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Citation: [The Journal of Chemical Physics](#) **4**, 469 (1936); doi: 10.1063/1.1749886

View online: <http://dx.doi.org/10.1063/1.1749886>

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## The Absorption Spectrum of Methyl Alcohol Vapor in the Photographic Infrared\*

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(Received May 18, 1936)

The absorption of methyl alcohol vapor in the photographic infrared has been explored under low dispersion. Absorption regions were found at  $\lambda 9500$  and  $\lambda 7300$ , which correspond to two harmonics of the O—H vibration, and at  $\lambda 12,000$  which is a harmonic of the C—H vibration. The

two O—H harmonic bands were investigated under high dispersion and a somewhat complex rotational structure was resolved. The complete interpretation of the spectrum must be postponed until the theory of the torsion oscillator rotator is further developed.

### INTRODUCTION

THE authors have noticed recently that it is sometimes difficult to decide from the spectrum whether a molecule has the most symmetrical structure compatible with its constitution or whether it deviates slightly from this configuration. Small deviations from the highest possible symmetry appear to cause almost negligible splitting of vibrations which would otherwise be degenerate, and although there will be a breakdown of the transition rules which apply strictly only to the case of high symmetry the new transitions allowed may appear so weakly as to escape casual examination. In particular we have had some difficulty in deciding whether or not methyl cyanide and methyl isocyanide have a threefold axis of symmetry.

We consequently decided to study the spectrum of a molecule in some respects similar to the ones just mentioned but in which the absence of a threefold axis of symmetry is quite certain, in order to observe the effect of this lack of symmetry on the spectrum. Methyl alcohol was chosen for this purpose and in the course of its investigation some very interesting bands have been observed, of a type which has previously received little attention, namely the vibration rotation bands of a torsion oscillator. The investigation has since then very naturally developed into a systematic study of the spectra of a special class of torsion oscillators, the alcohols, the results of which will appear shortly. Since methyl alcohol is the only case so far encountered in which a rotational structure in the ordinary sense has been resolved it seemed appropriate to describe the results on this substance separately.

\* This investigation is a part of a program of research made possible by a grant to one of us (R. M. B.) from the Penrose Fund of the American Philosophical Society, for which it is desired to express appreciation.

### EXPERIMENTAL

The methyl alcohol vapor was confined in a glass absorption tube ten feet in length except in the high dispersion work on the band at  $\lambda 7300$ , when a seventy-foot tube previously described<sup>1</sup> was used. The pressure of vapor was regulated by controlling the temperature of a side tube containing an excess of liquid, the absorption tube being kept at a somewhat higher temperature to prevent condensation. The pressures used ranged from one-quarter to three-quarters of an atmosphere though in the high dispersion work the lower pressures were found advantageous due to the pressure broadening of the lines.

In preliminary experiments the entire photographic infrared spectrum was mapped with a glass spectrograph of such dispersion that the region from the edge of the visible to the limit of sensitivity of photographic emulsions was included on one six inch plate. In the high dispersion work the first order of a 21-foot grating was employed. The plates used were the Eastman 1Z, 144Q or 144K as occasion demanded. A filter was always employed to eliminate disturbing wavelengths as far as possible.

In the work with the glass spectrograph certain sodium, potassium and barium lines were used as wave-length standards while in the fine structure investigations with the grating the water lines were found very convenient. It was never possible to eliminate these lines entirely from the spectrum and though they caused some interference they nevertheless made very satisfactory standards. As wave-lengths of the water lines we took the values given in the 1928 revision of Rowland's table of solar wave-lengths,<sup>2</sup> except

<sup>1</sup> Badger, Bonner and Cross, J.O.S.A. **25**, 355 (1935).

<sup>2</sup> Revision of Rowland's Preliminary Table, Carnegie Inst. (1928).

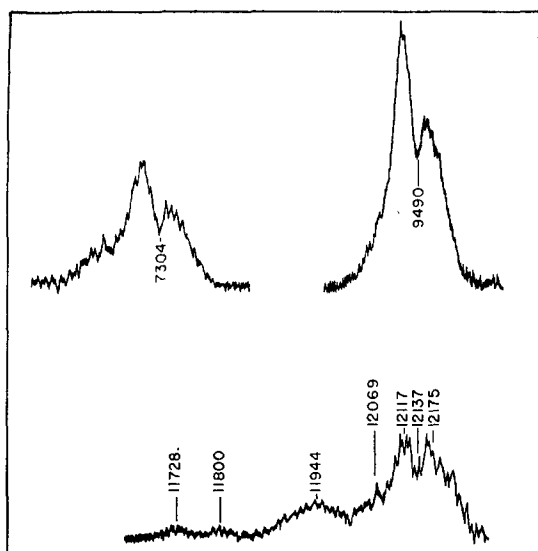


FIG. 1. Microphotometer curves of low dispersion plates of three absorption regions in methyl alcohol vapor. The curves have been corrected for a trend in plate sensitivity with wave-length.

that to the wave-lengths in the  $\lambda 9500$  region, given in the infrared extension of that table, we applied a correction of  $-0.072\text{\AA}$  to bring them into agreement with recent work of Babcock on certain of the solar lines in the farther photographic infrared.

#### THE LOW DISPERSION WORK

In Fig. 1 are reproduced microphotometer curves of the spectrograms taken with the glass spectrograph, which have been corrected for the trend in plate sensitivity with wave-length. These curves show certain features more clearly than those of the high dispersion plates, in particular a weak branch on the violet side of the  $\lambda 7300$  band, and indicate the general nature of the absorption in the harmonic of the C—H vibration at  $\lambda 12,000$ , which we have not been able to photograph satisfactorily under high dispersion. The small maxima and minima are without significance as they

TABLE I. Absorption maxima observed under low dispersion in the harmonic of the C—H vibration at  $\lambda 12,000$ .

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$
11,728	8524
11,800	8472
11,944	8370
12,069	8283
12,117	8251
12,175	8211

are due to plate grain, but there appear to be six definite maxima in the  $\lambda 12,000$  region, which probably belong to at least three distinct band structures. In Table I are given the wave-lengths and frequencies of these maxima.

#### HIGH DISPERSION WORK

We have photographed with high dispersion the bands at  $\lambda 9500$  and  $\lambda 7300$  which correspond to the transitions  $0 \rightarrow 3$  and  $0 \rightarrow 4$  in the O—H vibration, respectively, with results which are presented in Figs. 2 and 3, and Tables II and III. These two bands show considerable similarity of structure though there are some obvious differences. Both are rather complex and apparently consist of several branches which we have named rather arbitrarily for the sake of identification, as is shown in the figures.

At first sight both bands appear to resemble the parallel bands of methyl fluoride. There are apparently *P* and *R* branches and in the center of the band a *Q* branch, though in the  $\lambda 7300$  band this feature is certainly weak. However, somewhat to the long wave side of the band centers there are additional very strong lines which also resemble *Q* branches. These we have called the "*Q'*" branches. The "*P*" and "*R*" branches consist of lines which are approximately equally spaced and there is little if any convergence till one passes to the high frequency side of the maxima of the "*R*" branches. The line spacing near the centers of the bands averages about  $1.75 \text{ cm}^{-1}$  and  $1.60 \text{ cm}^{-1}$  in the  $\lambda 9500$  and  $\lambda 7300$  bands, respectively, which is very roughly what would be expected in a rotational structure in which only the large moments of inertia of the methyl alcohol molecule are involved. In the "*P*" branch of the  $\lambda 9500$  band there is some tendency for every third line to be more intense than the remainder. This is more evident in the plates themselves than in the microphotometer curves.

In addition to those just described each band has some additional considerably weaker branches. About  $45 \text{ cm}^{-1}$  to the violet side of the "center" of the main band there appears to be in each case a moderately strong line which we have called the "*Q''*" branch. Still farther out there is a moderately well developed branch which in the case of the  $\lambda 9500$  band consists of lines with a spacing about equal to that in the "*R*" branch.

In the  $\lambda 7300$  region this "side band" appears more intense relative to the other branches, but no structure could be resolved in it and we have recorded the apparent maximum of absorption which may be considerably in error. These side bands we have designated by " $R'$ ."

Most of the lines of the " $P$ " and " $R$ " branches of the  $\lambda 9500$  band are fitted within experimental error by the formula:

$$\nu(\text{cm}^{-1}) = 10,530.7 + J(B' + B'') + J^2(B' - B'') + 4J^3C,$$

in which  $(B' + B'') = 1.7142$ ,  $(B' - B'') = -0.0058$ ,  $4C = -0.000165$  and  $J$  takes the values of the positive and negative integers. The formula fails to fit well on the extreme red side of the " $P$ " branch. We are inclined to doubt whether the constants of the expression given have any great

significance, for two reasons. In the first place a different set of constants is required to fit the  $\lambda 7300$  band in a similar fashion, from which it is evident that  $B''$  cannot be interpreted as a quantity characteristic of the ground state of the molecule. Secondly, the relatively great intensity of the " $R$ " branch, especially in the  $\lambda 7300$  band, gives rise to the suspicion that we may have to do with the superposition of two or more types of structure, so that the observed spacing may be of somewhat doubtful meaning.

No theory has been developed, so far as we are aware, which predicts the rotational energy levels of a molecule of the type which we find in methyl alcohol. This molecule, with little doubt, consists of a  $\text{H}_3\text{CO}$  group with a threefold axis of symmetry, and an additional hydrogen atom about  $0.96\text{\AA}$  distant from the oxygen atom and so lo-

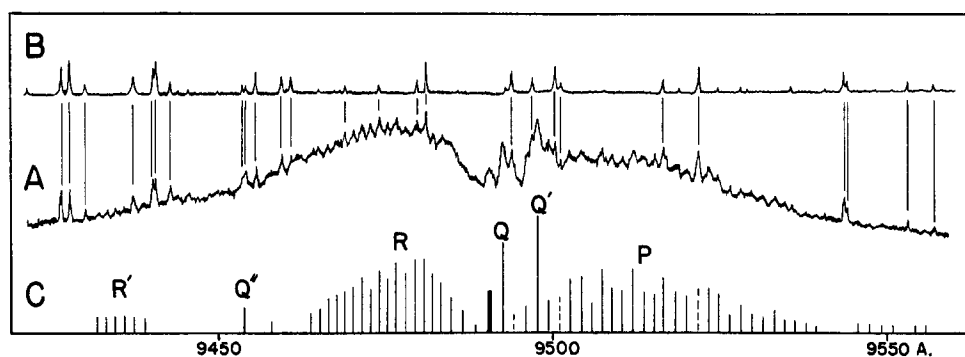


FIG. 2. The O-H harmonic band in methyl alcohol vapor at  $\lambda 9500$  under high dispersion. (A) microphotometer curve of the absorption band; (B) curve showing absorption of water vapor in the same region; (C) a representation of the maxima which were measured.

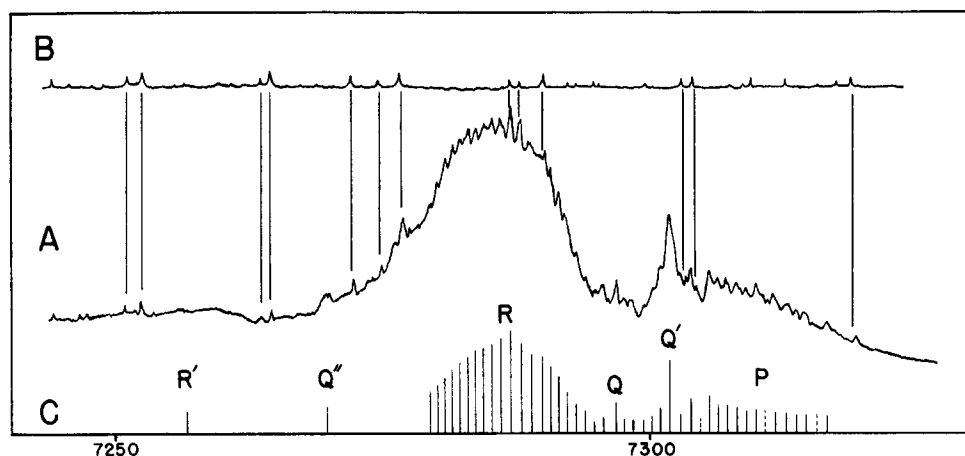


FIG. 3. The O-H harmonic band in methyl alcohol vapor at  $\lambda 7300$  under high dispersion. See Fig. 2 for explanation.

TABLE II. Wave-lengths, frequencies and intensities of the lines in the  $\lambda 9500$  band of methyl alcohol vapor.

Line No.	P branch			R branch		
	I	$\lambda(\text{\AA})$	$(\text{cm}^{-1})$	I	$\lambda(\text{\AA})$	$(\text{cm}^{-1})$
<i>Q</i>	10	9493.05	10531.1		—	—
1	0?	94.34 <sup>b</sup>	529.7	5	9491.11	10533.3
2	3	96.74	527.0		—	—
3	20	98.14	525.5	1	88.94	535.7
4	7	99.94	523.5	3	87.27	537.6
5	?	— <sup>b</sup>	—	5	85.22	539.8
6	9	9503.04	520.1	8	83.91	541.3
7	9	04.78	518.1	9	82.60	542.7
8	7	06.19	516.6	11?	81.50 <sup>b</sup>	544.0
9	10	07.78	514.8	10?	80.19 <sup>b</sup>	545.4
10	8	09.29	513.1	9	78.60	547.2
11	8	10.91	511.4	10	77.15	548.8
12	10	12.49	509.6	9	75.88	550.2
13	8	13.95	508.0	10?	74.78 <sup>b</sup>	551.4
14	8	15.56	506.2	9	73.32	553.1
15	9?	17.10	504.5	9	72.06	554.5
16	7	18.87	502.6	8	70.70	556.0
17	6	20.52	500.7	8?	69.43 <sup>b</sup>	557.4
18	?	22.13 <sup>b</sup>	499.0	7	68.31	558.7
19	7	23.69	497.2	6	66.96	560.2
20	6	25.23	495.5	5	65.71	561.6
21	4	26.82	493.8	4	64.51	562.9
22	5?	28.54 <sup>b</sup>	491.9		—	—
23	3	29.91	490.4		62.77	(unres.)
24	2	31.66	488.5		—	—
25	3	33.39	486.6		—	—
26	2	34.95	484.8		—	—
27	1	36.38	483.3		—	—
28	0	38.20	481.3		—	—
29	0	39.66	479.7		—	—
Some additional very doubtful lines				<i>R'</i> branch		
	0	9544.88	10473.9	0	9458.44	10569.7
	0	47.55	471.0	<i>Q''</i> 2	54.49 <sup>b</sup>	574.1
	0	49.46	468.9	1	39.20	591.2
	00	51.21	467.0	1	37.93 <sup>b</sup>	592.7
	00	54.50	463.4	1	36.52	594.2
	00	56.02	461.7	1	35.26	595.6
				1	33.90	597.2
				1	32.69	598.5

Note: for convenience we have numbered the lines in the "*P*" and "*R*" branches from the "*Q*" branch taken as arbitrary origin. Several blends with water vapor lines occur and are designated by *b*. In these cases the measurements and estimates of intensity may be in doubt.

cated that the angle between the C—O and the O—H bonds is around 105°. The hydroxyl hydrogen is presumably capable of more or less free rotation about the axis of the H<sub>3</sub>CO group, and although three maxima of potential energy will be passed through in such a complete rotation, they are probably not very high.

Now although the methyl alcohol molecule considered as a whole is not a symmetrical rotator it deviates rather slightly from being such, the departure being due only to the light hydrogen

atom which is located off the symmetry axis of the remainder of the molecule. Consequently it appeared possible that the considerations on the symmetrical torsion oscillator rotator made by Nielsen<sup>3</sup> might lead to a qualitative interpretation of the spectrum.

Consider first of all the case of completely free internal rotation, which our molecule may approach more or less closely. Nielsen has derived an expression for the rotational energy levels for the case in which the two portions of a molecule which are free to rotate with respect to each other have coincident symmetry axes which are at least threefold. We prefer to rewrite this expression in another form which appears to us more convenient:

$$W = (h^2/8\pi^2) \{ [J(J+1) - (K_1 + K_2)^2/A_x] + (K_1^2/A_z') + (K_2^2/A_z'') \}.$$

In this expression *J* takes the values 0, 1, 2, etc., and *K*<sub>1</sub> and *K*<sub>2</sub> the values 0, ±1, ±2, etc., subject to the restriction that  $J \geq |K_1 + K_2|$ ; *A*<sub>z</sub>' and *A*<sub>z</sub>'' are the respective moments of inertia of the two separate portions of the molecule about their symmetry axes, and *A*<sub>z</sub> is the moment of inertia of the molecule as a whole about an axis perpendicular to the former.

This expression was derived for a non-vibrating system, but let us extend it to the interpretation of vibration rotation bands on the assumption of little interaction between vibration and rotation. In particular let us consider some vibration which we shall regard as entirely confined to one of the two portions of the molecule which we shall assume to have a much smaller moment of inertia than the other, say *A*<sub>z</sub>' < *A*<sub>z</sub>'. It is evident that we may expect two types of band structure. In case the change in electric moment is parallel to the symmetry axes of the two rotating groups we have the selection rule  $\Delta J = 0, \pm 1$  and  $\Delta K_1 = \Delta K_2 = 0$ , which results in a band with *Q*, *P* and *R* branches, the spacing in the latter two being  $(h/4\pi^2 c A_z) \text{ cm}^{-1}$ . This structure is similar to that of the parallel bands of methyl fluoride and may be called the "parallel type" structure.

In case the change in electric moment is perpendicular to the symmetry axes of the groups, we have as before  $\Delta J = 0, \pm 1$  and  $\Delta K_2 = 0$ , but  $\Delta K_1 = \pm 1$ , which gives rise to a set of sub-bands

<sup>3</sup> H. H. Nielsen, Phys. Rev. **40**, 445 (1932).

the centers of which are given by the expression:

$$\nu(\text{cm}^{-1}) = \nu_0 \pm (h/8\pi^2c)(2K_1 + 1)[(1/A_z') - (1/A_x)],$$

in which  $K_1$  takes the values 0, 1, 2, etc. Each individual sub-band will consist of equally spaced lines with the same separation as found in the  $P$  and  $R$  branches of the "parallel type" band. Each line will really consist of a kind of  $Q$  branch with a number of other lines superposed on it. If  $A_z'$  is quite small the levels with large  $K_1$  will be little populated, due to the Boltzmann factor, and the number of observable sub-bands might be rather small.

Now indeed the methyl alcohol bands have somewhat the appearance of a superposition of the two types of structure just described, which might perhaps be expected since the O—H vibration will produce a change in electric moment with a small component parallel to the symmetry axis of the  $\text{H}_3\text{CO}$  group and a large one perpendicular to it. We might regard the ' $P$ ', ' $R$ ' and ' $R$ ' branches as being the three sub-bands of the perpendicular type structure corresponding to the transitions in  $K_1$ :  $1 \rightarrow 0$ ,  $0 \rightarrow 1$  and  $1 \rightarrow 2$ , respec-

tively, with the  $P$  and  $R$  branches of a weaker parallel type band superposed on the first two with the  $Q$  branch lying between.

However, this interpretation is by no means adequate. It does not take into account the multiplicity of  $Q$  branches, and we should expect the perpendicular type structure to be much more completely developed with at least a half dozen sub-bands intense enough to be observable. Certainly for a complete explanation we should have to take into account the asymmetry of the rotator and the fact that the internal rotation is not completely free. But probably even these refinements would not be sufficient, as we have been forced to conclude from our study on other alcohols. It will almost certainly be necessary to take into account a special kind of interaction between the O—H vibration and the internal rotation.

To cite a rather extreme case, it has been observed by Wulf<sup>4</sup> and ourselves that the harmonic bands of the O—H vibration in ortho chlor phenol each consist of two components, one strong and one weak. These have been interpreted by Pauling<sup>5</sup> who makes the likely assumption that the hydroxyl hydrogen is not very free to rotate and is likely to be found only in one or another of two orientations with respect to the remainder of the molecule, which correspond to potential minima. The difference in intensity of the two components is interpreted as due to the unequal depth of the two minima and the greater probability of finding the molecules in the lower energy state.

In the two orientations mentioned the frequency of the O—H vibration is considerably different and it may well be that the O—H equilibrium distance and the equilibrium angle between the C—O and O—H bonds are also affected, as well as to a lesser extent the configuration of the remainder of the molecule. In methyl alcohol the situation will no doubt be less extreme but even there the frequency of the O—H vibration will be to some extent dependent on the relative orientation of the two parts of the molecule, which will give rise to an interaction between the vibration and the internal rotation. To take these effects into account even approximately may be difficult but appears to be an interesting problem.

TABLE III. Lines in the  $\lambda 7300$  band of methyl alcohol vapor. (See Table II for explanation.)

Line No.	I	P branch		R branch		
		$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$	I	$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})$
$Q$	5	7296.9	13700.7	—	—	—
1	3	97.7	699.1	4	7295.7	13703.0
2	3	98.3	698.1	3	95.0	704.3
3	2	99.4	695.9	4	94.0	706.0
4	4	7300.2	694.4	6	93.2	707.6
5	5	01.0	692.9	8	92.3	709.3
6 $Q'$	10	01.8	691.6	11	91.7	710.5
7	3	02.7	689.8	14	90.8	712.1
8	5	03.6	688.1	16?	90.0b	713.6
9	?	— <sup>b</sup>	—	17	89.1	715.4
10	5	05.3	684.9	19?	88.1b	717.3
11	4	06.1	683.5	20?	87.3b	718.7
12	4	06.9	681.9	19	86.4	720.3
13	3	07.9	680.1	19	85.6	721.8
14	3—	08.8	678.4	18	84.9	723.2
15	4	09.8	676.5	17	83.9	725.0
16	?	—	—	17	83.4	726.0
17	3—	11.2	673.8	16	82.7	727.4
18	2+	12.4	671.6	16	82.1	728.6
19	2	13.2	670.1	15	81.3	729.9
20	2	14.0	668.5	13	80.7	731.1
21	?	—	—	9	80.0	732.4
22	1	16.1	664.8			
$Q''$ $R'$	(apparent maximum of broad unresolved structure)				70.5 57.7	750.4 774.7

<sup>4</sup> Wulf and Liddel, J. Am. Chem. Soc. **57**, 1464 (1935).

<sup>5</sup> L. Pauling, J. Am. Chem. Soc. **58**, 94 (1936).