

Rotational Spectra and Structures of Carbon Monoxides C₅O, C₇O, and C₉O

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Abstract: Rotational spectra of carbon-chain molecules C₅O, C₇O, and C₉O have been observed for the first time by using a Fabry–Perot type Fourier transform microwave (FTMW) spectrometer cooperated with a pulsed discharge nozzle (PDN). The molecules have been generated by the discharge of C₃O₂ diluted in Ar. The spectra consist of series of R-branch transitions typical of linear molecules in singlet electronic states. For C₅O, transitions for all the possible singly substituted ¹³C and ¹⁸O isotope species have also been detected in natural abundance. These measurements with an assumption of linearity have enabled a complete substitution structure to be derived: $r_s(\text{C}_{(1)}-\text{O}) = 1.1562(11) \text{ \AA}$, $r_s(\text{C}_{(2)}-\text{C}_{(1)}) = 1.2552(30) \text{ \AA}$, $r_s(\text{C}_{(3)}-\text{C}_{(2)}) = 1.2881(38) \text{ \AA}$, $r_s(\text{C}_{(4)}-\text{C}_{(3)}) = 1.2947(21) \text{ \AA}$, and $r_s(\text{C}_{(5)}-\text{C}_{(4)}) = 1.2736(10) \text{ \AA}$. The CC bond lengths in C₅O were found to be much more uniform than those in an isoelectronic molecule HC₅N. The canonical structure which reproduces observed internuclear distances in C₅O has been suggested. By assuming the same partial structure as that in the C₅O molecule, the averaged bond lengths for the rest of C–C bonds in C₇O and C₉O have been determined to be 1.270 and 1.274 Å, respectively. Along with the recent results of triplet C_nO ($n = 2, 4, 6, \text{ and } 8$) [Ohshima, Endo, and Ogata, *J. Chem. Phys.* **1995**, *102*, 1493–1500], the CC bonds in C_nO are found to become more uniform cumulene-type double bonds with increasing n and to converge to a constant length.

There exists intense interest during the past decades in structural chemistry centered on linear carbon-chain molecules. The series of cyanopolynes, HC_nN represent probably the most extensively studied molecules by microwave spectroscopy. The detailed molecular structure has been determined for cyanobutylene,¹ H–C≡C–C≡C–C≡N. The observed bond lengths revealed that the π -electron delocalization effects slightly shortened the single bonds and lengthened the triple bonds. For other carbon chain molecules, precise structures have been reported only for relatively short molecules. The polycarbon monoxides C_nO are one series of such species. Carbon monoxide, the simplest of the series, has been studied by various kinds of spectroscopy. The molecular structure of CO was determined by millimeter wave spectroscopy.² The magnitude of the electric dipole moment³ was determined by the Stark effect, and its polarity⁴ from negative carbon to positive oxygen was determined by the observation of isotope effect of the rotational g factor. The first spectroscopic evidence for the existence of C₂O was proved by Jacox *et al.*,⁵ who observed the infrared spectrum of C₂O in an argon matrix and confirmed a linear structure for C₂O by observing isotope effects on the vibrational frequencies. Subsequently, Devillers and Ramsay⁶ analyzed the transient absorption spectrum of C₂O in a region

from 5000 to 9000 Å in a flash photolysis of carbon suboxide. High resolution laboratory infrared⁷ and millimeter-wave spectra⁸ of C₂O have been observed by Yamada *et al.*, and subsequently the molecule was detected in interstellar space Taurus Molecular Cloud-1 (TMC-1) by Ohishi *et al.*⁹ The first laboratory study of the microwave spectrum of C₃O by Brown *et al.*¹⁰ in 1983 was followed quickly by the interstellar detection of this molecule in TMC-1 by Mathews *et al.*¹¹ in 1984. The millimeter wavelength region of this spectrum was observed by Tang *et al.*¹² and Klebsch *et al.*¹³ After that, Brown *et al.*¹⁴ also observed the microwave spectra of C₃O including all monoisotopically substituted isotopomers and determined the substitution structure. The linear geometry of C₃O was confirmed by the observed l -type doubling in the first excited state of the ν_5 bending mode. The ESR spectra of C₄O and C₆O in neon and argon matrices were observed by Van Zee *et al.*,¹⁵ and the zero-field electron spin splitting parameters were determined. However, no experimental study has so far been reported for C₅O, C₇O, or C₉O.

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For a linear C_nO molecule the simple molecular orbital picture predicts that the molecule contains $2n + 2$ π -electrons. For those species with odd n , these π -electrons constitute a closed shell and result in a $^1\Sigma^+$ electronic configuration. For n even, however, two of the π electrons are distributed over a pair of approximately nonbonding orbitals, so that the ground state of this open-shell configuration is $^3\Sigma^-$ (with low-lying excited $^1\Sigma^+$ and $^1\Delta$ states). Theoretical calculation by an *ab initio* MO method has been carried out on C_5O by Brown *et al.*¹⁶ However, they predicted that either a linear singlet state or a kinked triplet state could be the ground state with no clearcut distinction between them as the ground state. For this reason, the experimental determination of the multiplicity of the ground state and comparison of the detailed molecular structures for longer members of the C_nO series are particularly interesting.

Iida, Ohshima, and Endo have recently developed a powerful method for the study of gas phase unstable molecules by using a Fourier transform microwave (FTMW) spectrometer¹⁷ coupled with a pulsed-discharge-nozzle (PDN) and successfully applied the method to the laboratory detections of HC_9N ¹⁸ and C_nS ($n = 3-5$).¹⁹⁻²¹ Longer members of the C_nO series are good candidates to be detected by this method, since CO and C_2O have been found to be produced efficiently by the decomposition of carbon suboxide and longer C_nO can be expected to be produced by the subsequent carbon insertion reaction to the double bond.²² Many allene derivatives such as fluoroallenes²³ have been prepared by this method for microwave spectra measurements.

We have detected new carbon-chain molecules C_nO ($n = 4-9$) by using the PDN-FTMW spectrometer. In the present paper we report Fourier transform microwave spectra of C_5O , C_7O , and C_9O in the singlet ground electronic states. The other molecules in the triplet ground electronic states are published separately.²⁴

Experimental Details

Spectral measurements were carried out with a Fabry-Perot cavity type, Fourier transform microwave spectrometer originally designed by Balle and Flygare.²⁵ The spectrometer was modified to incorporate a pulsed discharge nozzle to produce short-lived molecular species in the present experiment. Detailed explanations of the FTMW spectrometer¹⁸ and the pulsed-discharge-nozzle^{18,19} have already been given elsewhere. A mixture of 1% carbon suboxide diluted in argon was employed to generate molecules to be studied. The mixture was expanded as a supersonic beam through a pulsed solenoid nozzle with a 1.2 mm diameter orifice. The stagnation pressure of the C_3O_2 /argon mixture was about 8×10^5 Pa (8 atm). The mixture beam passed through a 6 mm diameter channel constructed of a pair of electrodes separated by 2 mm, to which a pulsed DC voltage of about 1500 V was applied to induce a discharge to generate the desired short-lived species. The electrodes are electrically isolated from the solenoid valve

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and from each other with insulating spacers. Three mutually perpendicular Helmholtz coils were set around the spectrometer to apply the magnetic field for checking for paramagnetic behavior of lines. All the measurements were carried out with a repetition rate at 5 Hz. The precursor molecule, carbon suboxide, was synthesized by dehydration of malonic acid with phosphorous pentoxide and purified by repeated distillations under reduced pressure.²⁶

Results

Microwave Spectra. A spectral survey was initiated by searching for the $J = 7-6$ transition of C_5O in the 18.8-19.4 GHz region. Several of the observed lines were assigned to the $J = 2-1$ transitions of C_3O for normal and ^{13}C isotopomers already reported,¹⁴ and the discharge condition was optimized by monitoring a ^{13}C isotopomer line of C_3O . Many new lines not assignable to C_3O were observed. Each observed line was checked to make sure that it disappeared without the discharge. Several of the observed lines were broadened or split by an external magnetic field, indicating the molecular species were in a paramagnetic open-shell ground state. Thus molecules in the singlet electronic state were easily distinguished from those in the multiplet states by their diamagnetic behavior. Transitions of C_5O were first assigned based on the rotational constant and relative intensity among the observed lines, and later the assignment was confirmed by observing other isotopomers.

The transition frequencies of singly substituted isotopomers with ^{13}C or ^{18}O were predicted from the observed rotational constant for the normal species and shifts of the rotational constant due to the substitutions, which were estimated by referring to the geometry of an *ab initio* MO calculation.¹⁶ All the measurements was made in natural abundance. The low J transitions were observed within a few MHz from the predicted frequencies. Their diamagnetic behavior was also checked. In order to achieve a reasonable signal-to-noise-ratio we had to accumulate up to 1000 shots for ^{13}C species and 8000 shots for ^{18}O species as shown in Figure 1. The relative intensities of the observed lines for the isotopomers were well consistent with the natural abundances for ^{13}C (1.1%) and ^{18}O (0.2%). The observed transition frequencies of C_5O for the parent species and of all the six singly substituted isotopomers are listed in Table 1, together with the derived rotational and centrifugal distortion constants. The centrifugal distortion constants for the isotopomers were fixed at the value of the parent species in the least squares fits, because the number of the observed transition frequencies for the isotopomers was limited.

Although the lines of C_5O were weaker than those of C_3O by two orders of magnitude, comparable to the ^{13}C isotopomers of C_3O , they were observed with a fairly good signal-to-noise ratio even with a moderate data acquisition (100 shots, 20 s). This fact encouraged us to identify the next longer member of the singlet C_nO series, *i.e.*, C_7O . The rotational constant of C_7O was predicted by an extrapolation of those for CO, C_3O , and C_5O as was done by Oka for astronomical search for longer members of cyanopolyynes.²⁷ This prediction was fairly reliable as we could find the corresponding transitions with only a 0.1% deviation. The intensity of the C_7O spectrum was smaller by a factor of 5 than that of C_5O . The observed transition frequencies for C_7O are listed in Table 2. The spectrum of C_9O was also assigned in a similar way. For this species, the predicted rotational constant differs by only 0.03% from the observed one. The intensity of the C_9O spectrum was again smaller by a factor of 5 than that of C_7O . The observed transition frequencies are also listed in Table 2. The rotational and centrifugal distortion

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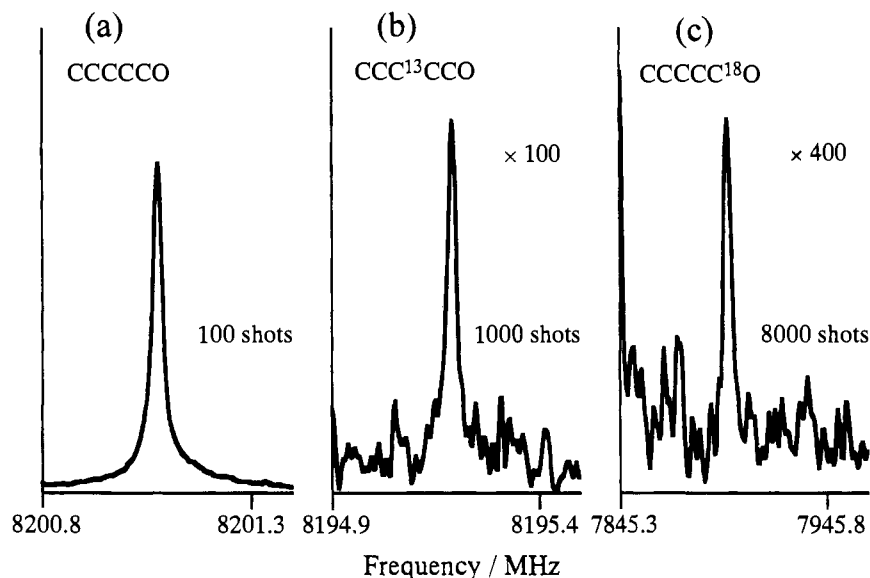


Figure 1. Observed rotational spectra of C₅O for normal, ¹³C and ¹⁸O isotope species. (a) The $J = 3-2$ transition of normal C₅O at 8201.078 MHz; (b) 3-2 of CCC¹³CO at 8195.192 MHz; (c) 3-2 of CCCCC¹⁸O at 7845.556 MHz. The spectra were obtained after 100, 1000, and 8000 shots accumulations at a repetition rate of 5 Hz, respectively. The vertical scales for CCC¹³CO and CCCCC¹⁸O are factored by 100 and 400, respectively, relative to that for the normal C₅O.

Table 1. Microwave Transition Frequencies and Spectroscopic Constants of C₅O^a

$J'' - J'$	C-C-C-C-O		¹³ C-C-C-C-O		C- ¹³ C-C-C-O		C-C- ¹³ C-C-O	
	obs/MHz	o-c/kHz	obs/MHz	o-c/kHz	obs/MHz	o-c/kHz	obs/MHz	o-c/kHz
2-1	5467.388	1						
3-2	8201.078	-1	7963.349	1	8108.474	0	8188.069	-1
4-3	10934.768	0	10617.794	1	10811.298	3	10917.422	-1
5-4	13668.454	0	13272.234	-1	13514.111	-2	13646.776	2
6-5	16402.136	1						
7-6	19135.810	-1						
8-7	21869.482	0						
9-8	24603.146	0						
B_0 /MHz	1366.84709(6)		1327.22525(9)		1351.41303(16)		1364.67909(15)	
D_0 /kHz	0.03505(51)		0.03505(assumed)		0.03505(assumed)		0.03505(assumed)	
$J'' - J'$	C-C-C- ¹³ C-C-O		C-C-C-C- ¹³ C-O		C-C-C-C-C- ¹⁸ O			
	obs/MHz	o-c/kHz	obs/MHz	o-c/kHz	obs/MHz	o-c/kHz	obs/MHz	o-c/kHz
3-2	8195.192	-3	8132.609	-1	7845.556	-6		
4-3	10926.925	3	10843.476	-1	10460.748	2		
5-4	13658.645	0	13554.340	1	13075.927	2		
B_0 /MHz	1365.86636(21)		1355.43566(10)		1307.59431(32)			
D_0 /kHz	0.03505(assumed)		0.03505(assumed)		0.03505(assumed)			

^a Error limits in parentheses are one standard deviation in the least squares fits and apply to the last significant figure quoted.

constants for C₇O and C₉O have been determined by the least square fits to the observed transition frequencies as listed in Table 3, together with those of shorter member of the series. In order to examine the variation of the rotational and centrifugal distortion constants for C_nO ($n = \text{odd}$), the values of $1/n\sqrt{B}$ and D/nB^3 were calculated from the determined rotational and centrifugal distortion constants and are plotted against n . The values $1/n\sqrt{B}$ represent the square root of the moment of inertia per bond and are expected to change smoothly with n unless a drastic change in the geometry occurs. On the other hand, Nielsen²⁸ has shown for a triatomic linear molecule that

$$\frac{D}{B^3} = 4 \left(\frac{\xi_{21}^2}{\omega_3^2} + \frac{\xi_{23}^2}{\omega_1^2} \right)$$

where ω_1 and ω_3 are the bond-stretching frequencies, and ξ_{21}

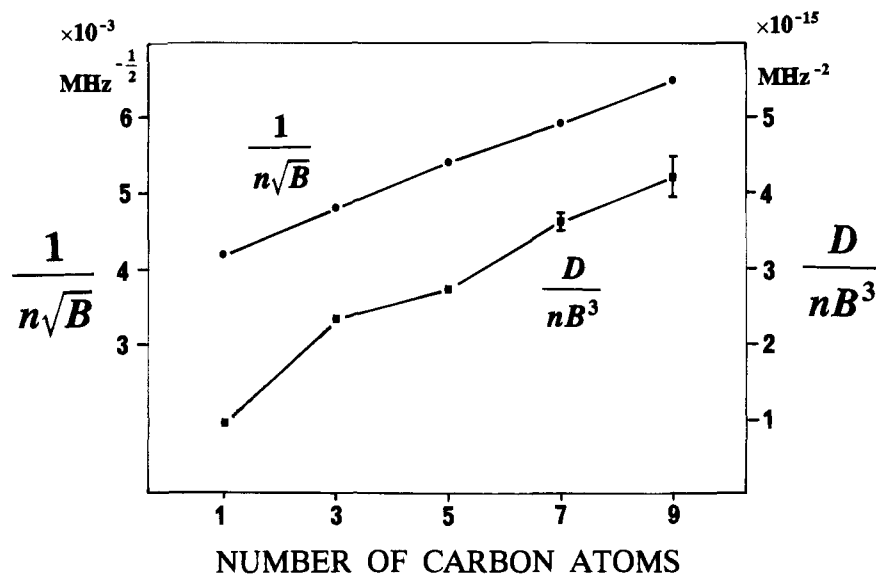
Table 2. Microwave Transition Frequencies of C₇O and C₉O

$J'' - J'$	C ₇ O		C ₉ O	
	obs/MHz	o-c/kHz	obs/MHz	o-c/kHz
4-3	4583.527	1		
5-4	5729.407	1		
6-5	6875.289	0		
7-6	8021.168	-1		
8-7	9167.046	-1	4699.776	0
9-8	10312.924	-2	5287.247	-1
10-9	11458.802	0	5874.717	-1
11-10	12604.680	2	6462.192	2
12-11	13750.553	0	7049.661	1
13-12	14896.428	2	7637.129	-2
14-13	16042.296	-1	8224.600	-1
15-14	17188.170	2	8812.072	2
16-15	18334.033	-3	9399.539	-1
17-16			9987.008	-1
18-17			10574.479	2
19-18			11161.947	1
20-19			11749.412	-2

Table 3. Spectroscopic constants of C₇O and C₉O and Related Molecules^a

	CO ^b	C ₃ O ^c	C ₅ O	C ₇ O	C ₉ O
<i>B</i> ₀ /MHz	57635.9660(17)	4810.88638(20)	1366.84709(6)	572.94105(5)	293.73611(4)
<i>D</i> ₀ /kHz	183.5053(29)	0.77833(30)	0.03505(51)	0.00475(15)	0.000956(66)

^a Figures in parentheses are one standard deviation in unit of the last significant figure. ^b Reference 29. ^c Reference 14.

**Figure 2.** Variations of the modified rotational constants $1/n\sqrt{B}$ and the modified centrifugal distortion constants D/nB^3 of C_{*n*}O against the number of carbon atoms.**Table 4.** Cartesian Coordinates of the Atoms in C₅O Obtained by Kratichman's Method (in Å)

atom ^a	C ₍₅₎	C ₍₄₎	C ₍₃₎	C ₍₂₎	C ₍₁₎	O
coordinate ^b	-3.3386(4)	-2.0650(6)	-0.7703(15)	0.5178(23) ^c	1.7730(7)	2.9292(4)

^a The atomic numbering is C₍₅₎-C₍₄₎-C₍₃₎-C₍₂₎-C₍₁₎-O. ^b Figures in parentheses are the errors determined by $\delta r_s \sim 0.0012/r_s$; ref 32. ^c The z-coordinate of C₍₂₎ was determined to be 0.4965(38) Å by the first moment condition $\sum_i m_i z_i = 0$.

and ζ_{23} are Coriolis coupling constants. For a linear XY₂ type molecule,²⁸ this equation is reduced to $D/B^3 = 4/\omega_1^2$. This simplified relation is the same that for a diatomic molecule. The stretching vibrational frequency is, however, often higher for a diatomic molecule than that for a linear polyatomic molecule, and D/nB^3 gives more constant value than D/B^3 . We have, therefore, attempted to apply this relation for the C_{*n*}O molecules with *n* more than 2. The results are plotted in Figure 2.

***r*_s Structure of C₅O.** All the spectroscopic constants observed for C₅O was consistent with those of a linear molecule; therefore, we have treated C₅O as a linear molecule for the structural determination. Having determined the rotational constants of six singly substituted isotopomers, substituting each nucleus in turn, we are able to determine the complete substitution structure of C₅O by using Kratichman's equations.^{30,31} The derived substitution coordinates are given in Table 4. Although several permutations of line assignments are possible, only those given in Table 4 are close to the predictions and yield a sensible set of bond lengths. The errors are calculated by using Costain's approximation,³² viz. $\delta r_s \sim 0.0012/r_s$. All the nuclei are over 0.5 Å away from the center of mass. All the coordinates should therefore be reliably determined. However, the center of mass condition, $\sum_i m_i z_i$, is not fulfilled exactly. The discrepancy of 0.249 uÅ is larger

than anticipated for such a favorable case. In the isoelectronic molecule cyanobutadiyne,¹ where the distance of all the nuclei to the center of mass are also more than 0.5 Å, the corresponding value is 0.042 uÅ. Such a situation has also been reported for C₃O, where the discrepancy was 0.169 uÅ,¹⁵ in contrast to the case of a isoelectronic molecule, cyanoacetylene, 0.018 uÅ.³¹ The substitution structure is given in Table 5, where the numbering of the atoms is C₍₅₎-C₍₄₎-C₍₃₎-C₍₂₎-C₍₁₎-O.

Discussion

As Figure 2 shows, the values $1/n\sqrt{B}$ and D/nB^3 increase almost monotonically with *n*, even though slight zig-zag variation is seen in D/nB^3 . There seems no special irregularity in the variation of the rotational and centrifugal distortion constants. Therefore, no drastic change in the linear geometry of C₅O, C₇O, and C₉O seems to be occurring.

Molecular Structure of C₅O. Since no experimental work has been reported on the structure of C₅O previously, it is compared with a result of an *ab initio* MO calculation.¹⁶ The bond lengths in the singlet electronic state with linear geometry are given in Table 5, which was obtained with MP3/D95** basis sets and gives the best agreement with the observation. These calculated bond lengths constitute the alternating short and long bonds, whilst the bonds are almost uniform length in the triplet electronic state.¹⁶ The theoretically calculated bond lengths agree well with those of the observed ones for $r(C_{(5)}-C_{(4)})$, $r(C_{(4)}-C_{(3)})$, and $r(C_{(1)}-O)$. Calculated $r(C_{(3)}-C_{(2)})$ and $r(C_{(2)}-C_{(1)})$ are, however, longer and shorter than the observed ones by 0.03 Å, respectively. That is, both structures agree quite well if the C₍₂₎ atom in the observed structure is shifted

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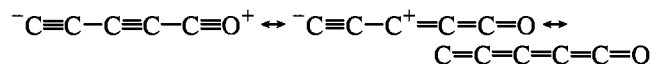
Table 5. Comparison of the Observed and the Calculated Bond Lengths of C₅O and Those of the Related Molecules (in Å)

C ₅ O	r(C ₅ -C ₄)	r(C ₄ -C ₃)	r(C ₃ -C ₂)	r(C ₂ -C ₁)	r(C ₁ -O)	ref
observed	1.2736(10)	1.2947(21)	1.2881(38) ^a	1.2552(30) ^a	1.1562(11)	b
<i>ab initio</i>	1.2779	1.2951	1.2580	1.2824	1.1576	c
Bond Lengths						
	C ₍₆₎ <u>1.2736</u> C ₍₄₎	<u>1.2947</u> C ₍₃₎	<u>1.2881</u> C ₍₂₎	<u>1.2552</u> C ₍₁₎	<u>1.1562</u> O	b
		C ₍₃₎ <u>1.254</u> C ₍₂₎	<u>1.306</u> C ₍₁₎	<u>1.150</u> O		d
				<u>1.12822</u> O		e
	HC ₍₅₎ <u>1.2087</u> C ₍₄₎	<u>1.3623</u> C ₍₃₎	<u>1.2223</u> C ₍₂₎	<u>1.3636</u> C ₍₁₎	<u>1.1606</u> N	f
		<u>1.2825</u> S	<u>1.2540</u> C ₍₃₎	<u>1.2696</u> C ₍₂₎	<u>1.1343</u> O	g

^a $r(C_3-C_2) = 1.2668(53)$ Å and $r(C_2-C_1) = 1.2765(45)$ Å were obtained from $z(C_2) = 0.4965(38)$ Å, which was determined by the first moment condition. ^b This work. ^c *Ab initio* MO calculation with MP3/D95** basis sets: ref 16. ^d Reference 14. ^e Reference 2. ^f Reference 1. ^g Reference 34.

away from the oxygen by 0.03 Å. Since the substitution coordinate of the C₍₂₎ atom was solely determined by the rotational constant of the CCC¹³CCO species, this shift of 0.03 Å is accomplished with an increase of *B* by 0.1 MHz. Therefore, we had made sure that there was no other line around the predicted transition frequencies with the rotational constant (*B* + 0.1) MHz.

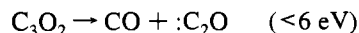
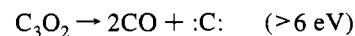
Carbon monoxide, the simplest of the C_{*n*}O series, consists of a triple bond judging from its bond energy, bond length, and force constant.³³ The small dipole moment of CO, $\mu = 0.112D$,³ with the negative carbon and the positive oxygen⁴ implies the migration of the lone pair electrons of the oxygen into the bond. The canonical structure of CO may be expressed as $^-C\equiv O^+$. By simply extending this canonical structure, the linear C₅O molecule in a singlet state may be written as $^-C\equiv C-C\equiv C-C\equiv O^+$. Polyene-type structures like $^-C\equiv C-(C\equiv C)_n-C\equiv O^+$, however, should not contribute much for the longer chains, because of the large charge separation implied by the structure. Cyanobutyne H-C≡C-C≡C-C≡N is isoelectronic with C₅O and gives an interesting comparison on molecular structure. The HC₅N molecule consists of alternating short triple bonds and long single bonds as shown in Table 5. The differences between the longest and the shortest C-C bond lengths in C₅O and HC₅N¹ are 0.0395 and 0.1549 Å, respectively. The π -electron delocalization effects, which shorten the single bonds and lengthen the triple bonds, seem much higher in C₅O than in HC₅N. The C₅O molecule has even more uniform CC bond distances than C₃O, as shown in Table 5. The CO bond lengths, 1.12822, 1.150, and 1.1562 Å in CO, C₃O, and C₅O, respectively, also shows the similar tendency. The observed $r(C_3-C_2) = 1.2881$ Å, $r(C_2-C_1) = 1.2552$ Å, and $r(C_1-O) = 1.1562$ Å in C₅O are not very different from 1.2540, 1.2696, and 1.1343 Å in S=C₃=C₂=C₁=O,³⁴ respectively. Although the bonds in C₅O are close to the cumulene-type double bonds rather than polyene-type, the observed irregularity in C₅O such as adjacent long bonds $r(C_4-C_3)$ and $r(C_3-C_2)$ and the adjacent short bonds $r(C_2-C_1)$ and $r(C_1-O)$ cannot be explained by the simple π -electron delocalization effects which make the polyene-type bonds, $^-C\equiv C-C\equiv C-C\equiv O^+$, into the cumulene-type bonds C=C=C=C=C=O. Structures which lengthen the $r(C_3-C_2)$ bond and shorten the $r(C_2-C_1)$ such as $^-C\equiv C-C^+=C=C=O$ need to be taken into account to explain the observed molecular structure. Accordingly, the observed bond lengths of C₅O cannot be expressed by a single canonical structure but should be attributed to resonance among several structures



In the above result for the *r_s* structure of C₅O, we have pointed out that the center of mass condition had not been fulfilled exactly but had a rather large discrepancy of 0.249 uÅ. We have suspected that the rotational constants especially for the ¹³C₍₂₎ species suffered from a small perturbation. We have, therefore, determined the *z*-coordinate of C₍₂₎ by the first moment condition $\sum_i m_i z_i = 0$. We got the result $z(C_2) = 0.4965(38)$ Å, leading to $r(C_2-C_3) = 1.2668(53)$ Å and $r(C_1-C_2) = 1.2765(45)$ Å, which then gave good agreement with the *ab initio* calculation of $r(C_2-C_3) = 1.2580$ Å and $r(C_1-C_2) = 1.2824$ Å, respectively. In this case, the experiment gives good agreement for all bond lengths with the *ab initio* calculation.

Structures of C₇O and C₉O. No experimental evidence suggests nonlinearity of the C₇O and C₉O molecules. The structures of C₇O and C₉O were calculated with the assumption that the partial structures of the C₍₅₎-C₍₄₎-C₍₃₎-C₍₂₎-C₍₁₎-O groups in C₍₇₎-C₍₆₎-C₍₅₎-C₍₄₎-C₍₃₎-C₍₂₎-C₍₁₎-O and C₍₉₎-C₍₈₎-C₍₇₎-C₍₆₎-C₍₅₎-C₍₄₎-C₍₃₎-C₍₂₎-C₍₁₎-O were the same that in the C₅O molecule. The averaged bond lengths in the rest of the C-C bonds in C₇O and C₉O were determined to be 1.270 and 1.274 Å, respectively, from the observed rotational constants. As discussed above for C₅O, the bonds in C_{*n*}O become more and more uniform cumulene-type with increasing *n*. Therefore, the CC bonds in C₉O and C₇O should have more uniform lengths than those in C₅O, and they seem to converge to a constant length.²⁴

Formation Mechanism of the Long Carbon-Chain Molecules C_{*n*}O. The discharge products contained many long carbon-chain molecules. These long-chain molecules could not be produced by a single step reaction from carbon suboxide but require several steps of reactions. The primary process of the discharge decomposition of carbon suboxide should be³⁵



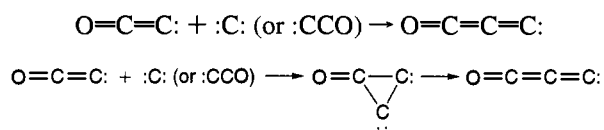
The produced :C: then reacted with other C_{*n*}O and produced longer carbon chains by either addition to the end carbon or

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insertion to any double bonds as follows:²²



The $:\text{C}=\text{C}=\text{O}$ radical also seems to be involved in the same process by an addition followed by loss of carbon monoxide. The fact that transitions of C_2O have been found to be less intense than those of C_3O in the present experiment seems to support these processes.²⁴ This kind of reaction had already been applied to the preparation for microwave measurements

of allene derivatives such as $\text{CHF}=\text{C}=\text{CH}_2$,²³ $\text{CF}_2=\text{C}=\text{HF}$,³⁶ $\text{CH}_3\text{CH}=\text{C}=\text{CH}_2$,³⁷ and $\text{CFCl}=\text{C}=\text{CH}_2$,³⁸ by photochemical reaction of C_3O_2 with ethylene compounds.

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