

Analysis of the 1– ν' Progression of the 3A Band System ($c^3\Pi$ – $a^3\Pi$) in the $^{13}\text{C}^{16}\text{O}$ Molecule Spectrum

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The 1–0, 1–1, and 1–2 bands of the 3A system of ^{13}CO ($c^3\Pi$ – $a^3\Pi$) have been recorded for the first time, in the form of discharge emission spectra photographed at high resolution. Preliminary rotational analysis suggests that the $\nu = 1$ level of the $c^3\Pi$ state is perturbed in a fashion similar to the $\nu = 0$ level, previously observed by Dabrowski *et al.* (1987. I. Dabrowski, M. Vervolet, and D. C. Wang, *Can. J. Phys.* **65**, 1171–1177). Rotational combination differences from the 1720 measured lines have been used to obtain rotational constants for the $\nu = 0$ –2 levels of the $a^3\Pi$ state, using the Hamiltonian of Brown *et al.* (1979. J. M. Brown, E. A. Calbourn, J. K. G. Watson, and F. D. Wayne, *J. Mol. Spectrosc.* **74**, 294–318). and the least squares formalism of Curl and Dane (1988. *J. Mol. Spectrosc.* **128**, 406–412), as modified by Watson (1989. *J. Mol. Spectrosc.* **138**, 302–308). Term values for the $c^3\Pi$, $\nu = 1$ level have then been obtained from the line frequencies, and a set of effective rotational constants for the $c^3\Pi$ ($\nu = 1$) level of ^{13}CO has been derived. © 2000 Academic Press

INTRODUCTION

The 3A band system arising as the result of the transition from the state $c^3\Pi$ to $a^3\Pi$ is observable within the emission spectrum of the CO molecule. The former belongs to a numerous group of triplet transitions of the aforementioned molecule. Only the 0– ν' progression in several isotopic variants has been noted so far.

The lower $a^3\Pi$ state of the 3A band also participates in other transitions such as that of the third positive system ($b^3\Sigma^+$ – $a^3\Pi$) (1), the Asundi system ($a'^3\Sigma^+$ – $a^3\Pi$) (2), the triplet system ($d^3\Delta$ – $a^3\Pi$) (3), the Cameron band system ($a^3\Pi$ – $X^1\Sigma^+$) (4), and the Herman system ($e^3\Sigma^-$ – $a^3\Pi$) (5). The $c^3\Pi$ state, in addition to the 3A band system, can be found in the $c^3\Pi$ – $b^3\Sigma^+$ bands (6) and intercombinational transition-forming systems of a lower intensity, namely, the Tilford system ($c^3\Pi$ – $X^1\Sigma^+$) (7) detectable in vacuum ultraviolet. It should be emphasized that the 3A system provides favorable conditions for the analysis of the $c^3\Pi$ state due to the location of the $c^3\Pi$ and $a^3\Pi$ states with respect to one another.

The 3A bands system was originally identified at lower dispersion by Asundi (8). At higher dispersion (about 1.3 Å/mm) it was obtained by Schmid and Gerö (9) and further studied by Gerö (10). Gerö investigated the rotational structure of the $\nu'-1$, $\nu'-2$, and $\nu'-3$ bands and calculated the preliminary value of the rotational constant of the $c^3\Pi$ state. Both Gerö and his predecessors regarded the c state as the $^3\Sigma^+$ state of an unobserved triplet splitting. This belief was contradicted by Tilford (7) and by Ginter and Tilford (11),

who proved that the c state is the $^3\Pi$ state. Nevertheless, they did not yet state measurable triplet splitting and did not specify the ν' value. It was only Danielak *et al.* (12) who photographed the 3A system within the spectrum of the $^{13}\text{C}^{16}\text{O}$ isotopic molecule. The observed isotopic shifts of bandheads in relation to the natural molecule enabled them to determine that the value of the quantum number ν' in the bands of the 3A system equals $\nu' = 0$. Kłopotek and Vidal (13) and Dabrowski *et al.* (6) determined a clear spin splitting of the $c^3\Pi$ state and introduced the correction to the data obtained by Ginter and Tilford (11).

A preliminary account of the 3A band system in $^{13}\text{C}^{16}\text{O}$, presented in Ref. (14), has been recently complemented by Hakalla *et al.* (15) with a detailed analysis of the 0– ν' progression in that isotope.

So far the 3A system has been exclusively investigated as the 0– ν' progression placed in the ultraviolet region within the 2400–2800 Å region. It was thus decided to detect and analyze the previously unobserved 1– ν' progression placed within the 2200–2500 Å region of that band system. The investigation of the 1– ν' progression started with the analysis of the $^{13}\text{C}^{16}\text{O}$ isotope, and the previously unknown bands 1–0, 1–1, and 1–2 have been obtained.

The major objective of the present paper is to (a) identify this spectrum region; (b) present a unified description of the $a^3\Pi$ state in $^{13}\text{C}^{16}\text{O}$ for the $\nu = 0, 1$, and 2 levels based on the Hamiltonian of Brown *et al.* (16); (c) conduct a preliminary investigation of the previously unknown $c^3\Pi$ ($\nu = 1$) level and specify its terms values and effective rotational constants; and (d) calculate new equilibrium constants on the basis of merging individual molecular constants for the $a^3\Pi$ state.

Supplementary data for this article are available on IDEAL (<http://www.idealibrary.com>) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

TABLE 1
Observed Wavenumbers (in cm⁻¹) and Rotational Assignment for the 1–0 Band
of the c³Π–a³Π System of the ¹³C¹⁶O Molecule^a

<i>J</i>	<i>R</i> _{11ee}	<i>R</i> _{11ff}	<i>P</i> _{11ee}	<i>P</i> _{11ff}	<i>R</i> _{12ee}	<i>R</i> _{12ff}
1	45381.775(-6)	45380.042(4)			45339.079(23)	45339.045(34)
2	45382.908*	45381.374*	45372.874(-19)	45371.123(28)	45339.909*	45340.100(12)
3	45385.124*	45383.600(-7)	45366.865(-35)	45365.200(-11)	45341.456*	45341.571(45)
4	45388.000(22)	45386.619*	45362.228(4)	45360.836*	45343.550(-2)	45343.634(-8)
5	45391.636(2)	45390.260(3)	45358.352(17)	45356.822(-15)	45346.168*	45346.298(-9)
6	45395.819(-16)	45394.750*	45355.005*	45353.785(10)	45349.317(-18)	45349.497(9)
7	45400.881(24)	45399.923(20)	45352.609*	45351.493*	45353.087(35)	45353.312(-9)
8	45406.408(-7)	45405.628(23)	45350.859(35)	45349.788(29)	45357.108(-30)	45357.431(-18)
9	45412.643(14)	45412.059(-5)	45349.604*	45348.876(-11)	45361.709(-14)	45362.191(10)
10	45419.630(-6)	45419.157(-35)	45349.220*	45348.442(-6)	45366.963(7)	45367.456(15)
11	45427.276*	45427.030(28)	45349.334*	45348.706(-33)	45372.400*	45373.195(-61)
12	45435.136(-42)	45435.493*	45349.848*	45349.698(25)	45378.610(40)	45379.477(-3)
13	45443.963(6)	45444.570*	45351.242(-18)	45351.274(8)	45385.206(-11)	45386.279(1)
14	45453.554*	45454.093*	45353.140(18)	45353.370(8)	45392.364(-12)	45393.682(21)
15	45463.746*	45464.257*	45355.652(-3)	45356.102(-16)	45399.957(10)	45401.603(16)
16	45473.580*	45475.163(-23)	45358.793(12)	45359.514(-21)		
17	45484.656(-4)	45486.526(-13)	45362.385(-10)	45363.548(-16)		
18	45496.378*	45498.756*	45366.575(0)	45368.153(23)		
19	45508.838*	45511.304*	45371.259(5)	45373.201(13)		
20	45521.505*	45524.331(-17)	45376.818*	45378.988*		
21	45535.014*	45538.336*	45382.685*	45385.189*		
22	45549.006*	45552.640(0)	45389.300(0)	45392.104(17)		
23		45567.659(0)	45396.310*	45399.602*		
24		45583.271(0)				
25		45599.507(0)				

<i>J</i>	<i>P</i> _{12ee}	<i>P</i> _{12ff}	<i>R</i> _{13ee}	<i>R</i> _{13ff}	<i>P</i> _{13ee}	<i>P</i> _{13ff}
2	45329.707*	45329.618(-28)	45304.419(-8)	45304.435*	45294.257(19)	
3	45323.235(4)	45323.103(-28)	45304.910(-53)	45305.035(1)	45286.688(14)	45286.726*
4	45317.813(14)	45317.646*	45305.702(-2)	45305.906(9)	45279.941(-10)	45280.080(-12)
5	45313.036*	45312.862(-24)	45306.895(20)	45307.089(27)	45273.610(35)	45273.805*
6	45308.605(4)	45308.588(-11)	45308.164(-26)	45308.528(-2)	45267.434(-22)	45267.553*
7	45304.899(0)	45304.852(5)	45309.916(-50)	45310.363*	45261.791(-22)	45261.964(-26)
8	45301.600(53)	45301.682*	45311.955(-1)	45312.454*	45256.338(-27)	45256.654(-36)
9	45298.821(-9)	45298.884*	45314.399*	45315.107(28)	45251.347*	
10	45296.476(1)	45296.817*	45317.104*	45318.008(-28)	45246.768(37)	
11	45294.448*	45295.090*	45320.310(-20)	45321.475(24)		
12	45293.411(-1)	45293.840(22)	45323.876(-16)	45325.188(-5)		
13	45292.558(38)	45293.005*	45327.976(8)	45329.454(15)		
14		45292.910*	45332.427*	45334.145*		

<i>J</i>	<i>R</i> _{21ee}	<i>R</i> _{21ff}	<i>P</i> _{21ee}	<i>P</i> _{21ff}	<i>R</i> _{22ee}	<i>R</i> _{22ff}
1	45388.764(13)	45386.922(0)			45346.041(16)	45345.903(8)
2	45394.055(11)	45392.173(-27)	45374.672(-14)	45372.979(12)	45350.942(0)	45350.727(-25)
3	45399.957(9)	45398.217*	45373.842(-28)	45372.151*	45356.312(33)	45356.047(10)
4	45406.764*	45404.906*	45373.186(-2)	45371.429(14)	45362.229(-16)	45361.e868(-12)
5	45414.147(15)	45412.346*	45373.079(-15)	45371.309(-39)	45368.707(-54)	45368.192(-28)
6	45422.406*	45420.225(40)	45373.810(17)	45372.014(1)	45375.715*	45375.003(-6)
7	45431.050(-16)	45428.850(-30)	45375.180(-23)	45373.370(27)	45383.279(18)	45382.270(-27)
8	45440.628(16)	45438.377(28)	45377.342*	45375.243(-37)	45391.226*	45390.068*
9	45450.796(34)	45448.340(-33)	45379.808*	45377.977*	45399.819(-37)	45398.523(34)
10	45461.508(-18)	45459.009(27)	45383.352(0)	45381.173(-19)	45408.802(-45)	45407.258(27)
11	45472.985(20)	45470.228*	45387.262*	45385.029(-18)	45418.410(29)	45416.353*
12	45485.092(26)	45482.211(9)	45391.956(45)	45389.490(28)	45428.283*	45426.126*
13	45497.825(15)		45397.108(-30)	45394.594(31)	45439.112(42)	45436.649(3)
14			45403.006(-4)	45400.221(-10)	45450.122(-12)	45447.429(10)
15			45409.454(-53)	45406.483(-3)	45461.702*	45458.719(-7)
16					45473.942(6)	45470.422*
17					45486.507*	45482.830*
18					45499.940*	45495.797*
19					45513.923*	45509.249(35)
20						45523.124*
21						45537.623*

^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.

TABLE 1—Continued

<i>J</i>	P_{22ee}	P_{22ff}	R_{23ee}	R_{23ff}	P_{23ee}	P_{23ff}
2	45331.665*	45331.506(-12)	45315.348(-42)	45315.282(48)	45296.045(14)	
3	45330.128*	45330.008(-8)	45319.827*	45319.544(-2)	45293.641(-2)	45293.468*
4	45328.697*	45328.422*	45324.529*	45324.062*	45290.948(34)	45290.745(-10)
5	45327.871*	45327.425(28)	45329.404(32)	45328.965(-11)	45288.307(-27)	45288.156(3)
6	45327.320(27)	45326.833(-3)	45334.624(-24)	45334.151*	45286.120(-29)	45285.893(14)
7	45327.307*	45326.789(29)	45340.173(-2)	45339.609*	45284.341(30)	45283.886(-17)
8	45328.029(24)	45327.126(2)	45346.090*	45345.305(24)	45282.757*	45282.137*
9	45329.038(0)	45328.008(28)	45352.410(-37)	45351.409(22)	45281.560*	45280.906(28)
10	45330.648(-25)	45329.447(6)	45359.175*	45357.741*	45280.937(8)	45279.996(-39)
11	45332.836*	45331.201*	45366.190(-19)	45364.685(-63)	45280.619(39)	45279.491(-5)
12	45335.322(19)	45333.566(-42)		45372.253*	45280.573*	45279.282(-39)
13	45338.433(34)	45336.595*			45281.115(-33)	45279.693(32)
14	45342.020(-22)	45339.869(1)				
15	45346.221(-4)	45343.887*				
16	45350.877(12)	45348.089(-9)				
17	45356.221*	45353.000(7)				
18	45361.833(-6)	45358.389(0)				
19	45368.244*	45364.458*				
20	45374.736*	45370.506*				
21	45382.364*	45377.866(-35)				
22	45390.396(0)	45385.369*				
23		45393.506*				

<i>J</i>	R_{31ee}	R_{31ff}	P_{31ee}	P_{31ff}	R_{32ee}	R_{32ff}
1	45399.384(-20)	45397.800(-59)			45356.712(32)	45356.839(7)
2	45408.381(-8)	45406.947(27)			45365.302(15)	45365.444(-27)
3	45418.003(-31)	45416.641(-9)	45384.523(-2)	45383.067(34)	45374.230*	45374.552(-18)
4	45428.330(1)	45427.125(20)	45387.403*	45385.965*	45383.984*	45384.190(1)
5	45439.448*	45438.237*	45391.224(44)	45389.994*	45394.003(-8)	45394.415(14)
6	45451.134(-1)	45450.327(32)	45395.437(-15)	45394.246*	45404.629(-6)	45405.003*
7	45463.679*	45462.846(-36)	45400.465(12)	45399.481(-43)	45415.665*	45416.349(49)
8	45476.505(17)	45476.149(26)	45406.037*	45405.280*	45427.103*	45427.971(4)
9	45490.021*		45412.412(-13)	45411.855(-10)	45439.136*	45440.268(-3)
10	45504.573(3)		45419.260(33)	45418.935(-32)	45452.288*	45452.757*
11			45426.760(-29)	45426.841(12)	45464.995*	45466.262(31)
12			45434.952(-3)	45435.198(20)	45478.416(-30)	

<i>J</i>	P_{32ee}	P_{32ff}	R_{33ee}	R_{33ff}	P_{33ee}	P_{33ff}
2			45329.760(25)	45329.961(8)		
3	45340.812(-44)	45340.939(-13)	45337.874*	45338.117(39)	45304.331(33)	45304.491(31)
4	45343.075(-32)	45343.232(13)	45346.063(7)	45346.480(37)	45305.175*	45305.452(-22)
5	45345.829(21)	45345.940(10)	45354.563*	45355.128(-30)	45306.387(-33)	45306.665(-21)
6	45348.944(-7)	45349.123(-22)	45363.509(19)	45364.132(-28)	45307.822(15)	45308.150(-37)
7	45352.643(-4)	45352.963(22)	45372.664(8)	45373.579*	45309.637*	45310.121(36)
8	45356.835(-11)	45357.236(3)	45381.903*	45383.018(-36)	45311.664(0)	45312.313(-8)
9	45361.435*	45361.926(-56)	45391.994*	45393.200(32)	45314.115(5)	45314.933(53)
10	45366.494(-53)	45367.287*	45402.108(-39)	45403.500(-40)	45316.806(2)	45317.848(39)
11	45372.234(29)	45373.006*	45412.734(-8)	45414.822*	45320.153*	45321.236(-41)
12	45378.545*	45379.321(-3)	45423.760(-8)	45425.912*	45323.708(39)	45325.060(23)
13	45384.902(-31)	45386.156(-21)	45435.298(36)	45437.545*	45327.722(39)	45329.328(-11)
14	45392.030(0)	45393.430(-16)	45447.178*	45449.694(25)	45332.190(38)	45334.011(16)
15	45399.659(-8)	45401.393(0)	45459.598(-2)	45462.362(-3)	45337.084(-28)	45339.216*
16			45472.364*	45475.528(-40)	45342.732*	45344.949(-25)
17			45485.805(-36)	45489.512(0)	45348.446(2)	45351.178(3)
18			45499.870*	45503.336*	45354.873*	45357.939(40)
19			45514.165*	45518.101*	45361.780(36)	45365.226*
20			45528.934*	45533.344(-6)	45369.117(0)	45373.029*
21				45549.211(35)	45377.033*	45381.163(0)
22					45385.480*	45389.919(6)
23						45399.295(-35)

EXPERIMENTAL DETAILS

The emission spectrum of the $c^3\Pi-a^3\Pi$ band system has been obtained in a water-cooled Geissler tube. The tube was filled with a mixture of the molecular gases $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$ with an approximate ratio of about 90 to 10%, respectively. The pressure in the tube was about 10 Torr. The tube was activated at 3 kV and 50 mA ac. The spectra were observed in the 11th order for the 1-0 band as well as in the 10th order for the 1-1 and 1-2 bands due to the use of a 2-m Ebert spectrograph (PGS-2) furnished with a 651-grooves/mm grating blazed at 1.0 μm (the total number of grooves equals 45 600). Reciprocal linear dispersion was equal to 0.040–0.048 nm/mm and theoretical resolving power was about 450 000–500 000. The exposure of ORWO UV-1 plates varied from 3 to 25 h.

The standard thorium lines (17) calculated from a number of orders and emitted by the water-cooled hollow-cathode tube were used as the calibration spectrum. Next, the plates with the appropriate spectra were measured by an automatic comparator constructed in our laboratory. The plates' position was interferometrically controlled, whereas the contour of lines was photoelectrically measured point by point.

The line center was calculated by the nonlinear least-squares procedure. The least-squares method was implemented to fit the wavenumbers of thorium lines, which allowed us to obtain the 9th order interpolation polynomial. The standard deviation of this fitting for 130–160 calibration lines was about $(3.6-5.4) \times 10^{-3} \text{ cm}^{-1}$. The same polynomial coefficients were then employed to calculate the values of wavenumbers of CO. The accuracy of a singular divided line with a good line/background ratio was evaluated to be about 0.005–0.010 cm^{-1} .

Many lines were nevertheless blended due to the complexity of the triplet spectrum, whose lines, even at high resolution (0.040–0.048 nm/mm), form joint contours which unfortunately are difficult to fit. The largest number of single lines can be encountered solely for the branches R_{33ee} and R_{33ff} from $J = 20$ to 25 and for the branches P_{13ee} and P_{13ff} from $J = 4$ to $J = 15$. However, it should be noted that those lines are very weak. All these reasons and the overlapping of the spectrum lines of $^{12}\text{C}^{16}\text{O}$ cause blending of the majority of lines in the 1- ν'' progression, particularly in the bandheads. Blended lines of

TABLE 5
Combination Differences

For $c^3\Pi$ state	For $a^3\Pi$ state
$F_{ix}(J+1) - F_{ix}(J-1)$	$F_{ix}(J+1) - F_{ix}(J-1)$
$F_{2x}(J+1) - F_{3x}(J-1)$	$F_{3x}(J+1) - F_{2x}(J-1)$
$F_{1x}(J+1) - F_{2x}(J-1)$	$F_{2x}(J+1) - F_{3x}(J-1)$
$F_{3x}(J) - F_{1x}(J)$	$F_{2x}(J+1) - F_{1x}(J-1)$
$F_{3x}(J) - F_{2x}(J)$	$F_{1x}(J+1) - F_{2x}(J-1)$
$F_{2x}(J) - F_{1x}(J)$	$F_{2x}(J) - F_{1x}(J)$
	$F_{3x}(J) - F_{2x}(J)$
	$F_{3x}(J) - F_{1x}(J)$

$i = 1, 2, 3.$

$x = e$ or f , respectively.

less precision are marked with an asterisk in the tables and were not used to calculate molecular constants.

The major results of this research are featured in Tables 1–3, which present the observed wavenumbers of lines, along with rotational assignments for the 1-0, 1-1, and 1-2 bands, respectively. Tables 2 and 3 are not printed here but are available as supplementary data. A measurement summary of the analyzed 1- ν'' progression of the 3A band system of the $^{13}\text{C}^{16}\text{O}$ isotopic molecule can be found in Table 4.

ANALYSIS AND CALCULATIONS

If one of the $^3\Pi-^3\Pi$ transition states is in Hund's case (a), whereas the other is close to Hund's case (b), i.e., the so-called "intermediate case," the selection rule $\Delta\Sigma = 0$ is not applicable. Thus, in the following equation representing wavenumbers of the lines as differences between terms of the upper state T' and the lower state T'' ,

$$\begin{aligned} \sigma &= T' - T'' \\ &= T'_e - T''_e + G'(\nu') - G''(\nu'') + F'_{vi}(J) - F''_{vj}(J), \end{aligned}$$

indices i and j can have values from 1 to 3 independently. The symbols used in this equation correspond to Herzberg's notation system (18). Thus, 27 branches, each of which is subject to Λ -doubling, are formally obtained. If the upper state passes to the pure case (b) and triplet splitting does not occur, some of the aforementioned branches will join together and only 15 N -numbered collective branches subject to Λ -doubling will appear (15, Table 5). The same kind of branching is observable in the case of the transition $^3\Delta-^3\Pi$.

In the 3A band system the lower state $a^3\Pi$ is in Hund's case (a), whereas the upper state $c^3\Pi$ is in an intermediate case close to Hund's case (b) with a slight measurable triplet splitting (6, 13). Hence 27 doubled branches should formally be obtained. Nevertheless, due to weak intensity of all the Q branches (20, Table 3.8), only 18 branches which are collective and doubled by Λ splitting, i.e., 36 in total, are observable.

TABLE 4
Summary of Observations and Analyses of the 1 - ν'' Progression of the 3A Bands of the $^{13}\text{C}^{16}\text{O}$ Molecule

Band	Remarks	Total number of lines	J_{max}	f^a	$\sigma_f \cdot 10^2^b$ (in cm^{-1})
1 - 0	first obs.	534	25	247	2.93
1 - 1	first obs.	569	25	254	3.02
1 - 2	first obs.	611	25	222	3.24

^a Number of degrees of freedom of the fit.

^b Standard deviation of the fit.

TABLE 6
Rotational Structure Constants (in cm^{-1}) for the $a^3\Pi$ ($v = 0, 1, \text{ and } 2$)
Levels of the $^{13}\text{C}^{16}\text{O}$ Molecule^a

Constant	$v = 0$	$v = 1$	$v = 2$
B_v	1.607616(82) ^b	1.589849(85) ^b	1.572298(73) ^b
	1.60767(15) ^c	1.58982(14) ^c	1.57213 (15) ^c
	1.60759(10) ^d	1.58991(12) ^d	1.572371(87) ^d
$D_v \cdot 10^6$	5.59(14) ^b	5.78(15) ^b	6.86(13) ^b
	5.82(31) ^c	5.60(21) ^c	6.60(21) ^c
	5.52(16) ^d	6.00(22) ^d	7.03(17) ^d
A_v	41.4510(23) ^b	41.2909(23) ^b	41.1163(21) ^b
	41.4569(39) ^c	41.2904(39) ^c	41.1145(46) ^c
	41.4477(29) ^d	41.2903(29) ^d	41.1144(23) ^d
$A_{Dv} \cdot 10^4$	0.002(250) ^b	-0.94(21) ^b	-1.44(22) ^b
	-0.26(47) ^c	-0.66(44) ^c	-1.88(50) ^c
	0.13(30) ^d	-0.95(24) ^d	-1.32(25) ^d
$\lambda_v \cdot 10^2$	3.80(19) ^b	3.03(20) ^b	2.49(17) ^b
	3.78(30) ^c	2.94(31) ^c	2.47(38) ^c
	3.77(24) ^d	3.09(26) ^d	2.46(19) ^d
o_v	0.8638(37) ^b	0.8480(37) ^b	0.8299(33) ^b
	0.8678(60) ^c	0.8529(61) ^c	0.8285(72) ^c
	0.8677(47) ^d	0.8528(47) ^d	0.8284(37) ^d
$p_v \cdot 10^3$	5.30(36) ^b	5.20(33) ^b	4.58(31) ^b
	3.67(62) ^c	4.34(62) ^c	4.65(72) ^c
	6.17(44) ^d	5.57(19) ^d	4.64(34) ^d
$q_v \cdot 10^4$	2.78(68) ^b	0.75(39) ^b	1.40(59) ^b
	1.8(14) ^c	-1.3(14) ^c	0.6(12) ^c
	3.22(79) ^d	1.12(43) ^d	1.51(68) ^d
$\sigma_f \cdot 10^2$	2.93 ^c	3.02 ^c	3.24 ^c

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit, σ is the standard deviation of the fit in cm^{-1} .

^b This work (merged results).

^c This work (individual results).

^d Hakalla *et al.* (15, individual results).

Since none of the Q branches have been detected, all the transitions are either of the $e-e$ or of the $f-f$ type.

The preliminary interpretation of newly observed bands 1-0, 1-1, and 1-2 has been based on preexisting information concerning the $a^3\Pi$ state (15), as well as the implementation of combination differences for the upper state and the lower state (Table 5). The preliminary analysis of the upper level $c^3\Pi$ ($v = 1$) employed sorted wavenumbers of the 1- v'' progression in the measured region as theoretically calculated on the basis of the foregoing measurements. These analyses and the evaluated differences imply the multifarious perturbation of the $c^3\Pi$ ($v = 1$) level. It seems to be a complex and multistate perturbation similar to that in the $c^3\Pi$ ($v = 0$) level explained by Ginter and Tilford (11), Dabrowski *et al.* (6), and Mellinger

and Vidal (19). That perturbation is the strongest for $10 < J < 20$ for both e and f parity with energy shifts of approximately $0.05-0.4 \text{ cm}^{-1}$, as well as the band origin of about 0.3 cm^{-1} . The other rotational levels also seem to be perturbed, but the observable effect is much smaller than that for $10 < J < 20$ and lies close to the experimental resolution.

Due to that multifarious perturbation the fitting of the spectrum and the calculation of the rovibronic structure constants were originally performed for the lower $a^3\Pi$ state. The spectrum for the individual bands has been reduced by a nonlinear least-squares fit with the effective Hamiltonians of Brown *et al.* (16). The corresponding elements of this Hamiltonian were taken from (21) and their detailed description can be found in (15, Table 6). This reduction was performed by a separate

TABLE 7
Observed Term Values (in cm^{-1}) for the $\nu = 1$ Level of the $c^3\Pi$ State of $^{13}\text{C}^{16}\text{O}^{a,b}$

J	F_{1e}	F_{1f}	F_{2e}	F_{2f}	F_{3e}	F_{3f}
1	45342.737(21)	45342.628(21)	45344.530(21)	45344.499(21)		
2	45345.677(13)	45345.643(15)	45352.646(15)	45352.528(17)	45363.301(13)	45363.465(13)
3	45352.926(15)	45353.070(21)	45363.889(13)	45363.733(13)	45378.234(15)	45378.452(13)
4	45363.966(17)	45364.039(14)	45378.725(15)	45378.550(14)	45396.811(15)	45397.083(14)
5	45378.680(14)	45378.875(16)	45397.373(16)	45397.113(16)	45419.031(14)	45419.422(14)
6	45397.266(16)	45397.459(15)	45419.763(14)	45419.372(15)	45445.013(18)	45445.554(15)
7	45419.415(14)	45419.765(17)	45445.873(22)	45445.285(17)	45474.714(15)	45475.395(17)
8	45445.418(17)	45445.933(20)	45475.627(17)	45474.909(18)	45508.107(20)	45508.911(17)
9	45475.006(17)	45475.611(20)	45509.203(19)	45508.355(18)	45545.078(20)	45546.129(18)
10	45508.312(24)	45509.110(20)	45546.444(20)	45545.418(19)	45585.898(26)	45587.200(21)
11	45545.486(23)	45546.355(21)	45587.377(21)	45586.145(21)	45630.421(22)	45631.860(23)
12	45586.195(25)	45587.373(23)	45632.073(22)	45630.670(26)	45678.607(26)	45680.348(26)
13	45630.644(24)	45632.016(26)	45680.532(27)	45678.885(27)	45730.520(25)	45732.464(31)
14	45678.892(26)	45680.449(28)	45732.745(26)	45730.817(30)	45786.187(29)	45788.468(38)
15	45730.866(32)	45732.679(32)	45788.625(31)	45786.437(32)	45845.638(0)	45848.138(35)
16	45786.467(33)	45788.662(33)	45848.306(0)	45845.800(33)	45908.674(36)	45911.556(37)
17	45845.776(44)	45848.330(35)	45911.696(34)	45908.864(42)	45975.453(0)	45978.732(39)
18	45908.732(38)	45911.637(37)	45978.824(0)	45975.744(0)	46046.072(42)	46049.893(44)
19	45975.665(0)	45978.896(0)	46049.642(0)	46046.121(0)	46120.328(55)	46124.361(0)
20	46046.259(0)	46049.677(0)	46124.501(0)	46120.557(42)	46194.310(0)	46202.691(57)
21	46120.504(57)	46124.197(45)	46202.823(53)	46194.611(0)	46275.661(0)	46284.764(54)
22	46194.680(0)	46202.675(0)	46285.109(0)	46275.960(0)	46360.734(0)	46370.705(60)
23	46276.019(0)	46284.750(53)	46371.006(0)	46361.029(0)	46449.532(0)	46460.709(0)
24	46361.079(0)	46370.630(58)	46460.663(0)	46449.824(0)	46542.060(0)	46554.153(0)
25	46449.861(0)	46460.256(64)	46554.083(0)	46542.346(0)	46638.319(0)	46651.366(0)
26	46542.369(0)	46553.661(72)	46651.269(0)	46638.599(0)	46738.315(0)	46752.350(0)

^a Term values for the $\nu = 1$ level of the $c^3\Pi$ state are given relative to the $J = 1e$, $\nu = 0$ level of the $a^3\Pi_0$ sub-state.

^b Uncertainties in parentheses represent one standard deviation in units of the last quoted digit, in cm^{-1} .

procedure suggested by Curl and Dane (22) and Watson (23) which allowed the separation of information for both states and the determination of individual molecular states for the lower state $a^3\Pi$ ($\nu = 0, 1$, and 2) and term values for the upper state $c^3\Pi$ ($\nu = 1$) calculated with regard to $J = 1$ in the e sublevel of the $\nu = 0$ level of the $a^3\Pi_0$ substate.

The individual constants calculated for the $\nu = 0, 1$, and 2 levels of the $a^3\Pi$ state in $^{13}\text{C}^{16}\text{O}$ have been compared to the corresponding individual molecular constants described in (15) and represented in Table 6. The term values of the newly observed $c^3\Pi$ ($\nu = 1$) level are featured in Table 7. The next step was to determine the constants of the lower state (calculated with high precision), whereas the matrix given in Ref. (21) was implemented to describe the upper state. Since a large number of perturbations have been observed in the course of analysis, and not all of the perturbed states have been identified, our model has been restricted to a simplified version; i.e., the additional perturbing matrix elements have not been taken into consideration. Only lines with $J < 10$ and $J > 20$ have been considered in the least-squares fit procedure separately for each band. The least-squares merge fit described by Albritton *et al.* (24) and Coxon (25) has been employed to calculate the

final molecular parameters for the observed levels of the $a^3\Pi$ state and for the $c^3\Pi$ ($\nu = 1$) level (Table 6 and Table 8, respectively).

Assuming their traditionally recognized polynomial dependence on the vibrational quantum number, the new equilibrium molecular constants for the $a^3\Pi$ state have been calculated on the basis of the obtained values of rovibronic constants and calculations based on the weighted least-squares method. The results are summarized in Table 9.

DISCUSSION AND CONCLUSION

The present attempt at the first observation of the 1–0, 1–1, and 1–2 bands of the $c^3\Pi$ – $a^3\Pi$ transition at high resolution and their analyses considerably broadens and deepens data concerning the $a^3\Pi$ and $c^3\Pi$ states by introducing preliminary information about the $c^3\Pi$ ($\nu = 1$) level. As a result of the spectrum analysis, over 1720 spectrum lines have been identified in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule. Those lines compose 1–0, 1–1, and 1–2 bands belonging to the newly observed 1– ν' progression in the 3A system.

The preliminary analyses suggest that the $c^3\Pi$ ($\nu = 1$) level

TABLE 8
Effective Rotational Constants (in cm^{-1})
for the $c^3\Pi$ ($v = 1$) Level of the $^{13}\text{C}^{16}\text{O}$
Molecule^a

Constant	Value ^b
B_v	1.85719(11)
$D_v \cdot 10^6$	- 5.64(13)
A_v	1.0684(86)
$A_{D_v} \cdot 10^2$	1.043(41)
λ_v	0.1310(30)
$o_v \cdot 10^2$	- 1.63(59)
$p_v \cdot 10^3$	4.58(40)
$q_v \cdot 10^3$	9.118(37)

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

^b Merged results.

is perturbed. It also appears to be a complex and multistate perturbation similar to the perturbation of the $c^3\Pi$ ($v = 0$) level (6, 19). The perturbation in question under consideration manifests itself mostly for $10 < J < 20$ and shifts band origins for about 0.3 cm^{-1} in the direction of longer wave numbers (this effect was first observed by Siwicz-Rytel (26) for the $c^3\Pi$ ($v = 0$) level in $^{14}\text{C}^{16}\text{O}$).

Due to these multistate perturbations, the fittings of the spectrum using the separative method proposed by Curl and Dane (22) and Watson (23) have been implemented. This procedure allows us to separate the spectroscopic information corresponding to the upper perturbed $c^3\Pi$ ($v = 1$) level from that concerning the regular lower $a^3\Pi$ ($v = 0, 1$, and 2) levels. The terms of the $c^3\Pi$ ($v = 1$) level (see Table 7) which had not been previously described and the individual molecular constants for the $a^3\Pi$ ($v = 0, 1$, and 2) levels (see Table 6) were thus obtained. These constants are in good agreement with the individual molecular constants presented in Ref. (15) with accuracy of up to one standard deviation, except for the A and p constants for the $v' = 0$ level. Those deviations can be attributed to a considerable number of overlapping lines in the investigated region. The application of the Hamiltonian of Brown *et al.* (16) to the analysis of the $a^3\Pi$ state levels made it possible to present a unified and improved specification of the regular levels of the $a^3\Pi$ state in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule.

Due to this complicated and unidentified perturbation for the

$c^3\Pi$ ($v = 1$) level only effective molecular constants have been calculated (see Table 8).

The empirical constant D deserves special attention. Its negative value, as well as its great impact on the calculation of effective constants, proves the hypothesis of Ginter and Tilford (11) as well as that of Dabrowski *et al.* (6) that in this case the constant D accounts for the perturbation rather than for the centrifugal distortion. The effective value $D = -5.64(13) \times 10^{-6} \text{ cm}^{-1}$ determined here for the $c^3\Pi$ ($v = 1$) level of $^{13}\text{C}^{16}\text{O}$ cannot be directly contrasted with those specified by Ginter and Tilford (11) $D = -36.2 \times 10^{-6} \text{ cm}^{-1}$ and Dabrowski *et al.* (6) $D = -60(6) \times 10^{-6} \text{ cm}^{-1}$, because their data concern the $c^3\Pi$ ($v = 0$) level of $^{12}\text{C}^{16}\text{O}$. It can nevertheless be stated that, first, the smallest absolute value of the D constant for the $c^3\Pi$ ($v = 1$) level of $^{13}\text{C}^{16}\text{O}$ in comparison to the value of the same constant for the $c^3\Pi$ ($v = 0$) level of $^{12}\text{C}^{16}\text{O}$ brings us to the following conclusions:

TABLE 9
Equilibrium Molecular Constants (in cm^{-1})
for the $a^3\Pi$ State of the $^{13}\text{C}^{16}\text{O}$ Molecule^a

Constant	Value
B_e	1.61641(11)
$\alpha_e \cdot 10^2$	1.7659(55)
$D_e \cdot 10^6$	5.27(18)
$\beta_e \cdot 10^7$	6.35(96)
A_e	41.5347(30)
$\alpha_{A_e} \cdot 10^1$	- 1.674(16)
$\lambda_e \cdot 10^2$	4.09(11)
$\alpha_{\lambda_e} \cdot 10^3$	- 6.51(62)
o_e	8.731(16)
$\alpha_{o_e} \cdot 10^2$	- 1.746(89)
$p_e \cdot 10^3$	5.59(28)
$\alpha_{p_e} \cdot 10^4$	- 3.7(16)
$q_e \cdot 10^4$	3.13(87)
$\alpha_q \cdot 10^5$	- 6.9(45)

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. All the constant values have been developed in accordance with the regular equation:

$$X_v = X_e + \alpha_e \left(v + \frac{1}{2} \right) + \dots,$$

except for the value of B constant which have been developed in accordance with the traditional formula:

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) + \dots$$

(1) The perturbation impact decreases in the heaviest $^{13}\text{C}^{16}\text{O}$ molecule in comparison to an ordinary molecule;

(2) the perturbation impact arising due to the increase in distance between the $c^3\Pi$ ($\nu = 1$) level and the perturbing levels decreases, which may be interpreted as follows: the level perturbing the $c^3\Pi$ ($\nu = 1$) level lie below the $c^3\Pi$ ($\nu = 0$) level. Second, the $c^3\Pi$ ($\nu = 1$) level has a negative centrifugal distortion constant D which may be explained in terms of a perturbation with a closely located $^3\Pi$ state at lower energy. This is most probably the $k^3\Pi$ (27, 28) state, which shifts our band origins, too. As all components of the $c^3\Pi$ ($\nu = 1$) level are affected, it may be assumed that the $^3\Pi$ is not the only perturber.

The small value of $A = 1.0684(86) \text{ cm}^{-1}$ proves the conclusion drawn by Klopotek and Vidal (13) that the $c^3\Pi$ electronic state is regular and exhibits only a weak spin-orbit interaction. This value also proves conclusion made by Dabrowski *et al.* (6) that the $c^3\Pi$ state is not entirely Rydberg in character. The relatively large value of the Λ doubling parameter $q = 0.009118(37) \text{ cm}^{-1}$ for the $c^3\Pi$ ($\nu = 1$) level in $^{13}\text{C}^{16}\text{O}$ is similar to the value specified in Refs. (6, 11, 19) for the $c^3\Pi$ ($\nu = 0$) level in $^{12}\text{C}^{16}\text{O}$. As the aforementioned constant contains direct information on the admixture of the $^3\Sigma$ electronic state, it seems reasonable to assume that one of the major perturbers (but not the only one) of the $c^3\Pi$ ($\nu = 1$) level is the closely lying $j^3\Sigma^+$ state.

The final molecular constants obtained as a result of the merge fit have been used to calculate new equilibrium molecular constants for the $a^3\Pi$ state in $^{13}\text{C}^{16}\text{O}$ (see Table 9). It follows from the considerations above that the present research makes a substantial contribution to the study of the $3A(c^3\Pi - a^3\Pi)$ band system, particularly the investigation of the previously unknown $c^3\Pi$ ($\nu = 1$) level.

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