

Rotational spectrum and structure of the HCN-(CO₂)₃ tetramer

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Microwave rotational transitions have been observed for HCN-(CO₂)₃, DCN-(CO₂)₃, H¹³CN-(CO₂)₃, HC¹⁵N-(CO₂)₃, HCN-(¹³CO₂)₃, HCN-(¹⁸OCO)(CO₂)₂, and HCN-(CO₂)(C¹⁸O₂)₂ with the pulsed Fourier transform, Flygare/Balle Mark II spectrometer. A symmetric top spectrum was observed for the parent isotopic species with rotational constants of $B_0 = 861.6392(1)$ MHz, $D_J = 0.681(5)$ kHz, and $D_{JK} = 0.821(12)$ kHz. The results for isotopic substitution indicate a zero-point, vibrationally averaged geometry having the C_3 symmetry of a cyclic (CO₂)₃ structure with the HCN along the symmetry axis and the N end closest to the (CO₂)₃. The C_3 symmetry is confirmed by the observation of states limited to $K = \pm 3n$, with $n = 0, 1, 2, \dots$, as predicted for threefold symmetry generated by bosons only. The (CO₂)₃ has a pinwheel configuration, as in the free trimer, and the three carbons lie in a plane $R = 2.758$ Å below the center of mass (c.m.) of the HCN. The C-C distance in this subunit is 3.797 Å which is 0.241 Å shorter than that found in the free (CO₂)₃ trimer. The individual CO₂'s in the (CO₂)₃ pinwheel are rotated out of the C-C-C plane by $\gamma = -36.9^\circ$, as determined from an inertial analysis, with the inner oxygens rotated away from the HCN. The HCN has an average torsional angle of 10.3°, as determined by isotopic substitution, and an observed χ_{cc} value of -3.891 MHz for the ¹⁴N. The c.m.(HCN) to C distance is 3.525 Å, compared to 3.592 Å in the HCN-CO₂ T-shaped dimer. The isotopic substitution by ¹⁸O perturbs the structure of the symmetric top clusters by a remarkable amount, decreasing γ to -28.9° and increasing R and R_{CC} to 2.797 and 3.814 Å, respectively. In the ¹⁸O substituted species, the CO₂'s are rotated in the C-C-C plane from C_{3v} symmetry by the pinwheel angle $\beta = \sim 32.5^\circ$.

INTRODUCTION

Carbon dioxide is nonpolar but has a large electric quadrupole moment. In it the oxygen atoms are negatively charged and the carbon is strongly positive. This provides two types of attractive sites to form structurally diverse, weakly bonded dimers or clusters with other quadrupolar or polar molecules. The linear, highly polar HCN molecule also has multiple attractive sites so one might expect the HCN/CO₂ clusters to be especially rich in variety, a view supported by our current work.

The first HCN/CO₂ species to be found was characterized in the ground vibronic state by molecular beam electric resonance techniques.¹ It is the T-shaped HCN-CO₂ (Fig. 1) in which the negative N is attracted to the positive C of the CO₂. More recently the linear OCO-HCN dimer was found by our group,² using a pulsed nozzle, Fourier transform microwave spectrometer.³ In the linear form, the H of the HCN is hydrogen bonded to one of the oxygens. Isomer relaxation and its strong dependence on the carrier gas for the pulsed nozzle indicate that the linear isomer is considerably less stable than the T-shaped form.⁴

Two nonpolar homoclusters of CO₂ have also been studied, both by high resolution, far infrared laser spectroscopy of pulsed jets.⁵ A dimer was found with a slipped parallel, planar geometry⁶ and a trimer having a planar, pinwheel structure with C_{3h} symmetry.⁷ Both are inaccessible to rotational spectroscopy; however, we have studied the ground vibronic state of the clusters formed by the addition of an HCN to each of these species. In both heteroclusters, the

(CO₂)_n structure is perturbed substantially by its interactions with the HCN. The findings for the HCN-(CO₂)₂ trimer will be reported separately.⁸ Here we consider the HCN-(CO₂)₃ tetramer.

The structure reported⁷ for the planar cyclic (CO₂)₃ trimer is shown in Fig. 1. If one neglects bending amplitudes of the CO₂'s, two parameters are needed to describe the geometry of the trimer, the carbon-carbon distance R_{CC} and the pinwheel angle β . The latter is the angle by which each CO₂ is rotated in the plane about its center of mass (c.m.) from C_{3v} symmetry. R_{CC} was found experimentally to be 4.0382(3) Å. A theoretical value of 43° was determined for β by placing the known electrical quadrupole moment of CO₂ on each carbon and minimizing the electrostatic interaction energy as a function of β .

We have found that HCN is attracted to the (CO₂)₃ trimer along its threefold axis, forming a symmetric top (Fig. 2) with the nitrogen end closest to the carbons as in the T-shaped HCN-CO₂ dimer. Several isotopic species of HCN-(CO₂)₃ were examined to assess the interactions between HCN and the (CO₂)₃. Among the most notable findings are contraction of the cyclic structure and rotation of the individual CO₂'s out of the carbon plane by the repulsion between the inner oxygens and the nitrogen. Also, ¹⁸O substitution perturbs the structure to an unusual degree.

EXPERIMENTAL

The microwave spectra of HCN-(CO₂)₃, DCN-(CO₂)₃, H¹³CN-(CO₂)₃, HC¹⁵N-(CO₂)₃, HCN-(¹³CO₂)₃, HCN-(¹⁸OCO)(CO₂)₂, and

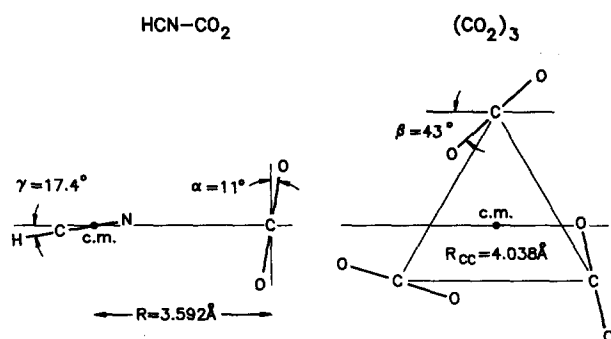


FIG. 1. The planar structures determined previously for the T-shaped HCN-CO₂ dimer and the cyclic (CO₂)₃ trimer. In the latter the oxygens consist of an inner and an outer set.

HCN-(CO₂)₂ (C¹⁸O₂)₂ were measured using the Balle-Flygare Mark II spectrometer.³ The parent species was found as a set of ¹⁴N hyperfine structure (hfs) centered at 5169.7 MHz while searching for rotational transitions of the HCN-(CO₂)₂ trimer.⁸ The signal was optimized at a higher concentration of CO₂ than required for transitions of the trimer, and the species was identified as described in the next section. The carrier gas was neon "first run" (Airco), a 70/30 mix of Ne and He, which we refer to here as Ne. The concentrations of HCN (Fumico) and CO₂ (Linde) at the nozzle were 0.1% and 2%, respectively, after coexpansion in 98% Ne. The backing pressure was 1.5 atm and the nozzle diameter was 1 mm.

The S/N ratio for a single free induction decay (FID) of the $J = 2 \rightarrow 3$ transition of HC¹⁵N-(CO₂)₃ (no hfs) in Ne is about 20:1. It was a factor of 10 worse when Ar (Linde) was used as the carrier gas, while use of pure He gave signals approximately as strong as Ne. Intensity comparisons indicate the concentration of the HCN-(CO₂)₃ tetramer to be roughly a factor of 5 to 10 smaller than that of the HCN-(CO₂)₂ trimer.

The isotopic derivatives HC¹⁵N and H¹³CN were prepared by reacting orthophosphoric acid with KC¹⁵N and K¹³CN (Cambridge Isotope Laboratories), respectively;

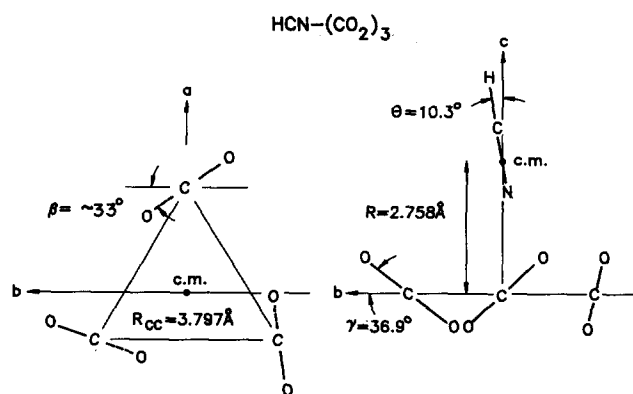


FIG. 2. Planar projections of the symmetric-top structure determined in this study for the HCN-(CO₂)₃ cluster. The pinwheel angle β is accessible only for the ¹⁸O species, in which it was found to be 32.5°.

and DCN from deuterated orthophosphoric acid and KCN. The fully labeled ¹³CO₂ and CO₂ with 50% ¹⁸O at random was purchased from Cambridge Isotopes. Also, CO₂ labeled 95% with ¹⁸O was obtained from Isotec.

RESULTS AND ANALYSIS

Identification, hfs, and rotational constants

The hfs associated with the transition at 5169.7 MHz was indicative of a single ¹⁴N nucleus with isotropic vibrational averaging of the HCN about the dipolar axis of the species. The splittings showed it to be a $J = 2 \rightarrow 3$, $K = 0$ transition, and the hfs given in Table I was fitted to the usual Hamiltonian employed for a symmetric top or linear molecule with a single quadrupole interaction, χ_{gg} along the symmetry axis,⁹

$$E(Q) = -\chi_{gg} Y(J, I, F), \quad (1)$$

where I is the nuclear spin and $F = J + I$. A more complex set of hfs was then found at $(4/3) \times 5169.7$ MHz for $J = 3 \rightarrow 4$, confirming a symmetric top species with $B_0 = 861.6$ MHz. Analysis showed the hfs to arise from $K = 0$ and ± 3 transitions (Table I). The absence of $K = \pm 1$ and ± 2 transitions proves the symmetry axis to be threefold, with only spin-zero nuclei off-axis.⁹ This is consistent with the HCN-(CO₂)₃ structure given in Fig. 2.

The $J = 4 \rightarrow 5$ transitions of the main (parent) isotopic species were also measured. The line centers (Table II) and χ_{cc} (Table I) were determined for all of the transitions by fitting the hfs. The line centers were then fitted to the semirigid Hamiltonian which for $J \rightarrow J + 1$ gives the expression⁹

$$\Delta E(J) = 2B_0(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2, \quad (2)$$

where B_0 is the ground state rotational constant and D_J and D_{JK} are the usual centrifugal distortion constants for a symmetric top.

TABLE I. Representative hyperfine structure for HCN-(CO₂)₃ and the values of χ_{cc} (¹⁴N) determined from it^a for the transitions observed.

Transition $J \rightarrow J'$	Component K	Obs. $F \rightarrow F'$ (MHz)	Diff. (kHz)	χ_{cc} (MHz)	
2→3	0	2→1	5168.5110	-1.0	-3.891
		3→3	5169.5700	1.9	
		1→1	5169.7625	-0.1	
		2→2	5169.8085	-0.4	
		1→3	5171.5130	-0.5	
3→4	0	2→1	6891.6410	-0.8	-3.890
		3→3	6892.8545	-0.6	
		1→1	6892.9314	-7.1	
		2→2	6892.9772	9.2	
		1→3	6894.6049	-0.8	
		1→3	6891.4258	1.0	
3	1→1	6892.0047	-2.0		
	2→2	6893.1623	2.3		
	3→3	6893.6054	-1.3		
4→5	0	-3.880	
	3	-3.876	

^aThe standard deviation for χ_{cc} is about 3 kHz.

TABLE II. Line centers determined for transitions *o*... symmetric top isotopic species of HCN-(CO₂)₃.^a

<i>J</i> → <i>J'</i>	<i>K</i>	HCN-(CO ₂) ₃	DCN-(CO ₂) ₃ ^b	H ¹³ CN-(CO ₂) ₃	HC ¹⁵ N(CO ₂) ₃	HCN-(¹³ CO ₂) ₃
2→3	0	5169.7626		5099.8379	5144.5330	5101.2185
	1	5101.2177
3→4	0	6892.9385		6799.7061	6859.3021	6801.5510
	1	6801.5486
	3	6892.8794		6799.6323	6859.2452	6801.4948
4→5	0	8616.0513	8 398.47	8499.5313	8573.9962	
	3	8615.9780		8499.4451	8573.9402	
5→6	0		10 078.14			
6→7	0		11 757.77			

^aDots indicate symmetry forbidden transitions searched for and not found.

^bApproximate line centers because of complex hfs.

With the B_0 for the parent species in hand from this fit and neglecting oscillation of the HCN, we used the following expression to estimate the B_0 's for the other four isotopic symmetric tops,¹⁰

$$I_b[\text{HCN}-(\text{CO}_2)_3] = I_0(\text{HCN}) + I_b(\text{CO}_2)_3 + \mu R^2, \quad (3)$$

where μ is the pseudodiatomic reduced mass of the cluster and R is the HCN center of mass (c.m.) to (CO₂)₃ c.m. distance. By assuming that in the cluster $I_0(\text{HCN})$ and $I_b(\text{CO}_2)_3$ are unchanged from their free state values (Table III),^{7,11,12} R was found to be approximately 2.601 Å. In turn, it was used with the $I_0(\text{HCN})$ and $I_b(\text{CO}_2)_3$ values for isotopically substituted species to predict B_0 's for the corresponding cluster. The transitions found in this manner are listed in Table II; they led to the isotopic rotational constants in Table IV.

A limited amount of structural information is obtainable from isotopic species which are symmetric tops. In particular the pinwheel angle β (Fig. 2) cannot be determined from the B_0 's for the HCN-(CO₂)₃ clusters with C_3 symmetry. Partial ¹⁸O substitution is required to accomplish this. But the variety of isotopic clusters with different numbers and locations of ¹⁸O is relatively large, making difficult the assignment of transitions. Therefore, the structural analysis was carried out as far as it could be without ¹⁸O data and the results were then used to predict rotational constants and transitions for the more probable ¹⁸O species. Even this approach met with difficulties because of changes in cluster

structure by ¹⁸O substitution. However, seven transitions in Table V were assigned to the mono ¹⁸O cluster in which one of the outer oxygens is substituted, and five to the HCN-(CO₂)(C¹⁸O₂)₂ cluster. These transitions were fitted by a computer program with the rotational constants A , B , and C and the symmetric top distortion constants D_J , D_{JK} , and D_K as adjustable parameters¹³ for the mono-¹⁸O species and only A , B , and C for the tetra-¹⁸O species. The results are included in Table V.

Structural determination

Symmetry and substitution positions of the HCN atoms

The absence of $K = \pm 1$ and ± 2 transitions for the four symmetric tops isotopically substituted only in the HCN (Table II) confirms the C_3 symmetry of the cluster and shows that the HCN lies symmetrically along the three-fold axis.¹³ The results for ¹³C substitution in all three CO₂'s are consistent with this. These clusters have three spin-1/2 nuclei symmetrically off axis and therefore no K values are forbidden. In keeping with this we found $K = \pm 1$ components for the $J = 2 \rightarrow 3$ and $3 \rightarrow 4$ transitions (Table II). The hfs for the $K = \pm 1$ components has virtually the same line center as for $K = 0$. However, the $K = \pm 1$ hfs is more widely separated than that for $K = 0$. Therefore the two sets were readily resolved and assigned.

The orientation of the HCN, with the N closest to the (CO₂)₃ subunit, is visible in the B_0 's for its four isotopic species which increase in the sequence DCN, H¹³CN, HC¹⁵N, and HCN. A more quantitative approach is to determine the substitution positions of the atoms in the

TABLE III. Spectroscopic and structural properties^a of free HCN, CO₂, and (CO₂)₃.

HCN ^b		CO ₂ ^c		(CO ₂) ₃ ^c	
Property	Value	Property	Value	Property	Value
B_0	44 315.975 7	B_0	11 698.2	B	1193.4380
$r_s(\text{H-C})$	1.063 17	$r_0(\text{C=O})$	1.162 08	C	596.7190
$r_s(\text{C-N})$	1.155 12			R_{CC}	4.0382
$\chi_0(^{14}\text{N})$	-4.707 9				

^aSpectroscopic properties are in MHz and distances in Å.

^bReferences 11 and 12.

^cReference 7.

TABLE IV. Rotational constants^a determined for the symmetric top species of HCN-(CO₂)₃.

	HCN-(CO ₂) ₃	DCN-(CO ₂) ₃ ^b	H ¹³ CN-(CO ₂) ₃	HC ¹⁵ N-(CO ₂) ₃	HCN-(¹³ CO ₂) ₃
<i>B</i> ₀ (MHz)	861.6392(2)	839.71	849.9824(14)	857.4345(9)	850.2154(8)
<i>D</i> _{<i>J</i>} (kHz)	0.681(5)	0.60	0.584(33)	0.692(23)	0.666(30)
<i>D</i> _{<i>JK</i>} (kHz)	0.82(1)		1.01(8)	0.69(6)	0.80(5)

^aNumbers in parentheses are the standard deviation in the last digit(s).

^bBased on three *K* = 0 approximate line centers and an assumed *D*_{*J*} of 0.60 kHz.

HCN by using the Kraitchman equation for single substitution on the axis of a linear or symmetric top molecule,⁹

$$I'_b = I_b + \mu_s c_i^2. \quad (4)$$

Here the prime indicates the substituted species, *I*_{*b*} is the moment of inertia of the parent species given by *I*_{*b*} × *B*₀ = 505 379.07 μÅ² MHz, μ_{*s*} is the reduced mass of the substitution, and *c*_{*i*} is the distance along the *c* axis of the substituted atom *i* from the c.m. of the parent molecule. The *c*_{*i*} values are averaged over the zero point vibrations, assumed to be unchanged by substitution. For HCN, the vibrations are largely the isotropic bending oscillations of the relatively rigid monomer about its c.m., and the positions are the projection of the atoms onto the *c* axis at the average displacement θ as seen in Figs. 1 and 2.

The atomic positions and effective bond distances were determined this way for HCN and the results are given in Table VI, confirming its orientation. The position of the hydrogen is not very accurate because of the large change in torsional oscillation caused by deuterium substitution. However, the C-N *r*_{*s*} distance of 1.1365 Å should be reliable.

Torsional amplitude and χ₀ of HCN

If the ¹⁴N quadrupole coupling constant in the free monomer χ₀^m did not change upon cluster formation, the projection operator

$$\chi_c^c = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \chi_0^m, \quad (5)$$

could be used to determine θ from χ_c^c, the experimentally determined projection of the quadrupole interaction constant along the cluster axis. However, incorporation of HCN in clusters has been found to change significantly the electric field gradient in it.¹⁴ In such cases the projection operator for the substitution C-N distance can be used^{14,15} to find θ:

$$r_c^c(\text{C-N}) = r_s^m(\text{C-N}) \langle \cos \theta \rangle, \quad (6)$$

where *r*_{*c*}^c(C-N) is the apparent distance in the cluster and *r*_{*s*}^m(C-N) is that in the free monomer. These quantities are 1.1365 and 1.155 12 Å, respectively (Tables III and VI), which give θ = 10.3°.

In contrast, Eq. (5) with the χ_c^c of -3.891 MHz found for the *J* = 2 → 3 transition, gives θ to be 19.9°, indicating that the magnitude of χ₀^m has been reduced appreciably in the cluster from its -4.7091 MHz value in the free monomer. By using the substitution value of θ in Eq. (5) we can determine χ₀^c, the quadrupole interaction constant for the rigid cluster. This turns out to be -4.087 MHz, a 13% reduction from the monomer.

Determination of *R*

The substitution positions of the ¹³C and ¹⁵N in the HCN enable us to find *R*, the HCN c.m. to (CO₂)₃ c.m. distance, by two different methods. We do not use the results for DCN in either case because deuterium substitution has a relatively large effect on the torsional amplitude of DCN. The simplest approach is based on the first moment condition. From the substitution positions of the C and N we find the position on the *c* axis of the HCN c.m. for the parent (normal) species with respect to the c.m. of the cluster. It is 2.2901 Å, using θ = 10.30°. In turn this requires the c.m. of

TABLE V. Line centers and rotational constants determined for two ¹⁸O substituted asymmetric tops.

Transition <i>J</i> _{<i>K_aK_c</i>} → <i>J</i> _{<i>K_aK_c</i>}	Observed (MHz)	Rotational constant	Determined value
HCN-(¹⁸ OCO)(CO ₂) ₂ ^a			
2 ₁₁ → 3 ₂₁	5066.4779	<i>A</i> (MHz)	861.626(2)
2 ₀₂ → 3 ₁₂	5091.1247	<i>B</i> (MHz)	838.367(3)
2 ₁₂ → 3 ₂₂	5099.8806	<i>C</i> (MHz)	668.420(28)
2 ₂₀ → 3 ₃₀	5108.6726	<i>D</i> _{<i>J</i>} (kHz)	0.47(16)
2 ₂₁ → 3 ₃₁	5136.1127	<i>D</i> _{<i>JK</i>} (kHz)	1.69(37)
3 ₃₀ → 4 ₄₀	6820.9236	<i>D</i> _{<i>K</i>} (kHz)	-1.60(24)
3 ₃₁ → 4 ₄₁	6850.3723		
HCN-(CO ₂)(C ¹⁸ O) ₂			
2 ₁₁ → 3 ₂₁	4904.0642	<i>A</i> (MHz)	835.639
2 ₀₂ → 3 ₁₂	4929.5302	<i>B</i> (MHz)	810.871
2 ₁₂ → 3 ₂₂	4939.5213	<i>C</i> (MHz)	642.984
2 ₂₀ → 3 ₃₀	4949.5280		
2 ₂₁ → 3 ₃₁	4978.2051		

^aWith the ¹⁸O in an outer position.

TABLE VI. Substitution atomic positions and derived structural parameters for the parent HCN-(CO₂)₃ cluster.

Atom or c.m.	Coord.	Position ^a	Parameter	Value
H	<i>c</i>	3.914 ^b	<i>r</i> (H-C) (Å)	1.074
C	<i>c</i>	2.8403	<i>r</i> (C-N) (Å)	1.1365
c.m.(HCN)	<i>c</i>	2.2901	θ (deg)	10.30
N	<i>c</i>	1.7038	<i>R</i> _{c.m.} (Å)	2.7588
c.m.(CO ₂) ₃	<i>c</i>	-0.4687 ^c	<i>R</i> _{CC} (Å)	3.7968
C	<i>a</i>	2.1921	γ (deg)	± 36.9

^aUnits are Å.

^bNot a reliable value.

^cFrom c.m.(HCN) and the first moment condition.

the (CO₂)₃ to be 0.4687 Å on the opposite side of the cluster's c.m. Their sum is $R = 2.7588$ Å.

The second approach is based on a pseudodiatom approximation for the moment of inertia about the b axis of a symmetric-top cluster. In the present case, we can write¹⁰

$$I_b(\text{cluster}) = I_b(\text{CO}_2)_3 + \frac{1}{2} \langle 1 + \cos^2 \theta \rangle I_0'(\text{HCN}) + \mu_c^i (R + \Delta_i)^2, \quad (7)$$

where μ_c is the reduced mass of the "diatomic" cluster, i designates the isotopic species of HCN, R is the c.m. to c.m. distance in the parent cluster HCN-(CO₂)₃, and Δ is the isotopic shift in the c.m. of HCN as projected on the c axis ($\Delta = 0, 0.019$ 83, and -0.020 73 Å for parent, ¹³C, and ¹⁵N substitution, respectively, using $\theta = 10.30^\circ$). Equation (7) assumes isotropic oscillation of the HCN about its c.m.

Isotopic substitution in the HCN end of the cluster will have at most a small effect on the moment of inertia for the (CO₂)₃ subunit, which we neglect. Accordingly we used Eq. (7) to fit the B_0 's observed for the HCN, H¹³CN, and HC¹⁵N species of the cluster (Table IV), with R and $I_b(\text{CO}_2)_3$ as adjustable parameters. This led to $R = 2.7543$ and $I_b(\text{CO}_2)_3 = 405.313 \mu\text{Å}^2$.

Determination of R_{CC}

The C-C distance in the (CO₂)₃ subunit (Figs. 1 and 2) may be determined from the B_0 values for the symmetric trisubstituted HCN-(¹³CO₂)₃ and the parent cluster by using Kraitchman's equations for off-axis multiple substitution retaining C_3 symmetry,⁹

$$\Delta I_a = \Delta I_b = \frac{3}{2} \Delta m a_i^2 + \mu_s c_i^2, \quad (8)$$

where ΔI_a and ΔI_b are the change in the moment of inertia due to the substitution, Δm is the change in mass for a single substitution, a_i is the distance of each substituted atom off the C_3 symmetry axis, c_i is the c coordinate of the substituted atom referred to the c.m. of the cluster, and $\mu_s = 3\Delta m M / (M + 3\Delta m)$ is the reduced mass of the substitution.

The symmetry of the CO₂ and (CO₂)₃ species requires that the carbons be coplanar with the c.m. of the (CO₂)₃. Therefore, for c_i we can use the value of -0.4687 Å determined in the preceding section for the c.m. (CO₂)₃ to c.m. cluster distance. Upon substitution of this and the other known quantities in Eq. (8) we find a_i to be 2.1921 Å, the C to c.m. (CO₂)₃ distance. By the geometry of the subunit this corresponds to a C-C distance R_{CC} of 3.7968 Å. The somewhat smaller value of 2.7543 Å obtained for R via Eq. (7) gives c_i to be -0.4680 Å, a_i 2.1924, and $R_{CC} = 3.7973$ Å.

This analysis not only assumes that ¹³C substitution does not affect the vibrational amplitudes of the (CO₂)₃ subunit but also it neglects those vibrations. The latter probably is an appreciable approximation in view of the 11° torsional amplitude estimated¹ for CO₂ in the T-shaped HCN-CO₂ dimer, a point considered in more detail later.

Nonplanarity of the (CO₂)₃ subunit

The threefold symmetry axis of the cluster limits the structural possibilities for the (CO₂)₃ subunit. If the latter

were planar as in the free trimer and rigid, an inertial analysis shows its moments would be given by

$$I_a = I_b = I_c/2 = 2m(\text{CO}_2)(R_{CC}/2)^2 + (3/2)I_0(\text{CO}_2). \quad (9)$$

Here $m(\text{CO}_2)$ is the mass of the CO₂ and $I_0(\text{CO}_2)$ is its moment of inertia.⁷ The pinwheel, in-plane rotational angle β of the individual CO₂'s does not affect the moments in the symmetric tops so there is only one adjustable parameter for a planar trimer, the C-C distance R_{CC} . Using for it the values determined in the preceding section, we calculate with Eq. (9) that $I_b(\text{CO}_2)_3$ should be $\sim 381.9 \mu\text{Å}^2$. However, this is much less than the value of $405.313 \mu\text{Å}^2$ found for it in the determination of R by fitting Eq. (7) to the experimental, isotopic B_0 's.

Therefore, the (CO₂)₃ subunit is nonplanar in the cluster. If one includes an out-of-plane rotation of each CO₂ about its c.m. by a vibrationally averaged γ , application of the parallel axis theorem¹⁶ and a bit of trigonometry lead to the following modification of Eq. (9):

$$I_a = I_b = 2m(\text{CO}_2)(R_{CC}/2)^2 + (3/2)I_0(\text{CO}_2)(1 + \sin^2 \gamma),$$

$$I_c = m(\text{CO}_2)R_{CC}^2 + 3I_0(\text{CO}_2)(1 - \sin^2 \gamma), \quad (10)$$

which is still independent of β . However, with γ as an additional adjustable parameter, we can now fit the experimental value of $405.313 \mu\text{Å}^2$ for $I_b(\text{CO}_2)_3$ in the cluster. Thereby the two values for R_{CC} found in the preceding section (3.7968 and 3.7973 Å) correspond to $\gamma = 36.97^\circ$ and 36.90° . A similar analysis of the B_0 found with HCN-(¹³CO₂)₃ gives $\gamma = 36.83^\circ$, for an average of 36.9° . The substitution positions and structural parameters obtained thus far are listed in Table VI. The pinwheel angle β and the direction of γ are still to be determined.

Inertial analysis of symmetric tops

A check on the substitution analysis was made by using a computer program to fit the B_0 's directly for the four symmetric tops, HCN-(CO₂)₃, H¹³CN-(CO₂)₃, HC¹⁵N-(CO₂)₃, and HCN-(¹³CO₂)₃ with R , R_{CC} , and γ as adjustable parameters. The torsional amplitude of the HCN was kept fixed at the same value 10.3° for all four isotopic species. The fit summarized in Table VII agrees reasonably well with the results of the substitution analysis (Table VI).

TABLE VII. A fit of the B_0 's for the isotopic symmetric tops with R , R_{CC} , and γ as adjustable parameters.

Species	B_0 Obs (MHz)	Obs - Calc kHz	Parameter	Value
HCN-(CO ₂) ₃	861.639	-1	$R_{c.m.}$ (Å)	2.7578(8)
H ¹³ CN-(CO ₂) ₃	849.982	-2	R_{CC} (Å)	3.8033(9)
HC ¹⁵ N-(CO ₂) ₃	857.435	3	γ (deg)	-35.5(2) ^a
HCN-(¹³ CO ₂) ₃	850.215	0		

^aThe negative sign is for the inner oxygen rotated away from the nitrogen.

TABLE VIII. Perturbation of the parent structure by ¹⁸O substitution. Rotational constants determined for the ¹⁸O substituted species compared with those predicted for the substituted species with the parent structure.^a

Rotational constant	HCN-(CO ₂) ₃ Parent	HCN-(¹⁸ OCO)(CO ₂) ₂ ^b		HCN-(CO ₂)(C ¹⁸ O ₂) ₂	
		Observed	Predicted	Observed	Predicted
<i>A</i> (MHz)	861.65 ^c	861.626	861.54	835.639	835.92
<i>B</i> (MHz)	861.65 ^c	838.367	837.36	810.871	809.33
<i>C</i> (MHz)	699.38 ^d	668.420	683.36	642.984	658.02

^aAs given in Table VII with inner oxygens rotated away from the N, and the pinwheel angle assumed to be 43°.

^bThis is for the ¹⁸O in the outer position.

^cObserved.

^dCalculated from the parent structure as in footnote a.

Effects of ¹⁸O substitution

In principle, the remaining angular aspects of the (CO₂)₃ subunit structure are readily obtainable by ¹⁸O substitution. However, unusual difficulties were encountered in finding and assigning transitions of ¹⁸O substituted species, in spite of having the ¹⁴N hfs as a guide. Rotational constants and transition frequencies were predicted for the various ¹⁸O species by using the values determined above for θ , R , R_{CC} , and γ with an assumed value of 43° for β . Also, a computational check was made on the sensitivity of the predicted rotational constants to the value of β , which was found to be only ~ 1 MHz/10°. However, the predicted rotational constants proved to be substantially in error.

Eventually two series of five lines were identified as the $K = 0$, ± 1 , and ± 2 components of the $J = 2 \rightarrow 3$ transitions of the near-symmetric tops HCN-(¹⁸OCO)(CO₂)₂ with the ¹⁸O in an outer position (Fig. 1), and HCN-(CO₂)(C¹⁸O₂)₂. These were fitted, and the rotational constants obtained for the mono-¹⁸O species were used to predict and readily find two of its $J = 3 \rightarrow 4$ transitions. The line centers and fitted rotational constants are summarized in Table V for the ¹⁸O species.

The rotational constants observed for the ¹⁸O substituted species are compared in Table VIII to the constants predicted for the two clusters if they had the symmetric top structure (Table VII) with the inner oxygens rotated away from the N and the pinwheel angle assumed to be 43°. The rotational constants are also given for the parent cluster as a base line. It is seen that the constants observed in the ¹⁸O species agree within about a MHz with the predictions for A and B , but those observed for C are 15 MHz smaller than predicted. None of the sets of constants predicted for the

numerous other ¹⁸O substituted species agree as well. Also, the A observed for the mono-¹⁸O species is close to that of the parent, as is expected for off-axis monosubstitution of a symmetric top.

Assuming the identity of the two ¹⁸O-substituted species to be as indicated, we fitted their rotational constants using the same procedure as in the B_0 analysis of the symmetric tops but with the pinwheel angle β included as an adjustable parameter. The best fit is given in Table IX. In it the initial value of γ was taken to be negative. A similar calculation with a positive initial value converged to a much poorer fit with $\gamma = +41(5)$ and an unreasonably short R , 2.55(11) Å.

The best fit gives a γ of $-28.9(11)^\circ$, significantly smaller than the 36.9° (or -35.5°) found for the symmetric tops. This decrease in γ is largely responsible for the small C in the ¹⁸O substituted species through the $(1 - \sin^2 \gamma)$ factor in Eq. (10). The decrease in $\sin^2 \gamma$ also causes half as large an increase in A and B , which is largely counteracted by an 0.04 Å increase in R , with some help from an 0.02 Å increase in R_{CC} . The fit also gives a value of 32.5° for the pinwheel angle β .

Support for the validity of this analysis is provided by using an isotopic substitution method on the rotational constants found for the mono-¹⁸O cluster. Ordinarily this method determines the location in the inertial frame of the isotopic mass change Δm , based on the assumption that the substitution does not affect the structure. We have just seen that ¹⁸O substitution changes materially the symmetric top structure.

By accident, however, the structural changes have little net effect on B_0 . The B_0 determined experimentally for the parent isotopic species is 861.64 MHz while that calculated

TABLE IX. A fit of the rotational constants for the ¹⁸O-substituted asymmetric tops with R , R_{CC} , γ , and β as adjustable parameters, compared with parameters from B_0 's of symmetric tops.

Species	Const.	Obs (MHz)	Obs-Calc (MHz)	Parameter	¹⁸ O species	Symmetric tops
Mono ¹⁸ O	<i>A</i>	861.626	-0.101	$R_{c.m.}$ (Å)	2.797(17)	2.758(1)
	<i>B</i>	838.367	0.092	R_{CC} (Å)	3.814(6)	3.803(1)
	<i>C</i>	668.420	-0.188	γ (deg)	-28.9(11)	-35.5(2)
Tetra ¹⁸ O	<i>A</i>	835.639	-0.019	β (deg)	32.5(10)	...
	<i>B</i>	810.871	0.036			
	<i>C</i>	642.984	0.191			

for HCN-(CO₂)₃ with the ¹⁸O structural parameters in Table IX is 861.76 MHz, a small difference compared to the changes in rotational constants caused by Δm alone. Therefore, the standard isotopic substitution analysis should apply and provide an internal consistency check on the structure obtained by fitting the six rotational constants.

In making this analysis the inertial axes were chosen so that the *ac* plane contains the substituted, outer oxygen (Fig. 2) in which case Eqs. (13.56) and (13.57) of Ref. 9 apply. With this choice the observed rotational constants give the coordinates of the ¹⁸O in the principal axis system of the parent to be $|a_i| = 2.866$, $b_i = 0$, and $|c_i| = 0.093$ Å. Comparison of these results with Fig. 2 shows that the substitution site is outside and "above" the carbons of the CO₂'s. Previously we found the carbons to be 2.192 Å from the figure axis, so at 2.866 Å the ¹⁸O is definitely outside. Also, we found the plane of the carbons to be 0.469 Å below the cluster's c.m. while the ¹⁸O is 0.093 Å either above or below the c.m. In either case, the outer ¹⁸O is far above the plane of the carbons, confirming that the CO₂'s have the inner oxygens rotated away from the nitrogens as shown in Fig. 2.

As a step in determining the pinwheel angle β we use the ¹⁸O substitution position to find the out-of-plane rotation angle γ . If the (CO₂)₃ subunit were rigid, the distance Δc_i between the ¹⁸O and the plane of the carbons would be given by

$$\Delta c_i = r(\text{C}=\text{O}) \sin \gamma, \quad (11)$$

where $r(\text{C}=\text{O}) = 1.1621$ Å is the bond distance in CO₂ (Table III) and $\Delta c_i = 0.469 \pm 0.093$ Å. This requires γ to be either -28.9° or -18.9° , of which -28.9° agrees with the result from fitting the six rotational constants (Table IX).

The pinwheel angle β is given by the cosine equation,

$$a^2 = r^2 + d^2 - 2rd \cos(90^\circ + \beta), \quad (12)$$

for the planar triangle in the (CO₂)₃ subunit (Fig. 2). Here a is the distance from the subunit's c.m. to the ¹⁸O, r is the c.m. to carbon distance, and d is the projection of $r(\text{C}=\text{O})$ by $\cos \gamma$ onto the plane of the carbons. For $\gamma = -28.9^\circ$ we find $\beta = 32.2^\circ$, while that from the fit of rotational constants is 32.5° (Table IX).

DISCUSSION

Probably the most interesting feature of this study is the change in structure of the (CO₂)₃ trimer caused by its interactions with the HCN in forming the cluster. The rotation of the CO₂'s out-of-plane by $\sim 36^\circ$ in the symmetric top clusters is spectacular. So is the large shrinkage of the C-C distance (by 0.241 Å) in the process. These structural changes are attributable to electrostatic interactions. The CO₂ has no permanent dipole moment but it does have a large electric quadrupole moment with the oxygens bearing a large negative charge and the carbon a positive charge of twice that magnitude. HCN has a strong dipole moment with the nitrogen negatively charged. Thus, formation of HCN-(CO₂)₃ can be viewed as attraction by the N of HCN to the C's of the (CO₂)₃.

The planar structure of free (CO₂)₃ is a balance between

neighboring CO₂'s of O-C attraction and O-O and C-C repulsion (Fig. 1). When the nitrogen end of the HCN approaches the (CO₂)₃ along the threefold axis from above, the three inner oxygens are closest to it with the three carbons next closest. The N-O repulsion rotates the inner oxygens out of the plane away from the N, while the N-C attraction pulls the carbons in, decreasing R_{CC} (Fig. 2). Comparison of the HCN to C distance in the cluster to that in the T-shaped dimer is complicated by the different geometry. In any event, the c.m. (HCN) to C distance is 3.525 Å in the cluster compared to 3.592 Å in the dimer.

Two features of the HCN are accessible and of interest, the torsional amplitude θ and the ¹⁴N quadrupole interaction constant χ_0 for the equilibrium geometry ($\theta = 0$). Torsional amplitudes of 12.4° and 10.3° , respectively, have been determined for the linear HCN-OCO dimer² and the HCN-(CO₂)₃ cluster, using the isotope substitution method of Eq. (6).

For the T-shaped dimer, the value of χ_a^d was observed to be -4.075 MHz, however a substitution determination of θ was not made.¹ For the linear dimer and the present cluster, χ_a^d and χ_c^c were found to be -4.2466 and -3.890 MHz. Part of the decrease in these values compared to that of free HCN, $\chi_0^m = -4.7079$ MHz, is caused by vibrational averaging. Correction for it with the substitution θ 's gives the decreases in χ_0 to be 0.146 and 0.62 MHz for linear dimer and cluster respectively. That for the T-shaped dimer is probably around 0.40 MHz indicating the interaction energies increase in the sequence linear, T-shaped, and the present cluster. The large decreases in the T-shaped dimer and cluster merit further study.

Also, it should be noted that the many values of χ_{cc} determined in fitting the hfs exhibited no significant changes with J or K . The results given in Table I for the parent cluster have what might be a very small change (~ 15 kHz) on going from $J = 2 \rightarrow 3$, $K = 0$ to $J = 4 \rightarrow 5$, $K = 3$; however, the results for the other isotopic species exhibited no such regularity.

The relatively large effects of ¹⁸O substitution were unexpected and they are intriguing. Considerable care was taken to verify the composition and structure of the ¹⁸O substituted species observed, and the effects appear to be real. The residues in fitting the six rotational constants for the ¹⁸O species are large, but there is good agreement between the results of the fit and the substitution values for the angles. Undoubtedly there are structural differences between the two ¹⁸O species, which we have neglected of necessity. Moreover, we have assumed that, except for mass distribution, the ¹⁸O species retain a threefold symmetry axis, which is oversimplified. The perturbation of the cluster's structure by ¹⁸O substitution merits further study in its own right. For example, it would be of interest to establish whether the structural differences persist in the various isotopic symmetric tops containing (C¹⁸O₂)₃. Also, more accurate determinations of rotational constants for a wider range of partially ¹⁸O substituted species could be revealing.

As is, the ¹⁸O effect consists of an 8° decrease in the out-of-plane angle γ , and 0.04 and 0.02 Å increases in R and R_{CC} , respectively, apparently of similar magnitude for

mono- and tetra-¹⁸O substitution. The coupling of γ with R_{CC} is consistent with R_{CC} being 0.24 Å longer in the planar (CO₂)₃ trimer ($\gamma = 0$) than in the HCN-(CO₂)₃ cluster ($\gamma = 37^\circ$). Also, the geometry of the cluster, which has the CO₂'s nearly perpendicular to the HCN, promotes strong coupling between γ and R . Rotation of the CO₂'s toward the N by decreasing γ will tend to push the HCN away, increasing R , as observed. But the manner in which ¹⁸O substitution decreases γ to the extent that it apparently does is not as evident.

Equation (10) treats γ as a static bend. However, the results are quite similar for vibration by $\Delta\gamma$ about an equilibrium angle γ_0 . In this case $\sin^2 \gamma$ is replaced by $\sin^2 \gamma_0$ plus a term in $\Delta\gamma^2$ so a reduction in vibrational amplitude is equivalent to a smaller static angle. Unfortunately, the vibrational amplitude for ¹⁸OCO is only 2% smaller than that of the parent CO₂, much too small of a difference to account for the observed decrease in γ . What seems to be involved is some cooperative mechanism for amplifying the structural effects of ¹⁸O substitution. Further experimental work is needed to characterize those effects. Also, potential surface calculations¹⁷ should be an aid in determining the mechanism for the effects as well as in understanding the interactions which distort the (CO₂)₃ trimer upon forming the HCN-(CO₂)₃ cluster.

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