

Precision Measurement of Dipole Moments and Other Spectral Constants of Normal and Deuterated Methyl Fluoride and Methyl Cyanide*

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From high precision measurements of first- and second-order Stark effects on both $\Delta M = 0$ and $\Delta M = \pm 1$ transitions, the molecular dipole moments of normal and deuterated methyl fluoride and methyl cyanide have been obtained as follows: for CH_3F , $\mu = 1.8572 \pm 0.0010$ D; for CD_3F , $\mu = 1.8682 \pm 0.0010$ D; for CH_3CN , $\mu = 3.913 \pm 0.002$ D; for CD_3CN , $\mu = 3.919 \pm 0.004$. A remeasurement of zero-field lines yields more accurate values of the spectral constants for three of these. They are: for CH_3F , $B_0 = 25\,536.148 \pm 0.005$ Mc/sec, $D_J = 60.4 \pm 0.10$ kc/sec, $D_{JK} = 439.26 \pm 0.05$ kc/sec; for CD_3F , $B_0 = 20\,449.854 \pm 0.012$ Mc/sec, $D_J = 34.2 \pm 0.4$ kc/sec, $D_{JK} = 221.7 \pm 0.9$ kc/sec; for CD_3CN , $B_0 = 7858.117 \pm 0.008$ Mc/sec, $D_J = 4.64 \pm 0.06$ kc/sec, $D_{JK} = 110.59 \pm 0.10$ kc/sec.

Previous measurements of the dipole moments of CH_3F (1) and CH_3CN (2) have been made. We undertook the present study to learn what changes in dipole moment are caused by substitution of deuterium for the hydrogens of the methyl group in these molecules and to find whether the changes in dipole moment with change of rotational state are large enough in these molecules to be measured with a high-precision Stark spectrometer. Since the parallel-plate cell used in the present work is more accurate than the normal waveguide Stark cell, these precise measurements of dipole moments made at millimeter wavelengths can serve as calibration standards for future measurements of dipole moments of other molecules made with a normal waveguide cell.

INSTRUMENTS AND PROCEDURES

The Stark cell was a parallel-plate cell constructed of silver-coated plate glass separated by optically ground quartz spacers. Focusing horns and lenses were used to direct the millimeter-wave energy between the plates. Two sets of horns were employed in the observations, one for the σ components ($\Delta M = \pm 1$) and

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the other for the π components ($\Delta M = 0$). Details of the construction of the horns and the other microwave components are described in earlier papers (1, 3) from this laboratory. The procedure for measurements of frequency and electric field is also described in these papers.

Several factors must be considered in estimation of the limits of probable error in the values of the dipole moments. As is true in most other measurements of the Stark effect, the limiting factors of accuracy are the uniformity and stability of the electric field and the ability to measure this field with precision. To insure uniformity of field, the glass plates were polished and tested for optical flatness by a simple wedge-interference test. Since the plates are supported only at the edges, they may bend slightly under the force of the electrostatic field. A calculation of this effect (1) shows, however, that a field strength of 30 000 V/cm is required to produce a deflection of 10^{-6} cm at the center of the plates. With the field strengths used in these experiments, this effect is negligible. The quartz spacers were carefully polished and were measured to an accuracy of 0.03%. The *K-2* potentiometer and standard cell used for measurement of dc voltage across the plates were recalibrated immediately before the measurements were made. The accuracy of the potentiometer is 0.01%. One source of error is the change in the battery voltage during the course of the measurement. To minimize the error as well as to estimate the magnitude of it, the voltage was measured immediately before and after each frequency measurement; the average voltage was used as the proper value. In consideration of the upper limits of the various sources of error in the field-measurements, the over-all error in the measurement of the field value for each line displacement is estimated to be less than 0.05%.

The largest source of error in the frequency measurements is the human error in the setting of the marker at the line center. To minimize this error, we measured each line at least three times with both a forward sweep and a reverse sweep; the average of these measurements was taken for the final value. In the region of the measurements, $\sim 100\ 000$ Mc/sec, the accuracy of the frequency measurements is estimated to be between ± 0.005 Mc/sec and ± 0.02 Mc/sec, according to the strength of the individual lines measured.

In the estimation of the probable limits of error which are assigned to the values of the dipole moments, the limiting errors inherent in the measuring instruments were taken into account. In addition, the consistency of the dipole moment values obtained with the same Stark components under different field values was used for an estimation of error limits. The standard deviation from the average as calculated from the deviation from the mean in the dipole moment values obtained with a given Stark component is calculated by Zurmuhl's method (4) to give a "confidence factor" of 99%. The error limits obtained by this method are consistent with the maximum error inherent in the instruments employed for measurement of the frequency displacement and of the electric

field. By averaging the values of the dipole moment thus obtained from different Stark components, we could gain a still lower standard deviation. This procedure is unjustifiable, however, because real differences in the dipole moments of different states are possible and because the estimated limits of error are then lower than the maximum error inherent in the measuring instruments.

CH₃F AND CD₃F

ZERO-FIELD SPECTRA AND SPECTRAL CONSTANTS

In the course of this work a remeasurement of the unperturbed zero-field lines of the $J = 1 \rightarrow 2$ and the $J = 3 \rightarrow 4$ transitions was made for both CH₃F and CD₃F. The observed zero-field lines are given in Table I. These measurements yielded more accurate values of the spectral constants B_0 , D_J , and D_{JK} than were previously available (5, 6). These new values are given in Table II. They were evaluated by a least-squares fitting of the frequencies to the formula

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

STARK EFFECT AND DIPOLE MOMENT

The dipole moment of CH₃F has been previously measured with high precision by Larkin and Gordy (1). In order to obtain a more direct comparison with the Stark splitting for CD₃F and to evaluate the small effects of deuterium substitution, we remeasured the Stark splitting of CH₃F. A slight improvement was

TABLE I
OBSERVED ZERO-FIELD LINES FOR CH₃F AND CD₃F

Transition $J \rightarrow J + 1$	K	Measured frequency (Mc/sec)	
		CH ₃ F	CD ₃ F
1 \rightarrow 2	0	102 142.656 \pm 0.006	81 798.332 \pm 0.005
1 \rightarrow 2	1	102 140.903 \pm 0.005	81 797.422 \pm 0.009
3 \rightarrow 4	0	204 273.730 \pm 0.016	163 590.068 \pm 0.010
3 \rightarrow 4	1	204 270.210 \pm 0.010	163 588.288 \pm 0.010
3 \rightarrow 4	2	204 259.678 \pm 0.010	163 582.941 \pm 0.012
3 \rightarrow 4	3	204 242.098 \pm 0.010	163 574.110 \pm 0.012

TABLE II
OBSERVED SPECTRAL CONSTANTS FOR CH₃F AND CD₃F

Constant	CH ₃ F	CD ₃ F
B_0	25 536.148 \pm 0.005 Mc/sec	20 449.854 \pm 0.012 Mc/sec
D_J	60.4 \pm 0.10 kc/sec	34.2 \pm 0.4 kc/sec
D_{JK}	439.26 \pm 0.05 kc/sec	221.7 \pm 0.9 kc/sec
μ	1.8572 \pm 0.0010 D	1.8682 \pm 0.0010 D

made in the value of the dipole moment of CH_3F . The dipole moment of CD_3F had not been measured before.

The first-order Stark energies of rotational lines of a symmetric-top molecule are given by

$$W_{JKM}^{(1)} = -\mu\epsilon MK/J(J+1). \quad (2)$$

Therefore, when $K \neq 0$, there is a first-order splitting of the rotational lines. The $\Delta M = 0$ Stark components are observed when the imposed dc field is parallel to the electric vector of the microwave field. The separation of this component from the corresponding zero-field frequency ν_0 is

$$\nu - \nu_0 = \alpha\mu\epsilon 2MK/J(J+1)(J+2), \quad (3)$$

where $\alpha = 0.50344$ when the frequencies are measured in Mc/sec, μ in Debye, and ϵ in V/cm. For the $J = 1 \rightarrow 2$ transition, the first-order effect is observed for the $K = 1$ line only. The $\Delta M = 0$ Stark spectrum for this line consists of three components, one of which coincides with the zero-field line. The other two are equally intense and spaced $\pm(\alpha\mu\epsilon)/3$ from this undisplaced component.

When the electric vector of the microwave radiation is perpendicular to the dc field ϵ , the $M \rightarrow M \pm 1$ components are observed. Their displacements from the corresponding zero-field lines are given by

$$\nu - \nu_0 = \alpha\mu\epsilon(2M \mp J)K/J(J+1)(J+2). \quad (4)$$

There are six $\Delta M = \pm 1$ transitions for the $J = 1 \rightarrow 2$, $K = 1$ line. In the first-order effect two sets of these transitions coincide so that the $\Delta M = \pm 1$ transitions give only four resolvable components for low-field values. These are symmetrically placed about the ν_0 line with relative intensities 1:9:9:1. The weaker components are spaced $(\pm\alpha\mu\epsilon)/2$; the stronger components, $(\pm\alpha\mu\epsilon)/6$ from the undisplaced ν_0 line. At higher fields, when the second-order effect becomes significant, the degeneracies of the coincident pairs are removed, and six $\Delta M = \pm 1$ components are observed.

For symmetric-top molecules without nuclear coupling, such as CH_3F , the second-order Stark splitting of the rotational levels for $J > 0$ is

$$W_{JKM}^{(2)} = \frac{\mu^2\epsilon^2}{2Bh} \left\{ \frac{(J^2 - K^2)(J^2 - M^2)}{J^3(2J-1)(2J+1)} - \frac{[(J+1)^2 - K^2][(J+1)^2 - M^2]}{(J+1)^3(2J+1)(2J+3)} \right\}. \quad (5)$$

For $K = 0$, the first-order effect vanishes, leaving only the second-order effect. When there is a first-order effect, it is very much larger than the second-order effect, which can generally be neglected except at high fields where it must be added as a small correction term to the first-order effect. We have used the second-order effect for $K = 0$ lines to obtain an independent evaluation of the

dipole moments for comparison with the values obtained with $K = 1$ lines. One purpose was to learn whether the rotation about the symmetry axis when $K = 1$ has a measurable effect on the dipole moment. However, this effect proved to be too small for measurement in any of the molecules studied in the present experiment. Tables III and IV illustrate the consistency of the data for measurements on the components of CD_3F . Similar results were obtained for CH_3F . The lines for $K = 1$, $M_J = 1 \rightarrow 2$ and $0 \rightarrow -1$ and those for $K = 1$, $M_J = -1 \rightarrow -2$ and $0 \rightarrow 1$, which are coincident in first-order Stark effect, are separated by the second-order effect at fields of 2000 V/cm by a few Mc/sec.

The summary of the experimental results of evaluation of the dipole moment for CH_3F and CD_3F is given in Table V. The final value for CD_3F is 0.6% larger than that for CH_3F . Lide (7) has observed the dipole moment of $(\text{CH}_3)_3\text{CD}$ to be 6.5% larger than that for $(\text{CH}_3)_3\text{CH}$.

CH_3CN AND CD_3CN

ZERO-FIELD SPECTRA AND SPECTRAL CONSTANTS

The microwave spectrum of methyl cyanide has been previously investigated (8, 9). The highly accurate set of molecular constants listed in Table VI was ob-

TABLE III
FIRST-ORDER STARK SPECTRUM FOR CD_3F
 $J = 1 \rightarrow 2$, $K = 1$, $\Delta M = \pm 1$ COMPONENTS

$\nu - \nu_0$ (Mc/sec)	\mathcal{E} (V/cm)	μ (D)
4.909	31.332	1.867
-4.915	31.331	1.870
9.149	58.384	1.868
-9.165	58.383	1.871
14.069	89.746	1.868
-14.079	89.746	1.870
18.374	117.140	1.869
-18.346	117.136	1.867
23.293	148.572	1.868
-23.284	148.633	1.867
27.175	173.312	1.869
-27.172	173.312	1.868
32.075	204.901	1.866
-32.105	204.881	1.868
37.431	238.976	1.867
-37.489	239.236	1.868
42.449	270.434	1.871
-42.390	270.578	1.867
-46.615	297.482	1.868
	Average	1.868

TABLE IV
SECOND-ORDER STARK SPECTRUM FOR CD₃F
 $J = 1 \rightarrow 2$, $K = 0$, $\Delta M = \pm 1$ COMPONENTS

$\nu - \nu_0$ (Mc/sec)	\mathcal{E} (V/cm)	$\mathcal{E}^2 \times 10^{-4}$ (V/cm) ²	μ (D)
2.230	1403.4	196.97	1.868
2.441	1465.2	214.67	1.871
5.037	2110.9	445.60	1.866
7.919	2640.5	697.24	1.871
12.700	3348.6	1121.33	1.868
14.117	3528.4	1244.98	1.869
17.113	3886.5	1510.49	1.868
7.940	1577.6	248.88	1.868
11.918	1931.9	373.22	1.868
16.666	2284.4	521.87	1.868
-4.235	1052.4	110.76	1.871
-5.223	1171.6	137.26	1.867
-7.530	1403.6	197.01	1.871
-8.181	1465.1	214.65	1.868
-14.212	1927.8	371.65	1.871
-16.958	2111.0	445.64	1.867
-19.934	2284.6	521.93	1.870
-23.175	2466.8	608.51	1.868
-26.533	2640.3	697.11	1.867
-30.316	2822.8	796.83	1.867
-34.128	2994.8	896.88	1.867
-38.353	3175.7	1008.51	1.866
-42.627	3349.0	1121.61	1.866
-47.386	3528.8	1245.26	1.867
		Average	1.868

TABLE V
SUMMARY OF EXPERIMENTAL RESULTS FOR CH₃F

Components $J = 1 \rightarrow 2$	Dipole moment μ (D)	
	CH ₃ F	CD ₃ F
First order, $\Delta M = 0$, $K = 1$	1.858 \pm 0.0010	1.868 \pm 0.0010
First order, $\Delta M = \pm 1$, $K = 1$	1.857 \pm 0.0011	1.868 \pm 0.0010
Second order, $\Delta M = 0$, $K = 0$	1.857 \pm 0.0010	1.868 \pm 0.0013
Second order, $\Delta M = \pm 1$, $K = 0$	1.857 \pm 0.0011	1.868 \pm 0.0011
Average	1.8572	1.8682

tained by Venkateswarlu *et al.* (9). In the present work the only transition measured with high precision was that for $J = 4 \rightarrow 5$. No improvement in the spectral constants could be made.

The dipole moment was measured first by Coles, Good, and Hughes (10), who

TABLE VI
OBSERVED SPECTRAL CONSTANTS FOR CH₃CN AND CD₃CN

Constant	CH ₃ CN	CD ₃ CN
B_0	9198.899 Mc/sec ^a	7858.117 ± 0.008 Mc/sec
D_J	3.81 kc/sec ^a	4.64 ± 0.06 kc/sec
D_{JK}	176.9 kc/sec ^a	110.59 ± 0.10 kc/sec
μ	3.913 ± 0.002 D	3.919 ± 0.004 D

^a Values for CH₃CN are taken from Venkateswarlu, Baker, and Gordy (9).

obtained the value $\mu = 3.97$ D. Later, Ghosh *et al.* (2), who also used the normal waveguide Stark cell, found from the second-order Stark effect on $K = 0$ the value $\mu = 3.92 \pm 0.06$ D. Kessler *et al.* (11) found the quadrupole coupling constant to be $eQq = -4.35 \pm 0.20$ Mc/sec.

Although the microwave spectrum of CD₃CN has been previously studied (11), the spectral constants obtained are not as precise as can now be obtained, and no value of D_J has been given before. To our knowledge, the dipole moment has not been previously measured.

In the present work, the Stark effect was investigated for the transition $J = 5 \rightarrow 6$. Also, the transition $J = 9 \rightarrow 10$ was measured for a recalculation of the rotational constants. The frequencies of these lines are listed in Table VII. These lines were used for calculation of the molecular constants for CD₃CN listed in Table VI.

STARK EFFECT AND DIPOLE MOMENTS

The spectrum of methyl cyanide is complicated by the hyperfine structure from nuclear quadrupole coupling. However, the coupling constant is so small that it is very easy to attain the strong-field case where $\mathbf{u} \cdot \boldsymbol{\epsilon} \gg eQq$. In the strong-field case the first-order energies are still given by Eq. (2). The frequencies for the $\Delta M_J = \pm 1$ are obtainable from Eq. (4). We must add to the frequencies the small differences caused by the nuclear quadrupole coupling in the strong-field case. These were calculated with the formula (12)

$$W_q^{(1)} = eQq \left[\frac{3K^2}{J(J+1)} - 1 \right] \left\{ \frac{[3M_J^2 - J(J+1)][3M_I^2 - I(I+1)]}{4I(2I-1)(2J-1)(2J+3)} \right\}. \quad (6)$$

The frequency differences obtained from this hyperfine structure, with $I = 1$, $eQq = -4.35$ Mc/sec for the N¹⁴ of methyl cyanide, are at most a few tenths of one Mc/sec for the $J = 4 \rightarrow 5$ transition. In these experiments, nuclear splitting generally was not resolvable although the hyperfine structure did produce a noticeable broadening of the lines.

In the measurement of the dipole moment of methyl cyanide, problems exist which were not present in the measurement for methyl fluoride: the value of B_0 is so much smaller that a higher J transition is required if the lines are to

TABLE VII
ZERO-FIELD FREQUENCIES OF CD₃CN

$J \rightarrow J + 1$		K	Measured frequency ^a (Mc/sec)
5	6	0	94 293.446 ± 0.008
5	6	1	94 292.069 ± 0.005
5	6	2	94 288.091 ± 0.010
5	6	3	94 281.646 ± 0.007**
5	6	3	94 281.227 ± 0.010*
5	6	4	94 272.474 ± 0.008**
5	6	4	94 271.748 ± 0.011*
5	6	5	94 260.670 ± 0.008**
5	6	5	94 259.535 ± 0.012*
9	10	0	157 143.838 ± 0.009
9	10	1	157 141.650 ± 0.008
9	10	2	157 135.024 ± 0.014
9	10	3	157 123.983 ± 0.010
9	10	4	157 108.509 ± 0.004
9	10	5	157 088.568 ± 0.009
9	10	6	157 064.353 ± 0.012**
9	10	7	157 035.578 ± 0.017**
9	10	8	157 002.554 ± 0.012**
9	10	9	156 964.981 ± 0.015**

^a The hyperfine structure is partially resolved for the higher K lines. The lines marked with a double asterisk correspond to the unresolved components $F = J - 1$ to $F = J$ and $F = J + 1$ to $F = J + 2$; those marked with a single asterisk correspond to the transition $F = J$ to $F = J + 1$.

occur within the operating range of our parallel-plate spectrometer. In the higher transition the Stark lines have many more components, hence presenting a confusing array of lines. Because the level splitting given by Eq. (2) varies inversely with $J(J + 1)$, it was necessary for us to use a relatively higher field strength even with the first-order Stark effect so that the frequency measurements would not limit the ultimate accuracy of the dipole moment. Nevertheless, the large dipole moment of methyl cyanide causes the second-order Stark effect to become significant for the fields necessary to produce the desired first-order splitting. Instead of including the second-order corrections in the calculations, which would have required the solution of a quadratic equation for each dipole moment computation, we devised a scheme to bypass this difficulty. For each Stark line with quantum number M_J , there is another Stark line with $-M_J$ which has the same $\Delta\nu$ for the first-order effect, except with a minus sign. Furthermore, these two lines are shifted the same amount and in the same direction by the second-order effect. Therefore, if the frequency difference between these two Stark components is used for $2\Delta\nu$ in the first-order Stark equations, the second-order effect is removed from the calculations.

TABLE VIII
IDENTIFICATION OF $J = 4 \rightarrow 5$ COMPONENTS USED FOR STARK MEASUREMENTS
OF CH_3CN

Symbol used	ν_+ transition			ν_- transition			Theoretical value ^a ($\nu_+ - \nu_-$)/2 (Mc/sec)
	K	$M \rightarrow M'$		K	$M \rightarrow M'$		
<i>A</i>	1	4	5	1	-4	-5	$0.50344 \mu \varepsilon$ 30
	1	0	-1	1	0	1	
<i>B</i>	1	3	4	1	-3	-4	$0.50344 \mu \varepsilon$ 60
	1	-1	-2	1	1	2	
<i>C</i>	2	4	5	2	-4	-5	$0.50344 \mu \varepsilon$ 15
	2	0	-1	2	0	1	
<i>D</i>	2	3	4	2	-3	-4	$0.50344 \mu \varepsilon$ 30
	2	-1	-2	2	1	2	
<i>E</i>	3	4	5	3	-4	-5	$0.50344 \mu \varepsilon$ 10
	3	0	-1	3	0	1	
<i>F</i>	3	3	4	3	-3	-4	$0.50344 \mu \varepsilon$ 20
	3	-1	-2	3	1	2	

^a When μ is in Debye and ε in V/cm.

TABLE IX
STARK SPECTRUM FOR CH_3CN

Sym- bol ^a	$K = 1$			$K = 2$			
	($\nu_+ - \nu_-$)/2 (Mc/sec)	ε (V/cm)	μ (D)	Sym- bol ^a	($\nu_+ - \nu_-$)/2 (Mc/sec)	ε (V/cm)	μ (D)
<i>A</i>	15.478	235.537	3.916	<i>C</i>	30.929	235.543	3.912
<i>A</i>	19.313	294.028	3.914	<i>C</i>	38.596	294.026	3.911
<i>A</i>	23.169	352.897	3.912	<i>C</i>	46.370	352.905	3.915
<i>A</i>	25.202	384.087	3.910	<i>C</i>	50.444	384.104	3.913
<i>A</i>	30.798	469.525	3.909	<i>C</i>	61.612	469.458	3.910
<i>A</i>	34.678	527.538	3.917	<i>C</i>	69.236	527.533	3.910
<i>A</i>	38.514	586.262	3.915	<i>C</i>	76.964	586.198	3.912
<i>A</i>	42.252	644.267	3.909	<i>C</i>	84.713	644.218	3.918
<i>A</i>	52.800	804.545	3.911	<i>D</i>	15.464	235.539	3.912
<i>B</i>	7.731	235.534	3.912	<i>D</i>	19.318	294.028	3.915
<i>B</i>	9.660	294.031	3.916	<i>D</i>	23.190	352.905	3.916
<i>B</i>	11.590	352.892	3.914	<i>D</i>	25.232	384.087	3.915
<i>B</i>	12.614	384.074	3.914	<i>D</i>	30.855	469.500	3.916
<i>B</i>	15.429	469.552	3.916	<i>D</i>	34.604	527.545	3.909
<i>B</i>	17.317	527.545	3.912	<i>D</i>	38.456	586.237	3.909
<i>B</i>	19.238	586.292	3.911	<i>D</i>	42.280	644.255	3.911
<i>B</i>	21.166	644.287	3.915	<i>D</i>	52.881	804.550	3.917
		Average	3.913			Average	3.913

^a See Table VIII.

Another problem for methyl cyanide comes from the hyperfine structure caused by the N^{14} quadrupole coupling. This is not resolved, however, for the Stark lines in the strong-field case. It does broaden the lines somewhat, but does not shift them. Calculations of the quadrupole splitting with Eq. (6) show that the fine structure lines are shifted about equally toward high and low frequency within a given Stark line.

Although the $\Delta M = 0$ transitions have fewer components, the $\Delta M = \pm 1$ lines proved easier to measure. Certain of the latter components are coincident for the first-order Stark effect. These lines therefore are fairly strong, whereas all the other transitions are much weaker than they. The net result is that for the

TABLE X
SUMMARY OF VALUES OF DIPOLE MOMENTS MEASURED FOR DIFFERENT
TRANSITIONS OF CH_3CN AND CD_3CN

$CH_3CN J = 4 \rightarrow 5$			$CD_3CN J = 5 \rightarrow 6$		
K	$M_J \rightarrow M_{J'}$	$\mu(D)$	K	$M_J \rightarrow M_{J'}$	$\mu(D)$
1	4 5	3.913 ± 0.003	1	4 5	3.919 ± 0.004
	0 -1			-1 -2	
1	-4 -5	3.913 ± 0.003	1	-4 -5	3.919 ± 0.004
	0 1			1 2	
1	3 4	3.914 ± 0.002	2	5 6	3.918 ± 0.006
	-1 -2			0 -1	
1	-3 -4	3.914 ± 0.002	2	-5 -6	3.918 ± 0.006
	1 2			0 1	
2	4 5	3.913 ± 0.003	2	4 5	3.919 ± 0.005
	0 -1			-1 -2	
2	-4 -5	3.913 ± 0.003	2	-4 -5	3.919 ± 0.005
	0 1			1 2	
2	3 4	3.913 ± 0.003	2	3 4	3.920 ± 0.005
	-1 -2			-2 -3	
2	-3 -4	3.913 ± 0.003	2	-3 -4	3.920 ± 0.005
	1 2			2 3	
3	4 5	3.913 ± 0.006	3	5 6	3.919 ± 0.004
	0 -1			0 -1	
3	-4 -5	3.913 ± 0.006	3	-5 -6	3.919 ± 0.004
	0 1			0 1	
3	3 4	3.913 ± 0.003	3	4 5	3.919 ± 0.005
	-1 -2			-1 -2	
3	-3 -4	3.913 ± 0.003	3	-4 -5	3.919 ± 0.005
	1 2			1 2	
Average		3.913	Average		3.919

high J transitions fewer lines are prominent for the $\Delta M = \pm 1$ transition than for the $\Delta M = 0$ transition.

The various $\Delta M = \pm 1$ transitions which were measured for CH_3CN are identified in Table VIII. The symbol ν_+ is used to represent a given line that is shifted to a higher frequency than the zero field line. The dipole moment measurements are illustrated for the $K = 1$ and the $K = 2$ lines in Table IX. The experimental results for CH_3CN are summarized in Table X. The average dipole moment found for CH_3CN is 3.913 ± 0.002 D. The previous value (2) of 3.92 D found from the second-order Stark effect in a conventional waveguide cell is in good agreement.

The $J = 4 \rightarrow 5$ transition for CD_3CN occurs at 78.6 Gc/sec, which is below the operating frequency of the spectrometer. Consequently, the higher transition $J = 5 \rightarrow 6$ was measured for CD_3CN . Only the $\Delta M = \pm 1$ transitions were measured for the first-order Stark effect. The same scheme was used to remove the second-order Stark shift from the calculations as was described for CH_3CN . The transitions that were measured are identified in Table X, along with the dipole moment obtained from each. Too much space would be required to list the individual measurements from which these dipole moments were computed. However, the internal consistency of the results is comparable to that shown for CH_3CN in Table IX. The average value for the dipole moment for CD_3CN is 3.919 ± 0.004 D. For methyl cyanide, as for methyl fluoride, the dipole moment for the deuterated species is larger than that for the normal species, but the difference is not as great for the cyanide as for the fluoride.

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REFERENCES

1. D. M. LARKIN AND W. GORDY, *J. Chem. Phys.* **38**, 2329 (1963).
2. S. N. GHOSH, R. TRAMBARULO, AND W. GORDY, *J. Chem. Phys.* **21**, 308 (1953).
3. B. BHATTACHARYA AND W. GORDY, *Phys. Rev.* **119**, 144 (1960).
4. R. ZURMUHL, "Praktische Mathematik für Ingenieure und Physiker," p. 277. Springer-Verlag, Berlin, 1961.
5. C. M. JOHNSON, R. TRAMBARULO, AND W. GORDY, *Phys. Rev.* **84**, 1178 (1951).
6. W. J. O. THOMAS, J. T. COX, AND W. GORDY, *J. Chem. Phys.* **22**, 1718 (1954).
7. D. R. LIDE, JR., *J. Chem. Phys.* **33**, 1519 (1960).
8. H. RING, H. EDWARDS, M. KESSLER, AND W. GORDY, *Phys. Rev.* **72**, 1262 (1947).
9. P. VENKATESWARLU, J. G. BAKER, AND W. GORDY, *J. Mol. Spectry.* **6**, 215 (1961).
10. D. K. COLES, W. E. GOOD, AND R. H. HUGHES, *Phys. Rev.* **79**, 224(A) (1950).
11. M. KESSLER, H. RING, R. TRAMBARULO, AND W. GORDY, *Phys. Rev.* **79**, 54 (1950).
12. W. LOW AND C. H. TOWNES, *Phys. Rev.* **76**, 1295 (1949).