PHYSICAL REVIEW VOLUME 84, NUMBER 3 NOVEMBER 1, 1951

Microwave Spectrum of Methyl Alcohol

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(Received June 4, 1951)

A series of absorption lines of $C^{12}H_3O^{16}H$ which was studied from $J=2$ to $J=10$ by Coles has now been followed up to $J=30$. The corresponding series for $C^{13}H_3O^{16}H$ and $C^{12}H_3O^{18}H$ have been found. The lines of the $C^{13}H_3O^{16}H$ series have been identified and measured from $J=2$ to $J=31$ and the lines of the $C^{12}H_3O^{18}H$ series from $J=2$ to $J=26$. Accurate Stark-effect measurements have been made of several low J lines of each of the above series and the coefficients tabulated. The frequencies of many other $C^{12}H_3O^{16}H$ lines between 20,000 and 40,000 Mc have been measured and tabulated. The order of the Stark effect, quantitative Stark-effect information, and J values of these lines are listed when known. The frequencies of several $C^{13}H_3O^{16}H$ lines which are not members of the above series are listed.

METHYL alcohol is one of the lightest and simplest molecules which is capable of internal rotation. In this molecule (Fig. 1), the OH group rotates around the axis of the CH_3 group. Since many of the alcohol absorption lines in the microwave region involve changes in both the internal and external rotations of the molecule, considerable information on both types of rotation is obtainable from the microwave spectrum. Because of the excellent resolution in the microwave region, it appears that microwave data are eminently suited for investigating the phenomenon of internal rotation in molecules.

Hershberger and Turkevich[1] and Dailey[2] have reported about twenty-five microwave absorption lines for ordinary methyl alcohol. Dailey discovered that some of the lines possess a linear Stark effect, and divided the lines between 20,000 and 26,000 Mc into those with symmetric Stark-effect patterns and those with asymmetric patterns. Five of the lines appeared to form a converging series. Coles[3] resolved the first "line" in this series into three separate lines and, by counting Stark components, was able to establish the J values of the lines from $J=2$ up to $J=10$. He measured the frequencies of these lines accurately and determined the coefficients of the first-order Stark effects. Dennison and Burkhard[4] have identified this series with the (absorptive) transitions $K=1\rightarrow 2$; $\tau=2\rightarrow 1$ and $J\rightarrow J$.

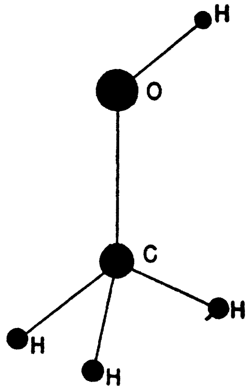

FIG. 1. Methyl alcohol molecule.

This paper describes a much more extensive study of ordinary methyl alcohol. Two other isotopic methyl alcohols have been prepared and studied. For their preparation see the Appendix. In particular, the aforementioned series has been found and traced in the spectra of $C^{13}H_3OH$ and $CH_3O^{18}H$. No attempt has been made to locate all the lines detectable on our spectrograph for these latter two isotopic molecules. Stark-effect studies of many of the lines are reported below.

Most of the methyl alcohol lines that we have observed exhibit a first-order Stark effect, similar to that exhibited by symmetric-top molecules. This appeared somewhat surprising to us, since the reported levels of rigid asymmetric rotors do not possess a linear Stark effect. In the case of very slightly asymmetric rigid rotors, the K-type doubling may be too small to resolve, so that they appear to have a first-order Stark effect, or a very close degeneracy may occur accidentally. But in any event, a necessary condition for a first-order Stark effect is a degeneracy of two rigid rotor levels of different symmetry species. In their theoretical treatment of the symmetrical rotator with hindered rotation (an approximation to the methyl alcohol molecule) Koehler and Dennison[5] pointed out that the internally rotating CH_3 group triples the number of energy levels, but at the same time brings about certain essential (and some nonessential) double degeneracies. The later theoretical discussion of methyl alcohol by Burkhard and Dennison (previous paper) deals with the modification in the levels and wave functions when an asymmetry is introduced. It is found that, in addition to a shift in the position of the levels, one-third of them are split into doublets and that this splitting is the exact analog of the splitting of the

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[1] W. D. Hershberger and J. Turkevich, Phys. Rev. **71**, 554 (1947).

[2] B. P. Dailey, Phys. Rev. **72**, 84 (1947).

[3] D. K. Coles, Phys. Rev. **74**, 1194 (1948).

[4] See the preceding paper. Their preliminary results were presented in 1948 and 1949 at the Ohio State Symposia on Molecular Structure.

[5] J. S. Koehler and D. M. Dennison, Phys. Rev. **57**, 1106 (1937).

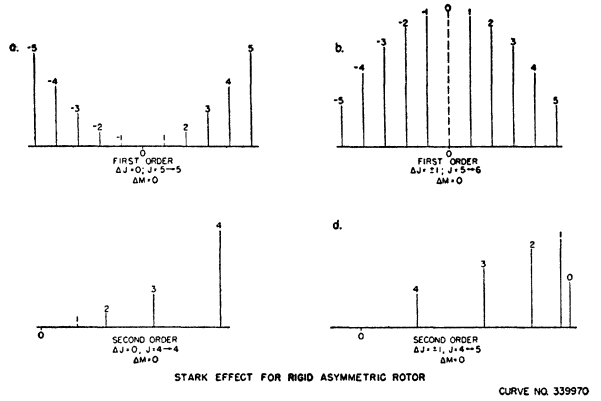

FIG. 2. Typical Stark effect patterns for asymmetric rotors. Methyl alcohol exhibits all types except c. This figure was drawn using the formulas given by S. Golden and E. B. Wilson, Jr., J. Chem. Phys. **16**, 669 (1948). The first-order Stark effect shown above is caused by a very close degeneracy of two asymmetric rotor levels of the same J. Dr. Kenneth Hurd has kindly pointed out to us that Fig. 2 does not include patterns due to a very close degeneracy of two levels of different J. An exact degeneracy of the type referred to by Dr. Hurd appears to be rather rare, however, in high resolution spectroscopy. It may be referred to as an "accidental" degeneracy. The type of degeneracy indicated in Figs. 2a and 2b may be called a "K-type" degeneracy—since it is due to a close coincidence of two levels with the same value of J and K. For many rigid molecules K-type degeneracy occurs for the higher values of K. For example, if the methyl alcohol were rigid, the two levels with $J=4$ and the same value of $K=4$ would be separated by about 0.0001 Mc. Higher values of $K=J<40$ would have a still smaller splitting. Such a very close K-type doublet would be observed as a single level possessing a first-order Stark effect.

levels of a rigid symmetric rotor when an asymmetry is introduced. They state that the lines of our series $K=1\rightarrow 2$, $\tau=2\rightarrow 1$, $J\rightarrow J$ arise from transitions between levels which are not split into doublets and they predict that these lines should show a first-order Stark effect in agreement with our observations.

Since the symmetric rotor possesses a first-order Stark effect while an asymmetric rotor with its K-type doubling does not, it seems very plausible that the doublet levels of the methyl alcohol molecule will not possess a first-order Stark energy. Burkhard and Dennison inform us that this appears to be the case although all of the details have not been worked out yet. Experimentally, about twelve lines have been found which do not possess a first-order Stark effect. In such lines only a small second- (or higher) order Stark effect is observed.

APPARATUS

A microwave spectrograph employing Stark-effect modulation[6] was used for all of these measurements. Sine-wave modulation at 85 kc was employed during most of the work although square wave modulation at 85 kc was used occasionally. The accurate frequency measurements were accomplished with a frequency standard very similar to that previously described.[6,7] A Collins 51-J receiver was used to interpolate between the 50-Mc reference frequencies obtained on the addition of a small 50-Mc voltage to the standard 500-Mc signal fed into the harmonic generator. It is believed that most of the frequencies quoted in the tables are within ±0.1 Mc and that many are closer than that.

THE SPECTRUM OF $C^{12}H_3O^{16}H$

A survey has been made of the spectrum of a sample of chemically pure methyl alcohol between 20,000 and 40,000 Mc. The spectrum is rich in strong lines and contains over one hundred lines with intensities greater than 10^{-8} cm^{-1}. Table I lists eighty-five lines, most of which are associated with $C^{12}H_3O^{16}H$. Lines known to be due to $C^{13}H_3O^{16}H$ and $C^{12}H_3O^{18}H$ are listed in Tables IV and V. Some of the weaker lines of Table I may be strong lines of the isotopic molecules, but all lines for which the J value has been specified are known to arise from the most abundant isotopic molecule. From the appearance of the lines on the Stark-effect microwave spectrograph, the lines are readily separated into those giving a first-order Stark effect and those giving a second-order Stark effect.

The existence of a series of several lines was first indicated by Hershberger and Turkevich[1] and later by Dailey[2] and Coles.[3] These lines exhibit first-order Stark patterns such as that shown in Fig. 2a, splitting up into $2J$ components symmetrically placed about the original line frequency. As the outer components are most intense and the intensities seem to be proportional to M^2, it appears that $\Delta J=0$ for these transitions. Dennison and Burkhard,[4] have suggested an interpretation for this series of lines. From the fact that the first line is $J=2$, they concluded that K changes from 1 to 2. From energy considerations they have identified this series as arising from transitions in which the external quantum number K changes from 1 to 2, the internal quantum number τ changes from 2 to 1, and

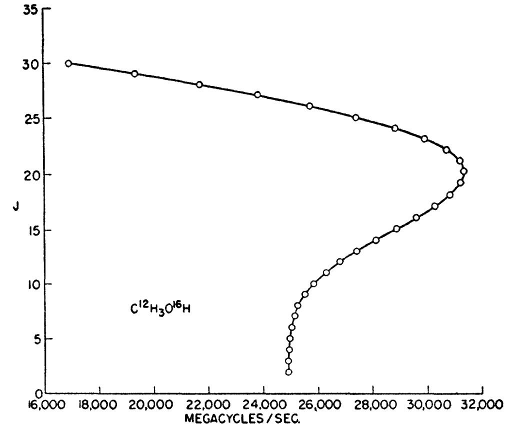

FIG. 3. Series of first-order Stark-effect lines in $C^{12}H_3O^{16}H$, arranged according to their rotational quantum number, J.

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[6] McAfee, Jr., Hughes, and Wilson, Jr., Rev. Sci. Instr. **20**, 821 (1949). A. H. Sharbaugh, Rev. Sci. Instr. **21**, 120 (1950).

[7] W. E. Good and D. K. Coles, Phys. Rev. **71**, 383 (1947).

TABLE I. Methyl alcohol spectrum (mainly $C^{12}H_3O^{16}H$).

Lower J	$\pm\Delta J$[a]	Frequency	Stark order	Intensity
30	0	16,941.6	1	*W*
...	...	17,911.1	...	...
29	0	19,390.18	1	*W*
...	...	20,171.07	...	*M*
...	...	20,346.83	1	...
high	...	20,908.87	1	...
10 or 11	1	20,970.65	2	*M*
...	...	21,244.2	...	*W*
10 or 11	1	21,550.31	2	*M*
28	0	21,708.68	1	*W*
8 or more	1	23,121.20	2	*M*
...	...	23,347.53	2	*W*
8 or 9	1	23,444.82	2	*M*
27	0	23,854.25	1	*W*
...	...	24,533.7	2	*W*
3	0	24,928.70	1	*M*
4	0	24,933.47	1	*M*
2	0	24,934.38	1	*M*
5	0	24,959.08	1	*S*
6	0	25,018.14	1	*S*
...	...	25,056.31	2	*W*
7	0	25,124.88	1	*S*
8	0	25,294.41	1	*S*
		25,322.98	1	*W*
9	0	25,541.43	1	*S*
26	0	25,787.12	1	*W*
10	0	25,878.18	1	*S*
9 or 10	1	26,120.50	2	*M*
11	0	26,313.11	1	*M*
...	...	26,550.15	...	*W*
...	...	26,778.9	...	*W*
...	...	26,783.18	...	*W*
12	0	26,847.27	1	*M*
...	...	27,227.02	...	*W*
12 or more	1	27,283.29	1	*S*
25	0	27,470.99	1	*W*
13	0	27,472.54	1	*M*
...	...	27,700.1	2	*M*
...	...	27,817.50	...	*W*
...	...	27,820.87	...	*M*
...	...	28,119.5	...	*W*
14	0	28,169.31	1	*M*
3	1	28,316.03	1	*M*
24	0	28,874.45	1	*W*
15	0	28,905.70	1	*M*
8, 9, or 10	1	28,969.9	2	*M*
...	...	29,113.76	1	*M*
16	0	29,636.91	1	*M*
...	...	29,889.33	1	
23	0	29,973.06	1	*W*
17	0	30,308.00	1	*M*
...	...	30,678.66	1	*W*
...	...	30,693.42	...	*W*
22	0	30,752.26	1	*M*
18	0	30,858.40	1	*M*
21	0	31,209.75	1	*M*
19	0	31,226.70	1	*M*
20	0	31,358.31	1	*M*
...	...	31,673.05±0.2	...	*W*
high J	...	31,757.42	1	*M*
...	...	31,977.82	1	*M*
...	...	32,379.37	1	*M*
...	...	32,398.44	...	*W*
...	...	33,089.91	1	*M*
...	...	33,414.1±0.2	...	*W*
...	...	33,566.20	...	*W*
...	...	33,568.2±2	...	*W*
18 to 22	1	33,691.63	2	*M*
18 to 22	1	33,693.74	2	Forbidden
18 to 22	1	34,001.35	2	Forbidden
18 to 22	1	34,003.69	2	*M*
14 or greater	1	34,236.91	1	*S*
...	...	34,417.86	1	*M*
...	...	35,161.6	2	
...	...	35,478.55	...	*W*
...	...	35,738.32	...	*W*
3	1	36,169.24	1	*M*
high	...	36,248.14	1	*M*
...	...	37,044.68	1	*M*
7	1	37,703.72	1	*M*
5	1	38,293.5	1	*M*
5	1	38,452.69	1	*M*

[a] All of the $\Delta J=0$ lines belong to a series identified by Burkhard and Dennison as $K=1\rightarrow 2$, $\tau=2\rightarrow 1$, and $J\rightarrow J$.

the over-all rotational quantum number J remains constant.

We have now extended this series from $J=10$ to $J=30$ (see Fig. 3). The $J=11$ and 12 lines were definitely identified by splitting the lines into components and counting them. This procedure becomes more and more difficult for larger J's because of the large number of weak components. As there are quite a few other first-order lines in the region of this series which do not belong to it, a method is needed for identifying the high J's. The high J's were identified by constructing a table of differences up to the seventh difference, by which means it was possible to predict the frequency of a line within a few megacycles. The series was not taken beyond $J=30$ because the equipment required to go below 16,000 Mc was not readily available.

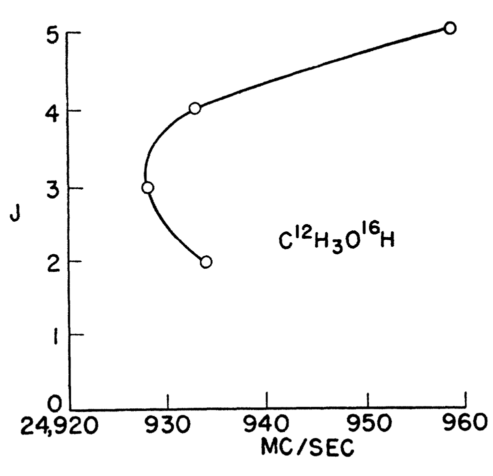

FIG. 4. Start of series of Fig. 3.

The plot of the series in Fig. 3 shows that the line spacing is very small for the lower members of the series, but tends to get larger with increasing J. The series changes direction at $J=20$. Figure 4 shows the start of the series. It will be noted the $J=2$ is at a higher frequency than $J=3$ and $J=4$. There is a possibility that some very weak lines in Table I are caused by J's around 40 for which values the (reversed) transition frequency may be back in this microwave region.

The intensities of these lines have not been measured. The lines appeared to become stronger from $J=2$ up to about $J=15$ and then to get weaker again. From the facts that the $J=5$ and 6 lines of $C^{12}H_3O^{18}H$ were several times noise in a naturally occurring methyl alcohol sample and that the sensitivity of the spectrograph is close to 10^{-8} cm^{-1}, the intensities of the $J=5$ and 6 lines are estimated to be between 1 and 5×10^{-6} cm^{-1}. The most intense lines are probably somewhat more intense than 5×10^{-5} cm^{-1}. The following ranges are assumed for the estimated intensities in Tables I, IV, and V: $S>10^{-5}$ cm^{-1}; $10^{-5}>M>5\times10^{-7}$ cm^{-1}; 5×10^{-7} cm$^{-1}>W$. The Stark effect of the first members of this series is discussed in detail in the section, "Quantitative Stark-Effect Measurements."

There are several other first-order Stark-effect lines in this spectrum. They show Stark-effect patterns such as that displayed in Fig. 2b for which the following formula applies:[8]

$$\Delta\nu_M(\text{Mc})=BME(\text{esu}), \qquad (1)$$

where $\Delta\nu_M$ is the frequency deviation of the Mth component from the original line frequency, and E is the field intensity in electrostatic units. All components except $M=0$ have a first-order Stark effect while the latter, shown dotted, has a second-order Stark effect. As the inner components on either side of the original line frequency are most intense, we assume that $\Delta J=\pm1$ for these transitions. The coefficients of ME for the components of these are listed in Table II. Twelve components were counted on each side for the line listed as $J=12$ or more, although it was difficult to determine the exact number of components because the outer ones became very weak. Despite the fact that the J value was not determined unambiguously, the coefficient B can be determined with certainty.

There is a set of four lines in the ordinary methyl alcohol spectrum which gives rise to a much more complicated Stark pattern than do any of the lines mentioned previously. These lines form a set very similar to that shown in Fig. 5 for $C^{13}H_3O^{16}H$, which we call a mirror image pattern. Two of the lines, those which occur at 33,691.63 and 34,003.69 Mc, are second order at low voltages with the components of one line moving in opposite directions from those of the other on the application of a weak field. At 33,693.74 and 34,001.35 there are forbidden lines which begin to appear only when a Stark field is applied. At a field of a few volts per cm a second-order line and its neighboring forbidden line seem to merge and the mixture gives a Stark effect which appears to be approximately first order. The coefficient of ME for the mixture of the two lines near 34,000 Mc has been determined to be 1.25 Mc/esu. From the fact that the first-order Stark effect pattern is similar to that of Fig. 2b, it is concluded that $\Delta J=\pm1$ during these transitions. Eighteen components were counted on one side of the Stark pattern, but the outer ones were so weak that the end of the pattern could not be determined. There were indications that there were more components and that the J value was probably somewhere between 18 and 22. A more complete description of a mirror image set of this type is given in the section on $C^{13}H_3O^{16}H$, since the $C^{13}H_3O^{16}H$ set was easier to study.

TABLE II. Linear Stark-effect coefficients for $C^{12}H_3O^{16}H$ lines with $\Delta J=\pm1$.

Lower J	Frequency (Mc)	B, coefficient of ME (Mc/esu)
12 or more	27,283.29	0.93
3	28,316.03	3.40
14	34,236.91	0.82
3	36,169.24	6.52
7	37,703.72	3.09
5	38,293.32	13.0
5	38,452.69	13.0

The two $J=5$ lines listed in Table II appear to be related. The lines are unsymmetrical at low voltages. They both appear to be first order at low voltages, but with stronger components on the low frequency side of the low frequency line and on the high frequency side of the high frequency line, giving the lines a mirror image appearance. On the application of increasing voltage the components on the sides of the same line become more equal in intensity, and there is some possibility that there is even an interchange in intensities with the weaker components becoming the stronger at the higher voltages. These lines may be the same type as those discussed in the previous paragraph, but with the separation between a line and its neighboring forbidden transition smaller than the resolution of the spectrograph.

Eleven lines with a second-order Stark effect have been observed in the methyl alcohol spectrum in addition to the two in the mirror image pattern discussed previously. For a typical Stark pattern refer to Fig. 2d. These lines appear to have Stark effects in fair agreement with the rigid rotor formula:[8]

$$\Delta\nu_M(\text{Mc})=(C+DM^2)E^2(\text{esu}), \qquad (2)$$

where $\Delta\nu_M$ is the deviation in Mc of the frequency of the component M from the original line frequency, and

TABLE III. Approximate Stark-effect coefficients of second-order lines.

Frequency	C[a] (Mc/(esu)^2)	D[a] (Mc/(esu)^2)	Lowest possible value of the smaller J
20,970.65	+	+	10
21,550.31	see following discussion		10
23,121.20	+	+	8
23,347.53	+	+	...
23,444.82	+0.16	+0.011	8
26,120.50	0.32	−0.038	9
27,700.1	+	−	...
28,969.0	+0.16	−0.034	8
35,161.6	+	+	...

[a] Refer to Eq. (2).

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[8] S. Golden and E. Bright Wilson, Jr., J. Chem. Phys. **16**, 669 (1948).

TABLE IV. Spectrum of $C^{13}H_3OH$.

Lower J	$\pm\Delta J$[a]	Frequency	Stark order	Intensity
31	0	17,870.5	1	*W*
30	0	20,329.32	1	*W*
29	0	22,672.90	1	*W*
28	0	24,860.62	1	*W*
27	0	26,855.01	1	*W*
12	1	26,979.03	2	*M*
12	1	26,980.40	2	forbidden
3	0	27,047.19	1	*M*
4	0	27,050.45	1	*M*
2	0	27,052.97	1	*M*
5	0	27,072.17	1	*M*
12	1	27,104.80	2	forbidden
12	1	27,105.93	2	*M*
6	0	27,122.76	1	*M*
7	0	27,215.60	1	*M*
8	0	27,364.12	1	*M*
9	0	27,581.65	1	*M*
10	0	27,880.04	1	*M*
11	0	28,267.71	1	*M*
26	0	28,621.04	1	*W*
12	0	28,747.67	1	*M*
...	...	28,869.59	1	...
13	0	29,315.20	1	*M*
14	0	29,955.72	1	*M*
25	0	30,127.80	1	*W*
15	0	30,643.69	1	*M*
16	0	31,342.31	1	*M*
24	0	31,350.19	1	*W*
17	0	32,004.43	1	*M*
23	0	32,271.10	1	*W*
18	0	32,575.53	1	*M*
22	0	32,883.47	1	*M*
19	0	32,998.94	1	*M*
21	0	33,192.97	1	*M*
20	0	33,220.05	1	*M*

[a] See footnote to Table I.

E is the electrostatic field strength in electrostatic units. C and D are roughly constant. It is believed that these lines are $J\rightarrow J\pm 1$, as the components of low M are strongest. Table III lists information about the second-order Stark-effect lines which have been studied in detail. Because of the experimental difficulties of observing the outer weak components and of the difficulty of resolving the inner components, the Stark coefficients and J values are only approximate. The line at 21,550.31 Mc has been studied in more detail and at least eleven components were seen. The pattern is best described by the following equation containing a fourth-order term:

$$\Delta\nu_M = 0.33E^2 + 1.74\times 10^{-2}M^2E^2 - 1.18\times 10^{-6}M^4E^4. \quad (3)$$

The E^4 dependence of the last term has not been definitely established.

Bak, Knudsen, and Madsen[9] have reported eighteen lines of methyl alcohol. Our results are in agreement with theirs if we assume that certain of their lines between 24,901 and 25,449 Mc are actually smeared-out Stark components produced by the high electric fields they employed.

Miss Girdwood has reported on the microwave spectrum of methyl alcohol in the *Canadian Journal of Research.*[10] She lists a large number of lines between 23,500 and 24,900 Mc which are not to be found in Table I. We have not been able to detect others than those listed in the table even on searching through the spectral region several times. Dr. A. L. Schawlow of Columbia University[11] has not been able to find the new lines nor does he detect the shifts in the line frequencies of methyl alcohol when water vapor is admitted to the wave guide, as reported by Miss Girdwood. We suspect that most of the lines in her tabulation (which are spaced regularly about sixty Mc apart) are due to standing waves in the apparatus, rather than to absorption by methyl alcohol.

The large number of accurately measured lines should make this substance useful for the rough calibration of wave meters throughout the region of from 20,000 to 40,000 Mc. Since many of these strong lines have a linear Stark effect, they should be useful as standards for the calibration of a Stark-effect wave guide at low voltages. A line especially recommended for this use is the $J=3\rightarrow 4$ at 36,169 Mc which is rather intense.

THE SPECTRUM OF $C^{13}H_3O^{16}H$

Table IV contains the lines which have been definitely proven to be given by $C^{13}H_3O^{16}H$. These are lines which are much stronger in a concentrated sample than they are in an ordinary methyl alcohol sample.

A series of first-order Stark-effect lines very similar to that for $C^{12}H_3O^{16}H$ shown in Fig. 3 corresponding to the transitions $K=1\rightarrow 2$, $\tau=2\rightarrow 1$, and $\Delta J=0$ has been found for this molecule. It starts just above 27,000 Mc instead of at 24,928 Mc as in the ordinary alcohol and reaches a maximum frequency at the same J value of 20. The members have been identified from $J=2$ up to $J=31$. The beginning of the series is very similar to that in Fig. 4, except that $J=4$ is midway between $J=3$ and $J=2$.

There is a set of four lines plotted in Fig. 5 which give rise to a complicated Stark pattern. The lines at 26,979.03 and 27,105.93 are second order at low voltages. As the components of the lower line move towards lower frequencies and the components of the high frequency line move toward higher frequencies, the lines appear to be mirror images. Near each of these lines there is a forbidden line which appears only when

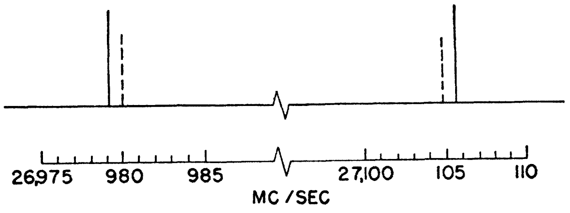

FIG. 5. Mirror image pattern in $C^{13}H_3O^{16}H$. The solid lines are allowed transitions, the dotted ones are forbidden transitions (in the absence of an electric field).

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[9] Bak, Knudsen, and Madsen, Phys. Rev. **75**, 1622 (1949).

[10] B. Girdwood, Can. J. Research **28**, 180 (1950).

[11] A. L. Schawlow, private correspondence.

a voltage is applied. With increasing voltage the "forbidden" line becomes stronger and stronger. At a field of a few volts per cm, each allowed line and its neighboring "forbidden" line seem to merge. At a slightly higher voltage the mixture gives a Stark effect which is approximately first order. A plot of the position of the components from the mixed lines near 26,980 Mc is shown in Fig. 6 for two voltages. As the lines at these voltages appear to be first order, the coefficient of ME is roughly determined to be 3.5 Mc/esu. The patterns are unsymmetrical, with frequency displacements on the low frequency side being ten percent greater than those on the high frequency side. The pair at 27,106 Mc, show the same Stark pattern with approximately the same coefficient. From the fact that the inner components are most intense, we conclude that $\Delta J = \pm 1$.

It appears that the observations on the "mirror image" lines can be brought into accord with the theory proposed by Burkhard and Dennison. These lines may correspond to transitions between doublet levels. (See Fig. 7.) Between two doublet levels four transitions are in principle possible but the selection rules, in the absence of external perturbations, exclude two of these. The Stark electric field does, however, perturb the system and hence these extra or forbidden lines may appear. From our experimental data it is impossible to tell whether the larger splitting belongs to the upper level, as shown in Fig. 7, or to the lower level.

The second-order Stark coefficient should be large because of the near degeneracy of the two lower levels. At rather low field strengths the two levels originally separated by 1.2 Mc merge and the Stark effect becomes first order. A theoretical discussion of the Stark effect of slightly asymmetric rigid rotors by Penney[12] seems to apply qualitatively to this particular group of levels, even though the over-all energy level scheme is greatly changed in methyl alcohol by the phenomenon of internal rotation.

One other line was found for the C^{13} concentrated sample. An extensive search for other lines was not made, because our primary objective was to provide information on the isotope effect of the long series of first order lines. Undoubtedly, there are other first-order lines and some second-order lines in this spectral region.

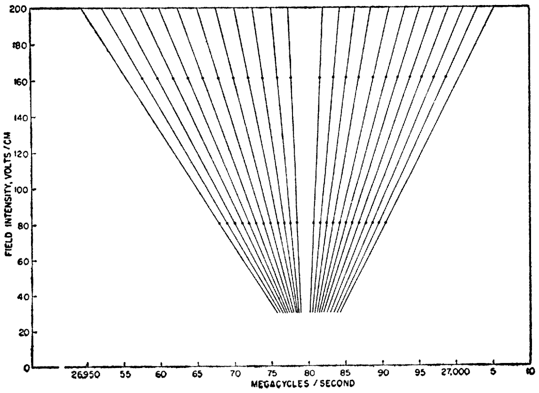

FIG. 6. Stark effect of lower frequency pair of lines in Fig. 5.

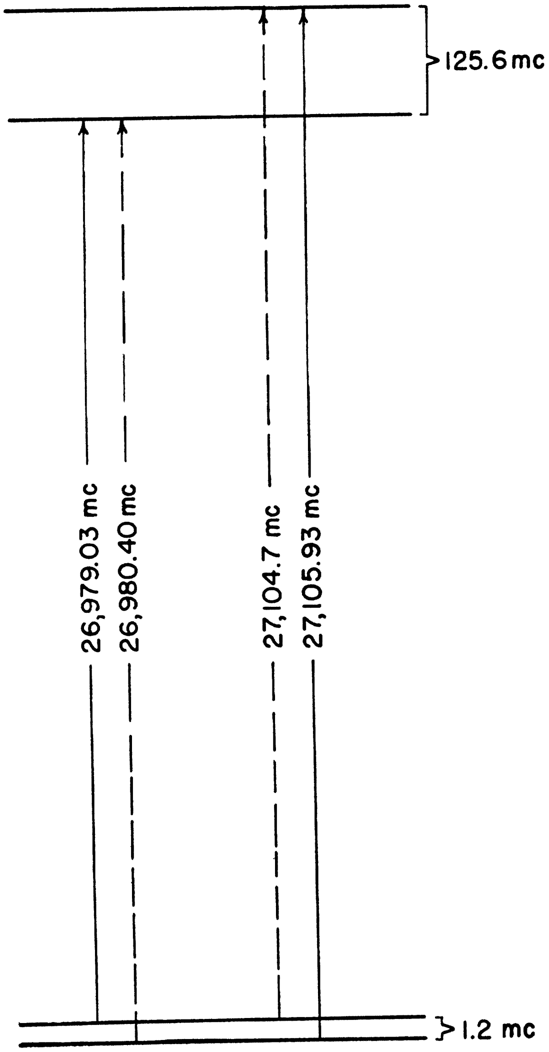

FIG. 7. A possible energy level diagram to explain the mirror image pattern of Fig. 5.

THE SPECTRUM OF $C^{12}H_3O^{18}H$

The spectrum of a sample containing twenty percent $C^{12}H_3O^{18}H$ and eighty percent $C^{12}H_3O^{16}H$ has been observed between 33,900 and 39,700 Mc. Table V lists the lines known definitely to come from $C^{12}H_3O^{18}H$. This list contains only lines belonging to the series $K=1\rightarrow 2$, $\tau=2\rightarrow 1$, and $J\rightarrow J$ which corresponds to that seen for the other isotopic molecules. This series, which starts at 33,918 Mc instead of at 24,928 for the ordinary molecule, has much the same appearance as that for the ordinary methyl alcohol shown in Fig. 3. Its beginning is different from that of the other two

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[12] W. G. Penney, Phil. Mag. **11**, 602 (1931).

TABLE V. Spectral lines of $C^{12}H_3O^{18}H$.

Lower J	$\pm\Delta J$[a]	Frequency	Stark order	Intensity
2	0	33,918.97	1	*M*
3	0	33,925.49	1	*M*
4	0	33,943.63	1	*M*
5	0	33,981.35	1	*M*
6	0	34,048.42	1	*M*
7	0	34,155.63	1	*M*
8	0	34,314.64	1	*M*
9	0	34,536.74	1	*M*
26	0	34,761.75	1	*W*
10	0	34,831.64	1	*M*
11	0	35,206.11	1	*M*
12	0	35,661.78	1	*M*
13	0	36,193.55	1	*M*
25	0	36,312.57	1	*W*
14	0	36,787.33	1	*M*
15	0	37,418.97	1	*M*
24	0	37,579.85	1	*W*
16	0	38,053.87	1	*M*
23	0	38,547.73	1	*W*
17	0	38,647.87	1	*M*
18	0	39,149.41	1	*M*
22	0	39,210.48	1	*M*
19	0	39,505.01	1	*M*
21	0	39,574.97	1	*M*
20	0	39,661.80	1	*M*

[a] See footnote of Table I.

isotopic species in that the $J=2$ transition has the lowest frequency. Although difficulty was experienced in finding the high J lines because of the low concentration of the $C^{12}H_3O^{18}H$, it has been studied from $J=2$ up through $J=26$. No extensive study has been made of the spectrum of this molecule. There must be other first-order lines and several second-order lines in the spectral region between 20,000 and 40,000 Mc.

QUANTITATIVE STARK-EFFECT MEASUREMENTS

Accurate Stark-effect measurements have been made on the early members of the first-order series of the three isotopic molecules. Less accurate measurements made of several of the other first-order lines as well as on some of the second-order lines in ordinary methyl alcohol have been discussed earlier.

A Stark-effect microwave spectrograph incorporating an X-band wave guide with a center electrode was used for these measurements. To determine the coefficients the line was split into components with dc fields of from ten volts/cm up to several hundred volts/cm. The dc voltage applied to the electrode was measured by a type K potentiometer after reduction by a voltage dividing network, giving voltage measurements better than 0.1 percent. A low 85-kc modulating voltage was used to make the components visible on the spectrograph. Frequencies were measured with the same standard used in making line frequency measurements. The wave guide was calibrated by measuring the Stark effect for methyl fluoroform, taking the measurements of Shulman and others[13] as standard. The dimension of the wave guide was also measured and found to correspond with that calculated from the above calibration with methyl fluoroform.

Coles[3] found that the frequency shift for a Stark component of a line of the $C^{12}H_3O^{16}H$ series is rather accurately described by the following formula:

$$\Delta\nu_{MJ}(\mathrm{Mc})=[A(J^2+J)^{-1}+B]ME(\mathrm{esu}), \qquad (4)$$

where $\Delta\nu_{MJ}$ is the shift of the Mth Stark component from the line center frequency in Mc, and A, B are constants.

A plot of the results of our measurements for the three series is shown in Fig. 8. Here a small contribution from a term proportional to M^2 was eliminated by taking the average shift of the components M and $-M$. An interesting point to note is that the three lines extrapolate to the same point at $J(J+1)=0$. A more surprising result is the pronounced increase in the slope, by 50 percent, on substituting O^{18} for O^{16}. From the above plot, the following equations have been derived for the Stark effects of the three series:

$C^{12}H_3O^{16}H$:

$$\Delta\nu_{MJ}(\mathrm{Mc})=[131.1/(J^2+J)+1.710]ME(\mathrm{esu}) \qquad (5)$$

$$C^{13}H_3O^{16}H\text{: }\Delta\nu(\mathrm{Mc})=[131.3/(J^2+J)+1.751]ME \qquad (6)$$

$$C^{12}H_3O^{18}H\text{: }\Delta\nu(\mathrm{Mc})=[131.0/(J^2+J)+2.646]ME. \qquad (7)$$

The coefficients obtained by Coles[3] for $C^{12}H_3OH$ differ from these values by about 2 percent, because he made no correction for the wave guide being different from its nominal size. In Eq. (2) of the same article, the factor $M/(J^2+J)^{\frac{1}{2}}$ should have been placed outside of the square bracket.

As mentioned previously, the displacement of each component has a small contribution from terms higher in order than the first. The coefficients of E^2 for some of the components of lines of $C^{12}H_3O^{16}H$ are given as follows:

J	M	Coefficient of E^2 (Mc/(esu)^2)
2	Av. of 2 and -2	0.37
3	-3	0.38

As these results are probably not much better than ±15 percent they should be considered only as order of magnitude determinations. No extensive studies of the E^2 dependence have been made of any of the other lines of ordinary methyl alcohol. It is probable that these terms also have an M^2 dependence, but not enough experimental evidence was obtained to prove this point.

The M^2 dependence has been studied for the $J=7$ and 9 lines of the series for ordinary methyl alcohol, however, at a fixed voltage with the follcwing results:

J	Field in esu	Coefficient of M^2 (Mc)
7	1.345	0.024
9	1.345	0.0165

These figures are believed to be accurate within ±10

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[13] Shulman, Dailey, and Townes, *Stark Effects in Microwave Spectroscopy*, Columbia Radiation Laboratory (1949).

percent. As no measurements were taken at different voltages, it is not known if this contribution comes from a M^2E^2 term.

CONCLUSION

Because of the additional complexity introduced into this spectrum by the internal rotation, a detailed analysis of the spectrum is a difficult problem. Interpretation of the main features of the spectrum has already been achieved by D. M. Dennison and associates.[4,5,14] For a complete solution it is desirable to have supplemental microwave information at higher frequencies, and some measurements on the deuterated compounds. Fortunately, considerable progress in these two directions has already been achieved at Duke University.[15] It appears that an analysis of these microwave data will provide a rather exact determination of the structure and hindering potential barrier in this molecule, the lightest and simplest representative of a large and important class of molecules capable of internal rotation.

APPENDIX

Preparation of $C^{13}H_3O^{16}H$

This material was prepared by the hydrolysis of methyl iodide containing C^{13}. At 80°C or higher water hydrolyzes methyl iodide, replacing the iodine by a hydroxyl group. Approximately 1 gram of Eastman Kodak concentrated C^{13} methyl iodide (roughly 50 percent $C^{12}H_3I$ and 50 percent $C^{13}H_3I$), 0.6 g of sodium hydroxide, and 1 g of water were put into a 500 ml flask cooled with dry ice to prevent loss of the volatile methyl iodide. The sodium hydroxide neutralizes the hydroidic acid formed during the reaction and may help increase the velocity of the reaction by increasing the hydroxyl ion concentration. After cooling the flask with liquid air, the air was pumped out and the flask sealed to prevent loss of the very volatile reactant and product during the prolonged heating. The flask was heated for several days at 90°C. Testing for methyl iodide by cooling the flask with liquid air and then observing the amount of dense oily methyl iodide present in warming the flask showed it to be present until the fifth day. After the mixture was cooled with liquid air, the noncondensible gases were pumped off. One-half hour of pumping on the sample at dry ice temperature was necessary to remove the small amount of methyl iodide still remaining.

Because of the small amount of product, excessive losses would occur during an ordinary distillation. The vapor pressure of alcohol is between 0.01 and 0.1 mm of mercury at dry ice temperature which is adequate for microwave spectroscopy. The pressure of water at dry ice temperature is not sufficient to dilute the alcohol vapor appreciably. After the sample had been cooled by a dry ice bath, its vapor was used to fill the absorption cell. Although this sample has been used to fill the guide many times, there is no apparent reduction in its delivery.

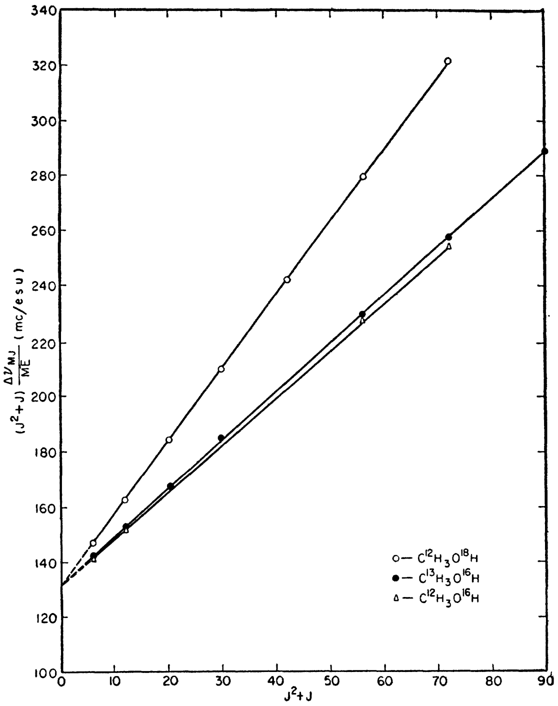

FIG. 8. Stark-effect coefficients for the series of first-order Stark-effect lines $K=1\rightarrow2$, $\tau=2\rightarrow1$, $J\rightarrow J$.

Preparation of $C^{12}H_3O^{18}H$

The compound was prepared by the hydrolysis of ordinary methyl iodide with H_2O^{18}. Dr. A. O. C. Nier of the University of Minnesota generously donated this heavy oxygen isotope in the form of oxygen gas, in which the ratio of $O^{16}O^{18}$ to O_2^{16} was 0.52.[16] The H_2O^{18} was formed as a by-product in the oxidation of ammonia to produce N_2O^{18}. As the addition of ordinary sodium hydroxide would have diluted the concentrated oxygen isotope too much, sodium hydroxide was formed by adding enough sodium to react with about half of the water and pumping off the generated hydrogen. As an excess of water with heavy oxygen remained, the solution was essentially the same as that in the preparation of $C^{13}H_3OH$. The hydrolysis treatment was the same as that in the preparation of C^{13} methyl alcohol, except that several more days were required for the completion of the reaction. Apparently the rate of reaction was slower because the amount of excess water was considerably less. As the oxygen gas had originally contained only 20 percent O^{18} atoms, the resultant alcohol was 80 percent ordinary methyl alcohol and only 20 percent $C^{12}H_3O^{18}H$. The filling of the microwave cell was the same as that for the C^{13} methyl alcohol.

We are grateful to Dr. G. R. Sprengling and Mr. David Lide of the Chemical Department of the Westinghouse Research Laboratories, who assisted in the preparation of the $C^{13}H_3O^{16}H$ and $C^{12}H_3O^{18}$ samples.

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[14] D. M. Dennison and E. Ivash (private communication).

[15] Edwards, Gilliam, and Gordy (to be published).

[16] A partially enriched O^{18} sample furnished by the AEC to Dr. A. O. C. Nier was further enriched by thermal diffusion in his plant at the University of Minnesota which was financed by the Committee on Growth of the National Research Council acting for the American Cancer Society.