	40240.295(15)	40240.581(-27)
6	40283.108(9)	40283.342(22)	40298.505(-2)	40299.222(-4)	40242.393(-9)	40242.805(0)
7	40287.484(-24)	40287.787(-14)	40308.524(-9)	40309.391(14)	40244.904(-29)	40245.429(-22)
8	40292.459(-8)	40292.908(-1)	40319.002(10)	40319.971(-17)	40247.889(24)	40248.594(24)
9	40298.067(-14)	40298.607(0)	40329.880(-10)	40331.086(-14)	40251.323(1)	40252.146(-2)
10	40304.307(33)	40304.926(9)	40341.323(-7)	40342.739(-14)	40255.220(-30)	40256.218(-8)
11	40310.993(-41)	40311.875(17)	40353.244(9)	40354.894(8)	40259.679(26)	40260.855(15)
12	40318.465(21)	40319.470(15)	40365.698(0)	40367.578(-5)	40264.622(-9)	40266.018(-11)
13	40326.439(25)	40327.615(-16)	40378.718(-9)	40380.816(-15)	40270.094(-9)	40271.747(20)
14	40335.027(5)	40336.452(-2)	40392.215(-26)	40394.630(-6)	40276.166(8)	40278.065*
15	40344.276(9)	40345.897(-7)	40406.295*	40409.025(-17)	40282.742*	40284.884(8)
16			40421.041(-8)	40424.051(-16)	40289.965(13)	40292.309(-8)
17			40436.415(7)	40439.754(3)	40297.735(-3)	40300.394(17)
18			40452.389(24)	40456.089(0)	40306.098(8)	40309.091(16)
19			40468.876(25)	40472.827(0)	40315.132(-7)	40318.446(-3)
20			40485.959(-24)		40324.778(-24)	40328.407*
21			40503.835(13)		40334.982(-25)	40339.016*
22			40522.303(0)		40345.897(24)	40350.294(0)
23			40541.376(0)		40357.446(-13)	40362.265(0)
24			40561.053(0)		40369.627*	40374.799(0)
25						

TABLE 4

Summary of Observations and Analyses of the $c^3\Pi$–$a^3\Pi$ Bands of $^{13}C^{16}O$ Molecule

Band	Remarks	Total number of lines	J_{max}	f [a]	$\sigma_f \cdot 10^2$ [b] (in cm^{-1})
0 - 0	first obs.	605	25	305	2.42
0 - 1	first obs.	637	25	332	2.48
0 - 2	reanalysis	585	24	381	2.13

[a] Number of degrees of freedom of the fit.

[b] Standard deviation of the fit.

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TABLE 5
Branches of the $^3\Pi$–$^3\Pi$ Transition and Their Correlations

Upper and lower states in Hund's case(a)			Upper state in Hund's case(b) with neglected spin splitting	Remarks
$\underline{P_{11}(J)}$			$P_1(N)$	
$P_{21}(J)$	$Q_{11}(J)$		$Q_1(N)$	
$\underline{P_{31}(J)}$	$Q_{21}(J)$	$R_{11}(J)$	$R_1(N)$	} N = J − 1
	$Q_{31}(J)$	$R_{21}(J)$	$S_1(N)$	
		$\underline{R_{31}(J)}$	$T_1(N)$	
$P_{12}(J)$			$O_2(N)$	
$P_{22}(J)$	$Q_{12}(J)$		$P_2(N)$	
$P_{32}(J)$	$Q_{22}(J)$	$R_{12}(J)$	$Q_2(N)$	} N = J
	$Q_{32}(J)$	$R_{22}(J)$	$R_2(N)$	
		$R_{32}(J)$	$S_2(N)$	
$\underline{P_{13}(J)}$			$N_3(N)$	
$P_{23}(J)$	$Q_{13}(J)$		$O_3(N)$	
$P_{33}(J)$	$Q_{23}(J)$	$\underline{R_{13}(J)}$	$P_3(N)$	} N = J + 1
	$Q_{33}(J)$	$R_{23}(J)$	$Q_3(N)$	
		$R_{33}(J)$	$R_3(N)$	

Note. Four underlined branches were observed for the first time.

TABLE 6
Matrix Elements of the Rotational Hamiltonian of the $a^3\Pi$ State in a Case (a) Basis[a]

	$\|0>$	$\|1>$	$\|2>$
$<0\|$	$-A+(B-A_D+2\lambda_D/3)(x+2)+2\lambda/3-2\gamma-D(x^2+6x+4)\mp(o+p+q)$	$-(2x)^{1/2}[B-\frac{1}{2}\gamma-\frac{1}{2}A_D-\lambda_D/3\mp\frac{1}{2}(p+2q)-2D(x+2)]$	$-[x(x-2)]^{1/2}(2D\pm\frac{1}{2}q)$
$<1\|$		$-4\lambda/3+(B-4\lambda_D/3)(x+2)-2\gamma-D(x^2+8x)\mp\frac{1}{2}qx$	$-[2(x-2)]^{1/2}[B-\frac{1}{2}\gamma+\frac{1}{2}A_D-\lambda_D/3-2Dx]$
$<2\|$			$A+(B+A_D+2\lambda_D/3)(x-2)+2\lambda/3-D(x^2-2x)$

[a] The basis functions have been abbreviated to $|\Omega>$. Upper and lower signs correspond to the e and f sublevels, respectively; x = J(J+1).

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TABLE 7
Rotational Structure Constants (in cm^{-1}) for the $a^3\Pi$ (v = 0, 1, and 2) Levels of the $^{13}C^{16}O$ Molecule[a]

Constant	$v = 0$	$v = 1$	$v = 2$
B_v	1.60759(10)	1.58991(12)	1.572371(87)
$D_v \cdot 10^6$	5.52(16)	6.00(22)	7.03(17)
A	41.4477(29)	41.2903(29)	41.1144(23)
$A_D \cdot 10^4$	0.13(30)	− 0.95(24)	− 1.32(25)
$\lambda \cdot 10^2$	3.77(24)	3.09(26)	2.46(19)
o	0.8677(47)	0.8528(47)	0.8284(37)
$p \cdot 10^3$	6.17(44)	5.57(19)	4.64(34)
$q \cdot 10^4$	1.22(79)	1.12(43)	1.51(68)
$\sigma_f \cdot 10^2$	2.42	2.48	2.13

[a] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit, σ is the standard deviation of the fit.

automatic interferometric comparator assembled in our laboratory. The positions of the line centers were calculated by means of an interactive graphic computer program using the least-squares procedure and assuming Gaussian profiles for the lines. Repeatability of the measurements was tested to be 0.3–0.5 μm according to the grain of the plates. The typical standard deviation of the least-squares fit for the 50–130 calibration lines was about (3.4–5.1) · 10^{-3} cm^{-1}. Consequently, the precision of the single molecular lines with a good line/background ratio was about 0.005–0.010 cm^{-1}. Unfortunately, the complexity of this spectrum transition, the appearance of heads in band branches, and the partial overlapping of the spectra from the $^{12}C^{16}O$ and $^{13}C^{16}O$ molecules meant that a relatively large number of spectral lines were blended. These lower precision, blended lines were not used for the calculation of constants.

Tables 1–3 present the observed wavenumbers of lines together with their rotational assignments for the 0–0, 0–1, and 0–2 bands, respectively. A summary of the measurements of the analyzed 3*A* bands of $^{13}C^{16}O$ is presented in Table 4.

ANALYSIS AND CALCULATIONS

A fully resolved $^3\Pi$–$^3\Pi$ transition spectrum in which both states belong to Hund's case (a) should contain 27 double branches (see Table 5). However, if the upper state belongs to the Hund's case (b) and exhibits a negligible spin splitting, then only 18 collective and doubled by Λ splitting, (i.e., 36) branches would be observed. The relative intensities of the branches for a $^3\Pi$–$^3\Pi$ transition were derived and discussed by Kovács (*12*, Table 3.8) assuming Hund's cases (a) and (b) for the lower and upper states, respectively. Preliminary analysis of the newly observed 0–0 and 0–1 and the reanalyzed 0–2 bands were performed by using earlier information about both $c^3\Pi$ and $a^3\Pi$ states (*8*, *13*). Results of the reanalysis include four previously unobserved branches being identified (underlined in Table 5), and the extension of the *J* range of the reanalyzed 0–2 band.

The fitting of the spectrum and calculation of the rovibronic structure constants were performed only for the lower $a^3\Pi$ state. Because of a strong, complex, and not fully identified perturbation of the upper $c^3\Pi$ (v = 0) level (*7*), the fitting of the spectrum was performed using a nonlinear least-squares method proposed by Curl–Dane–Watson (*14*, *15*), which yields the constants for the lower $a^3\Pi$ (v = 0, 1, and 2) state levels

TABLE 8
Equilibrium Molecular Constants (in cm^{-1}) for the $a^3\Pi$ State of the $^{13}C^{16}O$ Molecule[a]

Constant	Value
B_e	1.616375(63)
$\alpha_e \cdot 10^2$	1.7607(71)
$D_e \cdot 10^6$	5.09(22)
$\beta_e \cdot 10^8$	7.5(13)
A_e	41.5346(92)
α_{A_e}	− 0.139(11)
$\lambda_e \cdot 10^2$	4.089(24)
$\alpha_{\lambda_e} \cdot 10^3$	− 6.54(13)
o_e	0.8794(48)
$\alpha_{o_e} \cdot 10^2$	− 2.00(26)
$p_e \cdot 10^3$	6.71(23)
$\alpha_{p_e} \cdot 10^4$	− 7.9(14)

[a] Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. Only the B_v constant values were developed according to the traditionally applied formula: $B_v = B_e - a_e(v + \frac{1}{2}) + \ldots$, whereas the remaining constants were developed according to a normal polynomial formula: $X_v = X_e + a_{Xe}(v + \frac{1}{2}) + \ldots$.

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as well as term values for the $c^3\Pi$ ($v = 0$) state. In this procedure, regular levels of the $a^3\Pi$ state are represented by an effective Hamiltonian proposed by Brown *et al.* (*10*). The respective matrix elements of this Hamiltonian used in this work were taken from a work of (*16*) and collected in Table 6. Considering the precision of the observed wavenumbers of lines, a relatively large number of lines excluded from the calculation of constants, and the highest J value observed, it was statistically justified to use only the following molecular parameters for the description of the $a^3\Pi$ state:

1. rotational and centrifugal distortion constants B and D;
2. spin–orbit coupling constants A and A_D;
3. spin–spin interaction constant λ;
4. Λ-doubling constants p, q, and o.

The constants obtained for the $v = 0$, 1, and 2 levels of the $a^3\Pi$ state in $^{13}C^{16}O$ are listed in Table 7.

On the basis of the rovibrational constants in Table 7 the equilibrium molecular constants for the $a^3\Pi$ state were estimated using a weighted least-squares method. The resulting values are presented in Table 8.

DISCUSSION AND CONCLUSION

The present work provides a modern analysis of three selected 0–0, 0–1, and 0–2 bands of the $c^3\Pi$–$a^3\Pi$ transition in the $^{13}C^{16}O$ isotopic molecule recorded under high resolution. The result of the spectrum analysis was the identification of over 1820 spectrum lines comprising newly observed 0–0 and 0–1 bands. Also observed for the first time are the four branches P_{13}, R_{13}, P_{31}, and R_{31}. Finally, the rotational structure of the $v'' = 2$ vibrational level was considerably extended.

The fitting of the spectrum using the separative method proposed by Curl–Dane–Watson (*14*, *15*) made it possible both to separate the spectroscopic information relative to the upper, strongly, and repeatedly perturbed $c^3\Pi$ ($v = 0$) level and the regular lower $a^3\Pi$ ($v = 0$, 1, and 2) levels. The application of the Brown *et al.'s* Hamiltonian for the analysis of the $a^3\Pi$ state levels made it possible to present a unified and improved characterization of the regular levels of the $a^3\Pi$ state in $^{13}C^{16}O$ and to create a perspective of a global interisotopomeric analysis of this state. The analysis of the structure and of perturbations of the upper $c^3\Pi$ ($v = 0$) level and the recently recorded spectra involving the $c^3\Pi$ ($v = 1$) level (*17*) will be presented in a separate work.

ACKNOWLEDGMENTS

This work was supported in part by Grant-in-Aid for scientific research from the Committee of Scientific Research (Poland).

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