



# Microwave Spectrum of Acetyl Cyanide

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ence 2. Pauling has recently proposed that exchange interactions are responsible for barriers to internal rotation. His rough estimates for CH<sub>3</sub>COZ barriers are somewhat higher than the observed ones. More accurate calculations would be required for a conclusive test of his theory.

The bent bond description of double bonds predicts CCO and CCZ angles of 125°16' and 109°28', respectively for CH<sub>3</sub>COZ molecules. The pi-bond description on the other hand predicts angles of 120°. Neither description fits the experimental data very well. The pi-bond model is reasonably consistent with the observed angles for acetaldehyde, but the bent-bond model is more nearly consistent with the data on acetyl fluoride, chloride, and cyanide.

The CO bond length is considerably shorter (0.03 A)in acetyl fluoride than it is in acetaldehyde. This suggests that the ionic form



may be important. A contribution to the structure from this form is also consistent with the fact that the CCO angle is several degrees larger in acetyl fluoride than it is in acetaldehyde. However, as discussed in reference 2, this ionic form does not agree with bond moment data.

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## Microwave Spectrum of Acetyl Cyanide\*

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The microwave spectra of eight isotopic species of acetyl cyanide have been investigated in the region 8000 to 34 000 Mc. The hindered internal rotation of the methyl group splits some of the rotational lines into doublets. Analysis of these splittings for four isotopic species gives a barrier to internal rotation of 1270± 30 cal/mole.

From the rotational constants of CH<sub>3</sub>COCN, Cl<sup>3</sup>H<sub>3</sub>COCN, CH<sub>3</sub>COC<sup>13</sup>N, CH<sub>3</sub>CO<sup>18</sup>CN, CD<sub>3</sub>COCN, and CD<sub>3</sub>C<sup>13</sup>OCN the following structural parameters were determined:

СН	$1.086 \pm 0.005 \text{ A}$	∠HCH	108°44′±30′
C=0	$1.226 \pm 0.005$	∠C <sub>methy1</sub> CO	$124^{\circ}3' \pm 1^{\circ}$
C≡N	$1.164 \pm 0.005$	∠ CCC	114°59′±1°
$C_{methyl} - C_{carbonyl}$	$1.490{\pm}0.010$	∠ CCN	180° (assumed)
C <sub>carbony1</sub> —C <sub>cyanide</sub>	$1.466 \pm 0.010$ .		

A study of CH<sub>2</sub>DCOCN and CHD<sub>2</sub>COCN shows that in its equilibrium configuration, the acetyl cyanide molecule has a methyl hydrogen opposite the oxygen atom.

A dipole moment of 3.45D was obtained from Stark effect measurements.

#### INTRODUCTION

CCURATE values for the potential barriers A hindering internal rotation have been obtained for a number of molecules from frequency measurements in the microwave region.<sup>1</sup> The series of molecules consisting of a carbonyl group attached to a methyl group and another simple substituent, i.e., with the general formula CH<sub>3</sub>COZ, is particularly well suited to this method as the barrier heights fall in a range which allows a precise determination. The work on acetyl cyanide, described in the present paper, was undertaken as part of a systematic study of this "acetyl" series, which includes acetaldehyde,<sup>2</sup> acetyl fluoride,3 acetyl chloride,4 and acetic acid.5

<sup>\*</sup> The research reported in this paper was made possible by support extended Harvard University by the Office of Naval Research under Contract Nonr 1866, Task Order XIV. † National Science Foundation Fellow, 1955–1958; National Distillers Fellow, 1958–1959. <sup>1</sup> For a partial list, see E. Bright Wilson, Jr., Proc. Natl. Acad. Sci.U. S. **43**, 811 (1957).

<sup>&</sup>lt;sup>2</sup> Kilb, Lin, and Wilson, J. Chem. Phys. 26, 1695 (1957).
<sup>3</sup> L. Pierce and L. C. Krisher, J. Chem. Phys. 31, 875 (1959).
<sup>4</sup> K. M. Sinnott, Bull. Am. Phys. Soc. Ser. II, 1, 198 (1956).

<sup>&</sup>lt;sup>5</sup> W. J. Tabor, J. Chem. Phys. 27, 974 (1957).

The structure of acetyl cyanide is also of interest, not only in comparison with other members of this series, but also since it contains a conjugated system of alternate multiple and single bonds.

It is hoped that this process of determining the barriers in closely related molecules will provide some information about the nature of the forces involved.

## EXPERIMENTAL

Acetyl cyanide, CH<sub>3</sub>COCN, was prepared by refluxing equimolar acetyl bromide and cuprous cyanide as described by Migrdichian.<sup>6</sup> The product was separated with a fractionating column packed with helices.

All isotopic species were prepared by reacting a substituted acetyl bromide and cuprous cyanide in a sealed glass tube for 2 hours at 110°C. This method gives nearly complete conversion to acetyl cyanide. The same method, using acetyl chloride and silver cyanide, was found to give a much poorer yield and was abandoned for the preparation of isotopic species.

Cuprous cyanide enriched in C13 was prepared from KC<sup>13</sup>N (66%-Distillation Products, Eastman Kodak) by precipitation with CuSO<sub>4</sub> in the presence of ammonium bisulfite. The method used was analogous to that for the thiocyanate precipitation of copper described in various texts on analytical chemistry.7 The CuC13N was dried and reacted with CH3COBr as described above to give CH<sub>3</sub>COC<sup>13</sup>N.

The CD<sub>3</sub>COBr was prepared by refluxing CD<sub>3</sub>COOD (99%-Isotope Specialities Company) with PBr<sub>3</sub> and distilling the product.

The C<sup>13</sup>H<sub>3</sub>COBr and CD<sub>3</sub>C<sup>13</sup>COBr were prepared from samples of the corresponding acetyl chlorides, kindly provided by Dr. Louis Pierce. The substituted acetyl chlorides were reacted with a fivefold excess of liquid HBr at  $-80^{\circ}$ C for 6 hours, giving nearly complete conversion to acetyl bromides.

CH<sub>3</sub>CO<sup>18</sup>CN was prepared by first reacting H<sub>2</sub>O<sup>18</sup> (68%-Weizmann Institute, Rehovoth, Israel) with acetyl chloride to give substituted acetic acid. This procedure, of course, cuts the  $O^{18}$  enrichment to 34%. The resulting acetic acid was reacted with PBr<sub>3</sub>, and then CuCN as described above.

CH<sub>2</sub>DCOCN and CHD<sub>2</sub>COCN were prepared by reacting the corresponding species of acetic acid with PBr<sub>3</sub> and CuCN. The sample of CH<sub>2</sub>DCOOD was prepared by Kilb and Pierce.8 CHD<sub>2</sub>COOD was made by decarboxylating malonic acid which had been partially exchanged with D<sub>2</sub>O. The nuclear magnetic resonance spectrum was used to determine the extent of this conversion.

The microwave spectrometer used was a typical Stark effect type employing 100-kc Stark modulation. Both oscilloscope and recorder display were used. Frequency measurements were made with multiples of a 5-Mc standard which was monitored by a signal from the Cruft Laboratories of Harvard University. The Cruft signal is continuously compared against not less than four primary standards located in this and in other countries, including station WWV, an Atomichron, the British Post Office cesium standard, the Essen ring, and another Atomichron at Boulder, Colorado.

Both **a**-type and **b**-type rotational transitions of the various acetyl cyanide species were studied in the frequency range 8000 to 34 000 Mc. The observed frequencies are listed in Table I.

#### MOLECULAR STRUCTURE

The moments of inertia for the various isotopic species and the observed rotational constants are shown in Tables II and III. Certain R-branch transitions with  $J \leq 2$  involve only simple multiples of the rotational constants. The reported moments were obtained from these transitions, since the effects due to centrifugal distortion are greatly reduced for low values of J. For some observed Q-branch transitions involving J=12, this deviation from a rigid rotor prediction was as much as 20 Mc.

An isotopic substitution was made at every position in the molecule with the exception of the nitrogen atom. The structure of CH<sub>3</sub>COCN was calculated from the moments of these species with the assumptions that the molecule has a plane of symmetry, that the hydrogens are symmetrically placed around the C<sub>methyl</sub>- $C_{carbony1}$  bond, and that the group  $C-C \equiv N$  is linear.

The distance,  $r_{\rm H}$ , from the plane of symmetry to the out-of-plane hydrogen atoms can be shown to be, for a rigid model,

$$4m_{\rm H}r_{\rm H}^2 = I_a + I_b - I_c.$$

However, as has been pointed out by Laurie,<sup>9</sup> this relation contains a contribution from the "inertial defect,"  $\Delta'$ , due largely to low-frequency motions of the heavy in-plane atoms. Thus, a much better approximation to the equilibrium  $r_{\rm H}$  can be obtained by examining the moments of CH<sub>3</sub>COCN and CD<sub>3</sub>COCN according to the relations

$$4m_{\rm H}r_{\rm H}^2 = I_a{}^{\rm H} + I_b{}^{\rm H} - I_c{}^{\rm H} + \Delta'$$
$$4m_{\rm D}r_{\rm D}^2 = I_a{}^{\rm D} + I_b{}^{\rm D} - I_c{}^{\rm D} + \Delta'$$

where  $\Delta'$  is assumed to be unaffected by this isotopic substitution. This type of treatment gives  $r_{\rm H} = 0.883$  A, and  $\Delta' = 0.271$  amu A<sup>2</sup>. The  $\Delta'$  is similar in magnitude to values observed for  $\Delta_0$  in completely planar molecules, and is seen to increase as the Z group becomes larger in the CH<sub>3</sub>COZ series, while the  $r_{\rm H}$  values remain relatively unaffected.<sup>9</sup> It is felt that the  $r_{\rm H}$  calculated in

<sup>&</sup>lt;sup>6</sup> V. Migrdichian, The Chemistry of Organic Cyanogen Com-pounds (Reinhold Publishing Corporation, New York, 1947),

<sup>&</sup>lt;sup>7</sup> E.g., W. C. Pierce and E. L. Haenisch, *Quantitative Analysis* (John Wiley & Sons, Inc., New York, 1948), pp. 454-455.
<sup>8</sup> R. W. Kilb and L. Pierce, J. Chem. Phys. 27, 108 (1957).

<sup>&</sup>lt;sup>9</sup> V. W. Laurie, J. Chem. Phys. 28, 704 (1958).

Transition	CH3COCN	CH3COC13N	C <sup>13</sup> H <sub>3</sub> COCN	CH <sub>3</sub> CO <sup>18</sup> CN	CD₃COCN	CD <sub>3</sub> C <sup>13</sup> OCN
a-Type	12 165 50	12 002 00	12.000 (2	40.040.04	10 100 50	40.455.00
$I_{1,1}-Z_{1,2}$	13 105.78	13 083.99	12 900.02	12 842.31	12 192.50	12 177.98
$1_{0,1} - 2_{0,2}$ $1_{-2} - 2_{-2}$	14 170.15	15 362 32	15 959.01	15 044.50	13 128.23	14 380 50
$1_{1,0}^{-2_{1,1}}$	10 650 08	10 537 03	15 200.39	15 170.04	14 399.12	14 300.30
21,2 51,3	20 895 08 4 <sup>h</sup>	17 001.70			10 207 8°	
20,2 00,3	$20\ 894.60E^{i}$				17 277.0	
$2_{2,1} - 3_{2,2}$	21 481.42					
$2_{1,1} - 3_{1,2}$	23 112.13	22 946.19A			21 484.8°	
		22 945.22 <i>E</i>				
$3_{1,3}-4_{1,4}$	26 064.43	25 907.24	25 644.76	25 392.84	24 093.70	24 065.46
$3_{3,1}-4_{3,2}$	b 00.001.00					
$3_{3,0}-4_{3,1}$	28 981.60	20 204 56			20 410 02	
$3_{1,2}-4_{1,3}$	30 010.27A	30 394.30			28 410.93	
3 1	30 008.33L	27 110 03	26 817 10		25 106 62	25 076 04
$3_{0,3} - 4_{0,4}$		27 110.95	20 817.10		25 100.02	25 070.94
$3_{2,2} - \frac{1}{2,3}$		20 002.00	29 518 4		20 101.12	20 427.20
$4_{2,3} - 5_{2,4}$			2/ 010.1		32 867.29	32 826.45
$4_{1,4}$ - 51 5		32 181.45		31 519.18	29 895.95°	
40,4-50,5	33 344.70	33 161.23	32 773.38			
b-Type					<u></u>	
$0_{0} - 1_{1}$	13 188.21	13 170.70	12 858.27	12 577 <sup>f</sup>	11 500.72°	11 492.04
$1_{1,1} - 2_{0,2}$	8 142.5°					
$1_{0,1} - 2_{1,2}$	19 193.60	19 143.21	18 761.11	18 414.00	17 046.5	17 030.50
$2_{1,2} - 3_{0,3}$	15 871.37					
$2_{0,2}-3_{1,3}$		24 605.75	24 150.7°	23 733.95		
$3_{1,3}$ -40,4	23 479.26	23 270.4 <sup>d</sup>	00 000 16	23 174.95	22 297.6	
$3_{0,3}$ -41,4	02 500 00 4	29 478.10	29 228.46		26 903,58	26 877.25
$4_{2,3}-5_{1,4}$	23 529.29A 23 527 46 F					
4 5	23 327.402	30 524 12		30 186 53		
41,4=50.5	50 759.14	50.521.12		30 100.00	31 600 10	
30 2-31 2	10 705.27				01 000.10	
51 4-52 3	16 497.52					
52 3-53 2					23 897.3	23 888.35
61.5-62.4	17 576.96				15 192.6	
60,6-61,5	$24 \ 211.49A$					
	$24 \ 205.33E$					
$6_{2,4}$ - $6_{3,3}$	28 180.80	28 389.86		25 775.01E		
~ ~	10 020 42 4	10 020 54 4		25 774.16A	45 060 5	
/1,6-/2,5	19 939.43A	19 828.54A			17 969.7	
7 7	19 935.72E 26 380 04	19 024.90E	25 278 01	24 122 67		
$7_{2,5} - 7_{3,4}$	30 545 524	20 393.24	25 278.01	24 132.07		
10,7-11,6	30 537.91E					
81 7-82 6	23 716.83A	23 492.79A	23 541.99A	23 612.92A		
	23 711.10E	23 487.74E	23 536.65E	23 607.22E		
82.6-83.5	25 142.58A	25 301.05A	24 161.20	23 191.46	20 267.8	
	$25 \ 141.40E$	25 299.99E				
$9_{2,7} - 9_{3,6}$	24 901.87A	24 973.89A	24 109.5	23 403.71A	20 873.53	
	24 899.85E	24 971.91E		$23 \ 401.52E$		
$9_{1,8} - 9_{2,7}$	28 807.37A	28 521.60A	28 796.36A			
0 0	28 839.31E	28 513.87E	28 189.33E		20 000 66	
93,6 <sup>9</sup> 4,5	26 012 18 4	25 058 154	25 452 02 4	25 080 164	30 889.00	22 007 56
102,8-103,7	26 012.10A 26 008 42E	25 950.15A 25 954 50F	25 452.05A 25 448 26F	25 030.10A 25 076 08F	22 955.60	22 901.30
10, -10, .	20 000,1212	AU JUT.UJL	40 110.4015	20 010.00E	28 695 97	28 705 21
11, 9-11, 4	28 686.62A	28 473.03A	28 381.10A		26 550.51	26 507 05
	28 680.63E	28 467.34E	28 375.46E			
118.8-114.7	34 771 <b>=</b>		33 182.59	31 542.42		27 152.82
$12_{2,10} - 12_{3,9}$	32 987.34A	32 594.33A	32 927.01A			
4040	32 978.82E	32 586.38E	32 918.68E		A 4 <b>H</b> A 4 A -	
123,9-124,8	33 169.95	33 415.93		30 531.92	26 781.28	26 771.04

TABLE I. Observed transitions (Mc/sec).<sup>8</sup>

<sup>a</sup> Estimated uncertainty ±0.2 Mc unless otherwise indicated. <sup>b</sup> Line overlapped by a strong line.

° ±0.3 Mc. d ±0.4 Mc.

• ±0.5.

f ±2 Mc. <sup>g</sup> ±3 Mc.

<sup>h</sup> A, nondegenerate torsional level.

<sup>i</sup> E, degenerate torsional level.

TABLE II. Rotational constants (Mc).

<u>م محمد الم من الم م</u>	A	В	С
CH <sub>3</sub> COCN	10 185.46	4157.53	3002.75
CH <sub>3</sub> COC <sup>13</sup> N	10 184.58	4125.37	2986.21
C <sup>13</sup> H <sub>3</sub> COCN	9 906.07	4105.57	2951.68
CH <sub>2</sub> CO <sup>18</sup> CN	9 657.42	4085,73	2918.86
CD <sub>3</sub> COCN	8 728.40	3875,60	2772.32
CD <sub>3</sub> C <sup>13</sup> OCN	8 722.81	3870.29	2769.23
	Estimated uncert	ainty, $\pm 0.2$ M	C

this manner, rather than from a single species, is much closer to the actual equilibrium value.

The positions of the three isotopically substituted carbon atoms and the oxygen atoms were determined from observed changes in the rotational constants on substitution, by the method described in detail by Kraitchman.<sup>10</sup> It is well known that isotopic substitution generally gives useful information with regard to the substituted atom, and very little information about the positions of other atoms. Thus, the coordinates of the methyl carbon, oxygen, and the *a* coordinate of the cyanide carbon were determined with respect to the principal axis system of the normal species by examining the change in moments between normal CH<sub>3</sub>COCN and C<sup>13</sup>H<sub>3</sub>COCN, CH<sub>3</sub>CO<sup>18</sup>CN, and CH<sub>3</sub>COC<sup>13</sup>N, respectively.

The carbonyl carbon was substituted as  $CD_3C^{13}OCN$ in order to increase its distance from the principal axes. The Kraitchman method was used on the change in moments between the  $CD_3COCN$  and  $CD_3C^{13}OCN$ species, to give the position of the carbonyl carbon in the  $CD_3COCN$  principal axis system. It was then necessary to make the appropriate translation and rotation of axes to obtain the coordinates of this atom in the  $CH_3COCN$  system. This transformation, from the  $CD_3COCN$  to the  $CH_3COCN$  system, was accomplished by an iterative process which was continued until the change in rotation was less than 1'.

Determination of the out-of-plane hydrogen coordinate has been described. The remaining hydrogen coordinates were obtained by fitting the differences in moments between the  $CH_3COCN$  and  $CD_3COCN$ species.

<b>FABLE III.</b>	Moments	of inertia*	(amu A <sup>2</sup>	).
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	Ia	Ib	I <sub>c</sub>	$I_a + I_b - I_c$
CH4COCN	49.6326	121.594	168.356	2.871
CH4COC <sup>13</sup> N	49.6369	122.542	169.288	2.890
C <sup>13</sup> H <sub>3</sub> COCN	51.0324	123.133	171.269	2.897
CH <sub>3</sub> CO <sup>18</sup> CN	52.3464	123.731	173.195	2.883
CD <sub>3</sub> COCN	57.9179	130.439	182.349	6.008
CD <sub>3</sub> C <sup>13</sup> OCN	57.9551	130.618	182.553	6.021

<sup>a</sup> Conversion factor 5.05531×10<sup>5</sup> Mc amu A<sup>2</sup>.

<sup>10</sup> J. Kraitchman, Am. J. Phys. 21, 17 (1953).

TABLE IV. Molecular structure of acetyl cyanide.

$C-H = 1.086 A \pm 0.005$ $C=0 = 1.226 \pm 0.005$ $C=N = 1.164 \pm 0.005$ $C_{methyl} - C_{arbonyl} = 1.490 \pm 0.010$	$\angle$ HCH = 108°44′±30′ $\angle C_{methy1}CO = 124°3′±1°$ $\angle CCC = 114°59′±1°$
$C_{carbony1} - C_{cyanide} = 1.466 \pm 0.010$	$\angle CCN = 180^{\circ}$ (assumed)

The *b* coordinate of the cyanide carbon is very small and the Kraitchman method is impractical here. This coordinate and the two nitrogen coordinates were obtained by assuming linearity of the C—C $\equiv$ N group and using the first moment equations

$$\sum_{i} m_{i} a_{i} = 0$$
$$\sum_{i} m_{i} b_{i} = 0.$$

The molecular structure of CH<sub>3</sub>COCN, determined in this manner, is given in Table IV, and Fig. 1. One check is available, namely, the value of the product of inertia,  $\sum m_i a_i b_i$ , which should vanish. The final coordinates give a value of 0.5 amu A<sup>2</sup>.

The limits of error are based on the estimated experimental errors. The deviation of these values from the true equilibrium parameters is not known, but is



FIG. 1. The structure of acetyl cyanide showing the location of the atoms with respect to the a and b principal axes, and the orientation of the dipole moment. Arrowheads give assumed negative ends.

TABLE V. Internal barriers and structural constants.

	CH₃COCN	CH3COC13N	C¹³H₃COCN	CH <sub>3</sub> CO <sup>18</sup> CN
F	1.6668×10⁵ Mc	1.6665	1.6667	1.6632
$\lambda_a$	0,4872	0.4872	0.5047	0.4575
λ	0.8733	0.8733	0.8633	0.8892
$I_{\alpha}$	3.1421 amu A	<sup>2</sup> used for all sp	pecies	
$V_3$	1271 cal/mole	1273	1285	1263

believed to be little greater than the error limits shown.<sup>11</sup> The observed data on the four CH<sub>3</sub> species allow an estimation of the change in inertial defect on isotopic substitution,  $\delta$ , where

$$\delta = \Delta' - \Delta = \Delta I_{c} - \Delta I_{A} - \Delta I_{B}$$

for the various pairs of isotopic species. This  $\delta$  is nearly 0.02 amu A<sup>2</sup> for certain pairs, and this fact places a rather serious limit on the accuracy that can be obtained by the Kraitchman method.

#### BARRIER TO INTERNAL ROTATION

The low J transitions of the CH<sub>3</sub> species and the entire spectra of the two CD<sub>3</sub> species are typical of rigid asymmetric rotors. For the four CH<sub>3</sub> species studied, several higher J transitions were resolved into doublets, arising from the interaction of internal and overall rotation. The height of the barrier hindering this internal rotation was determined from these splittings, using the theoretical treatment of Kilb, Lin, and Wilson<sup>2</sup> and Herschbach.<sup>12</sup> The notation of Herschbach will be used in the following discussion. An alternate treatment of this type of data is described by Hecht and Dennison.13

The analysis assumes a molecular model consisting of a rigid asymmetric framework (COCN group) with an attached symmetric rotor (CH<sub>3</sub> group). The threefold potential barrier hindering the internal rotation of these two groups is taken to be

$$V = \frac{V_3}{2}(1 - \cos 3\alpha) + \frac{V_6}{2}(1 - \cos 6\alpha) + \cdots,$$

where  $\alpha$  is the angle describing the relative orientation of the rotor and framework. Experimental evidence indicates that this potential converges rapidly<sup>14,15</sup> and only the  $V_3$  term was retained in this case.

In the infinite barrier limit, each torsional level "v" is triply degenerate. However, as the barrier is lowered, the tunnel effect partially splits this degeneracy giving

a nondegenerate  $v_A$  level and a doubly degenerate  $v_B$ level. The rotational energies in these two levels are slightly different and the A rotational transitions follow a pseudorigid rotor pattern, while the E transitions have slightly different effective rotational constants and also possess odd-order perturbation terms. The splitting between the A and E members of a doublet is a very sensitive function of the barrier height and affords a precise determination.

For acetyl cyanide, the asymmetry splitting is generally sufficiently large so that the odd-order terms have a negligible effect. Only second-order perturbation corrections were necessary, except for one transition. For the four CH<sub>3</sub> species, a value of  $\Delta W^{(2)}$  was found directly from each doublet splitting, according to Eq. (13) through Eq. (16) of Swalen and Herschbach.<sup>16</sup> If we use Herschbach's notation

$$\Delta A = A_A - A_E = (h\lambda_a^2 I_\alpha / 8\pi^2 r I_a^2) \Delta W^{(2)},$$

and similarly for  $\Delta B$ , where  $I_{\alpha}$  is the moment of inertia of the methyl group about its symmetry axis,  $\lambda_q$  are direction cosines of the top axis with respect to the principal axes,  $I_a$  are the principal moments of the entire molecule, and

$$r=1-\sum_{g}\lambda_{g}^{2}I_{\alpha}/I_{g}$$

The energy level differences are expanded as

$$\Delta W = W_{A} - W_{B} = (\partial W/\partial A) \Delta A + (\partial W/\partial B) \Delta B$$

 $+ (\partial W/\partial C)\Delta C.$ 

The frequency separation of a doublet is the difference in the  $\Delta W$  values for the two levels involved in the transition. Each observed splitting is simply  $\Delta W^{(2)}$ times a factor depending on the particular transition and the structural parameters.

The barrier

where

$$F = h/8\pi^2 r I_{\alpha}$$

 $V_3 = (9/4) F_{s_1}$ 

is now determined from the structure and the value of scorresponding to the average of the  $\Delta W^{(2)}$  values from the various splittings. Splittings of less than 1 Mc were not included in this analysis of the barrier height since many larger splittings were available and the relative accuracy of measurement is, of course, proportionally greater.

For one observed transition, the  $6_{2,4}-6_{3,3}$  of CH<sub>3</sub>CO<sup>18</sup>CN, the first-order perturbation term causes a significant shift in the E level. The  $6_{3,3}$  and  $6_{3,4}$  levels are close together and the term linear in  $\mathcal{P}$  shifts the  $6_{3,3}$  E level to higher frequency by 0.7 Mc (calc) compared to the observed splitting of 0.85 Mc. The n=2 terms are negligible here.

<sup>&</sup>lt;sup>11</sup> C. C. Costain, J. Chem. Phys. 29, 864 (1958).
<sup>12</sup> D. R. Herschbach (to be published).
<sup>13</sup> K. T. Hecht and D. M. Dennison, J. Chem. Phys. 26, 31 (1957); see also, D. R. Lide, Jr., and D. E. Mann, *ibid.* 26, 1057 (1957). (1957).

<sup>&</sup>lt;sup>14</sup> Tannenbaum, Johnson, Myers, and Gwinn, J. Chem. Phys. 22, 949 (1954). <sup>15</sup> R. E. Naylor, Jr., and E. Bright Wilson, Jr., J. Chem. Phys.

<sup>26, 1057 (1957).</sup> 

<sup>&</sup>lt;sup>16</sup> J. D. Swalen and D. R. Herschbach, J. Chem. Phys. 27, 100 (1957).

The barrier heights calculated for the four different isotopic species are shown in Table V. The agreement is very satisfying since the splittings differ due to changes in the  $\lambda_q$  and F values for the various isotopes. It is felt, however, that a much larger error is introduced by uncertainty in the structure, so that a reasonable value for the barrier would be  $1270 \pm 30$  cal/mole (444 cm<sup>-1</sup>).

#### DIPOLE MOMENT

The dipole moment was determined from Stark effect measurements on the  $1_{0,1}-2_{0,2}$  and  $2_{0,2}-3_{0,3}$ transitions of CH<sub>3</sub>COCN. Theoretical Stark coefficients were calculated by the method of Golden and Wilson,<sup>17</sup> using the line strengths tabulated by Schwendeman and Laurie.18 The components of the dipole moment along the principal axes are  $\mu_a = 2.42D$  and  $\mu_b = 2.46D$ , giving a resultant moment,  $\mu = 3.45 \pm 0.06D$ . It is reasonable to assume that  $\mu_a$  and  $\mu_b$  are negatively directed toward the cyanide group and oxygen respectively, so that the resultant moment makes an angle of  $15^{\circ}20'$ with the  $C_{methyl} - C_{carbonyl}$  bond. The orientation is shown in Fig. 1.

#### EOUILIBRIUM CONFIGURATION

The six isotopic species of acetyl cyanide used for calculation of the molecular structure all have symmetric internal rotors, either  $CH_3$  or  $CD_3$  groups. The moments of inertia of these molecules are independent of the angle  $\alpha$ , which describes the relative orientation of the internal rotor and framework. For the species with asymmetric internal rotors, CH<sub>2</sub>DCOCN and CHD<sub>2</sub>COCN, however, the overall moments do depend on this orientation, and a study of these spectra was undertaken in order to determine the equilibrium configuration of acetyl cyanide.

Using the structure given in Table IV, two sets of moments of inertia were calculated for CH<sub>2</sub>DCOCN and CHD<sub>2</sub>COCN: Case I, a methyl hydrogen eclipses the oxygen; Case II, a methyl hydrogen eclipses the cyanide group.

The observed spectra of these two molecules are shown in Table VI. For each isotopic species, and a given type of configuration, two rotational isomers are possible, one possessing a plane of symmetry (sym), and one with no elements of symmetry (asym); e.g., for CH<sub>2</sub>DCOCN the sym form has the D atom in the plane of symmetry of the COCN framework, and the asym form has the D atom out-of-plane. The asym form is attained in two of the three equilibrium values of the internal angle,  $\alpha$ . The potential energy for these two asymmetric positions is identical, so the wave functions may be expected to mix and give rise to doublets in the rotational spectrum. Doublets were observed only in the CH<sub>2</sub>DCOCN spectrum.

TABLE VI. Spectra of CH2DCOCN and CHD2COCN, comparison of (A-C)/2.

Transition	sym- CH₂DCOCN	asym- CH₂DCOCN	asym- CHD₂COCN
21 1-31 2	22 174.5 Mc	22 748.5	1
20 2-31 2	23 976.34	23 591.75	
31 8-40 4	22 417.94	23 451.09	
60 5-61 5		24 014.94	22 $833 \pm 1$
7. 5-7.2 4		23 044.93	23 321.5
81 7-8° 6	22 617.57	23 570.53	22 351.7
-1,1 -2,0		23 568.45	
82 6-83 5		22 276.07	22 358.8
92 -93 6	24 655.85	22 726.47	22 454.2
10, 1-10, 7		24 692.58	23 911.19
		24 691.50	23 897.77
(A-C)/2			
Observed	3545 Mc	3257.5	3235.5
Calc., Case I	3546	3259.5	3237
Calc., Case II	3245	3409	3103

Most of the observed transitions belong to b-type Q-branch series which afford a good determination of the quantity (A-C)/2. Table VI shows the observed values of (A-C)/2 for the various species, as well as the values calculated for the two orientations listed above.

This comparison shows conclusively that Case I represents the equilibrium configuration, i.e., the oxygen is eclipsed by a methyl hydrogen. This result is analogous to that found for the other members of the acetyl series.

#### DISCUSSION

The structure of acetyl cyanide, Table IV, indicates a  $C_{earbony i} - C_{eyanide}$  bond distance of 1.47 A, which is somewhat shorter than the standard sum of covalent radii value of 1.54 A. Herzberg and Stoicheff<sup>19</sup> and more recently Stoicheff and Costain<sup>20</sup> have found that the length of the C—C bond depends linearly on the number of attached atoms. Their value for the



case is 1.43 A which deviates by 0.04 A from that observed here, which is probably somewhat outside the combined experimental errors in these molecules.

Table VII shows the barriers and structural parameters determined for the various members of the acetyl series, CH<sub>3</sub>COZ. The methyl group parameters and the C-C bond lengths are the same for all the compounds, within the experimental error.

The C==O bond length, however, appears to increase in the order Z=F, Cl, H, CN by an amount which is believed to be greater than the experimental uncertainty. This belief is strengthened by the fact that the

<sup>&</sup>lt;sup>17</sup> S. Golden and E. Bright Wilson, Jr., J. Chem. Phys. 16, 699 (1948).

<sup>18</sup> R. Schwendeman and V. W. Laurie, Line Strengths for Rotational Transitions (Pergamon Press, London, 1958).

 <sup>&</sup>lt;sup>19</sup> G. Herzberg and B. P. Stoicheff, Nature 175, 79 (1955).
 <sup>20</sup> B. P. Stoicheff and C. C. Costain, Symposium on Molecular Spectroscopy, Ohio State University, June, 1958.

	CH <sub>3</sub> COF <sup>a</sup>	CH₃COCl <sub>P</sub>	CH₃CHO⁰	CH₃COCN
C=0	1.181	1.192	1.216	1.226
С—Н	1.084	1.083	1.086	1.086
C—C	1,503	1.499	1.501	1.490
∠HCH	109°30′	108°34′	108°16′	108°44′
∠ CCO	128°21′	127°5′	123°55′	124°3′
∠ ČČŽ	110°18′	112°39′	117°29′	114°59′
$V_3$	1041	1300	1150	1270

TABLE VII. Structural parameters and barriers of the acetyl series.

<sup>a</sup> See reference 3.

<sup>b</sup> See reference 4.

<sup>c</sup> See reference 2.

carbonyl stretching frequency, near 1800  $\rm cm^{-1}$  in the infrared, decreases from F, Cl, H to CN. The relation can be made semiquantitative by using Badger's rule<sup>21</sup> connecting a vibrational force constant and the bond length, provided that the variation of the carbonyl frequency is assumed to be entirely due to the change in the force constant and not to mass effects. On this basis

#### $\nu^2 r^3 \cong \text{const}$

where r is the bond length and  $\nu$  the frequency. Table VIII and Fig. 2 show that this relation applies quite well to the acetyl series.

The molecules listed in Table VIII are the only ones of the CH<sub>3</sub>COZ series for which accurate carbonyl distances are available. The bond distance for acetone is that given by Allen, Bowen, Sutton, and Bastiansen,<sup>22</sup> and was determined by the sector method of electron diffraction. The other carbonyl distances were determined from microwave data (see Table VII for references).

The carbonyl stretching frequencies for acetyl chloride and acetone are those measured by Hartwell, Richards, and Thompson.<sup>23</sup> The frequency for acetaldehyde is that given by Evans and Bernstein,<sup>24</sup> who also report data on CH<sub>3</sub>CDO. The small shift of about  $2 \text{ cm}^{-1}$ between the carbonyl bands of CH<sub>3</sub>CHO and CH<sub>3</sub>CDO indicates that mass effects are of minor significance here. The carbonyl frequencies of acetyl fluoride and



FIG. 2. Plot of carbonyl bond distance (angstroms) vs  $\nu^{-\frac{3}{2}} \times 10^{3}$ where  $\nu$  is the carbonyl stretching frequency, for CH<sub>3</sub>COZ molecules. The points are labeled by the appropriate Z.

acetyl cyanide were measured under comparable conditions by one of us (L.C.K.) and Thomas James on the grating instrument of Dr. W. A. Klemperer.

Another structural trend, listed in Table VII, is the increase in the angle CCZ and the decrease in the angle CCO along the series as Z=F, Cl, CN, H, which differs from the order of the C=O lengths in the interchange of H and CN. This difference, however, is probably not outside the experimental error for the angle; i.e., H and CN might be reversed in the sequence. Any explanation of this angular trend must be compatible with the observation that the angle OCZ is relatively constant.

The fact that the carbonyl bond distance and stretching frequencies fall on a smooth curve suggests that there is only one important parameter determining these quantities, and that an explanation would involve a superposition of two structures. However, it seems difficult to find structures which are compatible with the observed data. For example, to explain the carbonyl distance, it is tempting to postulate the importance of the structure

TABLE VIII. Carbonyl bond distances and stretching frequencies.

	$r_{C=0}(A)$	$\nu_{\rm C=0}({\rm cm}^{-1})$	$\nu^2 r^3 \times 10^{-6}$
CH <sub>*</sub> COF	1.181	1867	5.74
CH <sub>3</sub> COCl	1.192	1822	5.62
CH <sub>3</sub> CHO	1.216	1743	5.46
$(CH_3)_2CO$	1.22	1742	5.51
ĊH₃COCN	1.226	1740	5.58

 R. M. Badger, J. Chem. Phys. 3, 710 (1935).
 Allen, Bowen, Sutton, and Bastiansen, Trans. Faraday Soc. 48, 991 (1952)

<sup>23</sup> Hartwell, Richards, and Thompson, J. Chem. Soc. 1948, 1436.

<sup>24</sup> J. C. Evans and H. J. Bernstein, Can. J. Chem. 34, 1083 (1956).



TABLE IX. Dipole moment data (debyes).

	CH3COF	CH₃CHO	CH₃COCN
Observed compo	onents		
µa 1	2.83	2.55	2.42
μь	0.88	0.87	2.46
Calculated bond	d moments (CH <sub>3</sub> =	=0.4)	
C==0	2.97	2.57	2.67
ČŽ	1.95	0.37	3.43

which would increase with the electronegativity of Z, as has been done by Kagarise.<sup>25</sup> If this is a correct description, the angle RCO should also increase with the electronegativity of Z. The microwave data show an increase in the order Z=F, Cl, CN, H. However, as stated above, the angles for the CN and H cases probably do not differ by more than the experimental uncertainty so that the order for the angles and C==O bond lengths could be the same. It is not so obvious how this explanation can account for the relative constancy of the OCZ angle.

The above discussion, however, is incompatible with bond moment data. By assuming a bond moment for the methyl group, we can calculate bond moments for the C=O and C-Z groups from the observed components of the dipole moment along the principal axes. Table IX shows these bond moment values where we have assumed a methyl group moment of 0.4D, directed along the C-C bond with the negative end toward the carbonyl carbon. These calculated values are reasonable but the C=O moment is largest for CH<sub>3</sub>COF, and this is of course incompatible with a large contribution from the ionic structure postulated above, which would be necessary to account for the short C=O distance in acetyl fluoride. Further calculations, assuming a methyl moment of 0.25D, zero, and 0.4D(i.e., with the polarity reversed) give somewhat different calculated moments, but the carbonyl moment in CH<sub>3</sub>COF is always the largest in the series. This points out the dangers of trying to account for a small number of data by a superposition of structures.

The problem of correlating the internal barrier values is very difficult. Some of the shortcomings of various models have been discussed.<sup>1</sup> Throughout the series, the equilibrium configuration of the methyl group is such that the oxygen is eclipsed by a methyl hydrogen, even when Z is changed from H to F. The small change in barrier from one molecule to another is notable and seems incompatible with the hypotheses that the barrier arises primarily from steric repulsions or from electrostatic interactions between attached groups.

#### ACKNOWLEDGMENT

The authors are indebted to Dr. Louis Pierce for samples of  $C^{13}H_3COCl$  and  $CD_3C^{13}OCl$ .

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# Equilibrium in the Exchange of Hydrogen between Arsine and Water\*

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The equilibrium constant for the reaction  $AsH_2D(g) + H_2O(l) \Rightarrow AsH_3(g) + HDO(l)$  has been measured at 25.4° and found to be 1.89 $\pm$ 0.02, corresponding to a value in the gas phase of 1.77 $\pm$ 0.02. With the known vibrational spectra of AsH<sub>3</sub> and AsH<sub>3</sub>-d<sub>3</sub> the gas phase equilibrium constant was calculated at 25.4°,  $K_2 = 0.777e^{258/T} = 1.84$ .

#### INTRODUCTION

AS was demonstrated by Urey and Rittenberg<sup>1</sup> equilibrium constants for isotopic exchange reactions may be calculated from spectroscopic data. Kimball and Stockmayer<sup>2</sup> made such a calculation for a reaction of ammonia involving hydrogen exchange. Recently, Weston and Bigeleisen<sup>3</sup> made a similar calculation for the exchange of hydrogen between phosphine and water where the necessary spectrum of  $PH_3-d$  was unknown. During a study of the acid and base catalysis of exchange of hydrogen between arsine and water the equilibrium constant for the following reaction,

$$AsH_3(g) + HDO(l) \rightleftharpoons AsH_2D(g) + H_2O(l),$$

was determined and compared with the calculated value.

#### EXPERIMENTAL

AsH<sub>3</sub> was prepared by allowing H<sub>2</sub>O (degassed by repeated freezing and thawing in vacuum) to drip on finely ground Li<sub>3</sub>As alloy. The AsH<sub>3</sub> which formed was flushed into a vacuum system by He gas and condensed in cold traps at liquid N<sub>2</sub> temperature. The AsH<sub>3</sub> was distilled three times at  $-100^{\circ}$ C (the

<sup>\*</sup> This research was performed at the Los Alamos Scientific Laboratory under the auspices of the U. S. Atomic Energy Commission.

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<sup>&</sup>lt;sup>1</sup> H. C. Urey and D. Rittenberg, J. Chem. Phys. 1, 137 (1933). <sup>2</sup> G. E. Kimball and W. H. Stockmayer, SAM Rept. 100 XR-

<sup>1657 (</sup>October 14, 1942). This work is outlined in reference 4, p. 55. <sup>a</sup> R. E. Weston and J. Bigeleisen, J. Chem. Phys. 20, 1400 (1952).