

InfraRed and Raman Spectra of Polyatomic Molecules XVII. Methyl Alcohol and Methyl Ether

Hermann D. Noether

Citation: *The Journal of Chemical Physics* **10**, 693 (1942); doi: 10.1063/1.1723650

View online: <http://dx.doi.org/10.1063/1.1723650>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/10/12?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[InfraRed and Raman Spectra of Polyatomic Molecules XVIII. Trideuteronitromethane](#)

J. Chem. Phys. **11**, 361 (1943); 10.1063/1.1723859

[InfraRed and Raman Spectra of Polyatomic Molecules XIV. Propylene](#)

J. Chem. Phys. **9**, 319 (1941); 10.1063/1.1750903

[InfraRed and Raman Spectra of Polyatomic Molecules XII. Methyl Acetylene](#)

J. Chem. Phys. **8**, 526 (1940); 10.1063/1.1750706

[InfraRed and Raman Spectra of Polyatomic Molecules. IV. Allene](#)

J. Chem. Phys. **6**, 686 (1938); 10.1063/1.1750152

[InfraRed and Raman Spectra of Polyatomic Molecules. III. Ethane](#)

J. Chem. Phys. **6**, 682 (1938); 10.1063/1.1750151



THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

DECEMBER, 1942

NUMBER 12

Infra-Red and Raman Spectra of Polyatomic Molecules

XVII. Methyl- d_3 -Alcohol- d and Methyl- d_3 -Alcohol

HERMANN D. NOETHER

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

(Received September 8, 1942)

CD_3OD and CD_3OH have been prepared and their infra-red spectrum in the range from 2.5μ to 18μ has been measured. The Raman spectrum of CD_3OD has been observed. CH_3OH and CH_3OD have been reinvestigated and an assignment for all four methyl alcohols has been given.

METHYL alcohol and methyl alcohol- d have been subjected to a thorough investigation in the Raman¹ as well as in the infra-red spectrum.² Methyl alcohol can be treated theoretically since it is a comparatively simple molecule. One degree of freedom involves the torsion about a single bond. From an accurate assignment of all the other fundamental frequencies it should be possible to evaluate the value of the torsional vibration with the use of heat capacity data. The hindrance potential to free rotation around this single bond could thus be determined. Methyl alcohol is an asymmetric top molecule of only small asymmetry, thus differing only slightly from a molecule of the point group C_{3v} . Molecules of this group have a class of doubly degenerate frequencies. The degeneracy would naturally be lifted, if the asymmetry of the molecule had any effect on the methyl group of the molecule. Then the highest symmetry of the methyl alcohols would be C_s . The splitting of these frequencies therefore gives a measure of the asymmetry of the molecule.

¹ J. O. Halford, L. C. Anderson, and G. H. Kissin, *J. Chem. Phys.* 5, 927 (1937).

² A. Borden and E. F. Barker, *J. Chem. Phys.* 6, 553 (1938).

To obtain more data the isotopic molecules CD_3OD and CD_3OH were investigated in the infra-red. CD_3OD was also investigated in the Raman spectrum.

EXPERIMENTAL PART

The infra-red spectrometer used has been described before.³ The polished rocksalt windows of the absorption cells (30 cm long, 2.5 cm in diameter) were sealed on with Apiezon wax. Blanks were recorded over the whole range. The alcohol was kept in a side arm and was sealed off to avoid as far as possible any contact with air and stopcock grease which tend to exchange with the deuterium of the hydroxyl group. Later on, when different fractions of the alcohol were measured to obtain a change in relative intensities of CD_3OD and impurity bands, the system was closed by a stopcock. This caused some exchange in the OD group. The vapor pressure was regulated by immersing the side arm into cooling mixtures. The Raman spectrum was taken with a cell containing ~ 0.4 cc CD_3OD . On some plates the 4047A

³ H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* 6, 194 (1938).

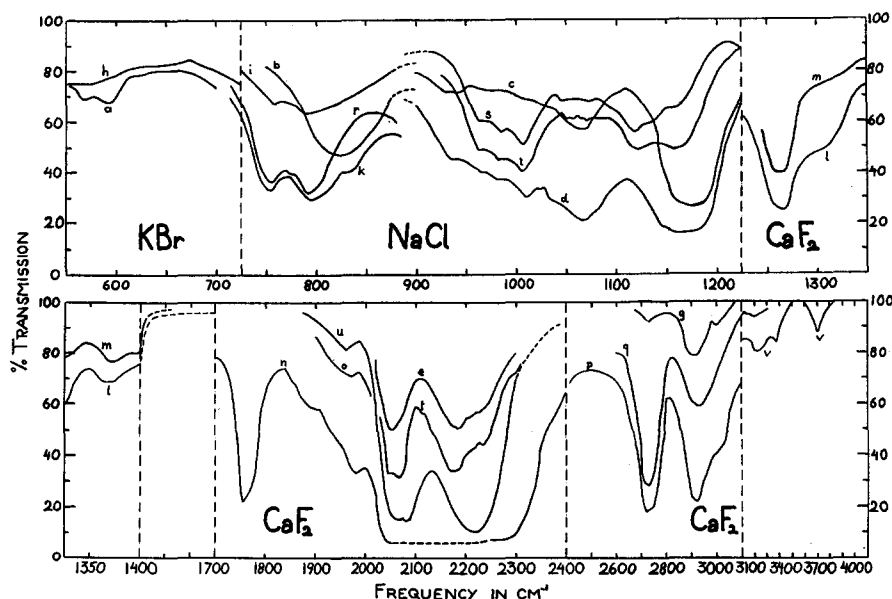


FIG. 1. Absorption bands in CD_3OD . Curves (a) to (g): These curves show mainly the bands of the impurity (bands at $\sim 580, 836, 933, 1069, 1160, 2056, 2196, 2925$, and 3000 cm^{-1}). (a) First fraction (0°C); (b) same, CD_3OD had been stored in a 300-cc flask and only the gas phase was condensed in the trap of the absorption cell. Thus mostly the impurity was collected. (c) ($\sim -50^\circ\text{C}$); (d) high pressure run of the sample, collected as described under (b); (e) (-50°C); (f) (-32°C); (g) sample as under (b) high pressure run. Note the slight absorption in the OD stretch range; there is no absorption in the range from 3100 to 4100 cm^{-1} . Curves (h) to (p): middle and third fraction containing the impurity with bands at $1260, 1370$, and 1762 cm^{-1} . (h) (0°C); (i) (-8°C); (k) (5 – 10°C ?); (l) later record with some CD_3OH present; (m) (0°C) early record with nearly no CD_3OH in sample; (n) sat. pressure; (o) (15°C ?); (p) sat. pressure ?; (q) (0°C). (r) to (v): third fraction and nearly pure CD_3OD with some CD_3OH . (r) (-1°C); (s) low pressure nearly pure CD_3OD ; (t) (-11°C); (u) (12°C); (v) ($\sim 25^\circ\text{C}$) some CD_3OH present. The temperatures given are those of the cooling mixtures in which the cell trap was immersed.

excitation was eliminated by a Wratten 2A filter, while a Rhodamine 5GDN Extra (DuPont)⁴ solution cut down the green mercury lines.

CD_3OD was prepared from CD_3Br by hydrolysis with a D_2O solution of NaOD on the steam bath in a sealed tube. The D_2O and CD_3OD were separated by fractional distillation. CD_3OH was prepared from CD_3OD by exchange with H_2O followed by fractional vacuum distillation of the CD_3OH . CH_3OD was prepared by reacting D_2O (99.6 percent) with dry $\text{Mg}(\text{OCH}_3)_2$.⁵ The CH_3OH used in this preparation and for some infra-red measurements was chemically pure (Merck) and had been distilled from $\text{Mg}(\text{CH}_3\text{O})_2$ after refluxing for several hours.

⁴ J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. 6, 12 (1938).

⁵ See reference 1.

Frequencies of CD_3OD and CD_3OH

The frequencies of the absorption maxima measured for CD_3OD in the range from 2.5μ to 18μ are given in Table I. However, many of

TABLE I. Infra-red and Raman frequencies in the CD_3OD spectrum (frequencies of impurities in parentheses).

Infra-red		Raman
$\sim(580)$	(1263) s	(576) m (6)
754 } s	? 1290 w	~ 821 v.w. (4)
Q ? 775 } s	(1372) m	989 s (9)
793 } s	(1760) s	1072 v.w. (7)
(836) m	1966 w	1131 v.w. (2-3)
879 v.w.	(2054) s	(1168) v.w. (2-3)
	2081 s	
(933) w	(2196) s	2082 s (10)
968 } s	2227 s	2162 m (3)
987 } s	2725 s	2245 br (8)
1005 } s		In brackets number of times observed. l and k excitation.
? 1045 w	(2925) s	
(1069) m	(3000) s	
? 1075 w	3232 w	
1121 s	~ 3680 m	
(1160) s		

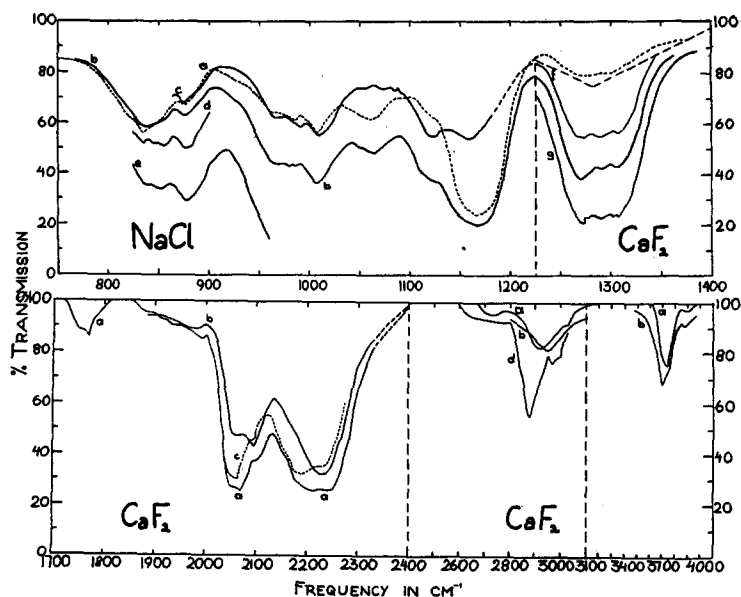


FIG. 2. Absorption bands of CD_3OH . Curves: 750–1400 cm^{-1} range: (a) ($\sim -35^\circ\text{C}$) from exchange of first fraction of CD_3OD ; (b) same fraction at 25°C ; (c) from exchange of third fraction of CD_3OD (-14°C) (strong change in the intensity of the 1060 and 1165 cm^{-1} bands); (d) third fraction (4°C); (e) third fraction (25°C); (f) third fraction (-10°C); (g) third fraction (0°C). There is no absorption from 1400 to 1700 cm^{-1} . Range 1700–4100 cm^{-1} : (a) second fraction (25°C); (b) third fraction (-3°C); note the change in relative intensities in the 2100 cm^{-1} bands; (c) second fraction ($\sim 15^\circ\text{C}$); (d) first fraction (25°C). The first two fractions contain a considerable amount of the impurity with bands at ~ 580 , 833, 933, 1060, 1165, 2062, 2186, and 2888 cm^{-1} . The third fraction contains only a small amount of it.

these apparently belong to two impurities which were difficult to eliminate completely because of the small quantity of material available. Certain bands were strong in the first distillation fraction (either plain vacuum distillation or vacuum distillation from charcoal),⁶ weak in the middle fraction, and practically absent in the last fraction. (See Fig. 1 for

TABLE II. Frequencies in the infra-red spectrum of CD_3OH (frequencies of impurities in parentheses).

(~ 580) w	1270 s
(833) s	1289 s
856 m	1308 s
878 m	(1355) v.w.
? (933) v.w.	(1767) w
967 } s	1975 w
990 } s	(2062) s
1009 } s	2094 s
? 1055 w	(2186) s
(1060) s	2232 s
? 1080 w	(2888) m
1123 s	(2940) m
(1165) s	~ 3680 m

⁶ H. D. Noether, J. Chem. Phys. 10, 664 (1942).

CD_3OD and Fig. 2 for CD_3OH). Therefore it is fairly certain that these bands belong to a more volatile impurity. This is substantiated by low temperature runs in which only the bands of this impurity could be observed. They are at ~ 580 , 836, 933, 1069, 1160, 2056, 2196, 2925, and 3000 cm^{-1} . This assignment is confirmed by the fact that when these bands are strong the 987 and 2725 cm^{-1} bands which quite definitely belong to CD_3OD are weak or missing. The bands at 1290 and 3700 cm^{-1} also occur in the spectrum of CD_3OH (see below) and are only found in later records of CD_3OD where some exchange in the OD group had taken place. The bands of the other impurity which is present in the last fraction of the charcoal distillation of CD_3OD and CD_3OH had already been determined and separated in the measurement of the spectrum of CD_3Cl and CD_3Br .⁶ These bands occurred originally quite strongly at 1263, 1362, and 1760 cm^{-1} , but became much weaker after the charcoal treatment.

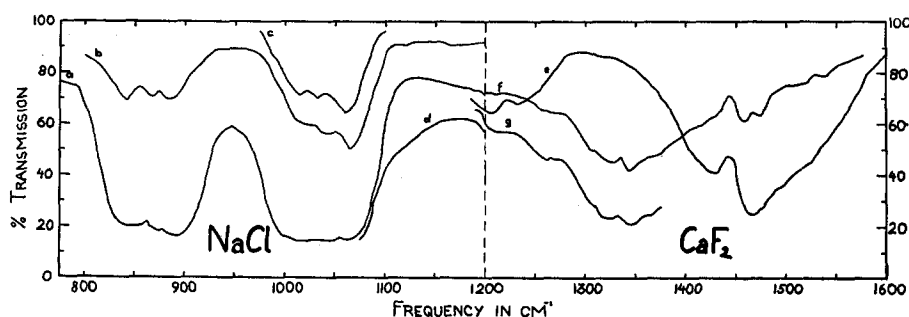


FIG. 3. Infra-red bands of CH_3OH and CH_3OD . Curves: (a) CH_3OD (20°C); (b) CH_3OD (-16°C); (c) CH_3OH (-22°C) the curve is shifted upwards by 10 percent to avoid superposition with curve (b); (d) CH_3OH (19°C); (e) CH_3OD (20°C); (f) CH_3OH (4°C); (g) CH_3OH (12°C). Temperatures in brackets are those of the cooling mixtures in which the cell trap was immersed.

For the CD_3OH measurements (Fig. 2, Table II), three different fractions of CD_3OD were exchanged with H_2O . The first fraction gave strong bands at 580, 833, 1060, 1165, 2062, 2186, and 2900 cm^{-1} . These are exactly the bands which were found to belong to the impurity in CD_3OD . The CO band at 990 and the OH band at 3680 are medium strong, proving the presence of CD_3OH . In the other exchanged fractions the same shifts in intensities of the bands occur as already observed in CD_3OD , thus supporting the conclusions drawn for the bands of the CD_3OD spectrum. The second impurity is present only in quite small concentration as shown by the weakness of its 1760 band.

Frequencies of CH_3OH and CH_3OD

The infra-red spectra of CH_3OH and CH_3OD were measured to find the exact shape and intensities of the fundamental bands of these compounds in our spectrograph (see Tables III and IV, Fig. 3). The bands agree in general very well with those measured by Borden and Barker² and Barker and Bosschieter.⁷ There are a few very weak bands in the 1230 region which have not been reported by these authors. They are at 1209 and 1260 cm^{-1} for CH_3OH and at 1207 and 1232 for CH_3OD . They were taken at saturation vapor pressure at 20°C . Comparing the 1450 range of CH_3OH and CH_3OD , it could be assumed that there is another weak band around 1430 cm^{-1} which is partly covered by the very strong 1340 absorption. This band is quite

clear in the CH_3OD molecule where the two bands of Barker and Bosschieter at 1459 and 1480 cm^{-1} seem to form one strong band at 1468 cm^{-1} due to our insufficient resolution.

The intensities of the bands in CH_3OH and CH_3OD are as follows: The 1033 and 1040 bands have exactly the same shape, the R branch being stronger than P and Q . The 863 band is very strong, and the 1340 band is much stronger than those in the 1460 range. The CH stretches are strong and have about the same intensity.

Assignments

We can expect 12 frequencies for the methyl alcohol molecule of which 3 pairs should be either doubly degenerate, if the molecule behaves like a symmetrical top molecule, or should show a slight splitting, if the OH or the OD group makes the molecule asymmetric. The degenerate or nearly degenerate frequencies represent the carbon-hydrogen stretches, bendings, and rockings of the methyl group, all connected with a change of electric moment perpendicular to the C axis. Then there are three frequencies for which the electric moment changes parallel to

TABLE III. Infra-red frequencies of CH_3OH .

Own measurements	Borden & Barker	Own measurements	Borden & Barker
P 1014 } s	1010	1456	1455
Q 1033 } s	1034	1470	1477
R 1060 } v.s	1058	Q 2056 } m	2054
1209 } w		R 2081 } m	
1260 } w		2888 } s	2845
P 1322 } s		2960 } s	2978
Q 1340 } s	1340	3615 } m	3683
R 1365 }			
? 1425-1430			

⁷ E. F. Barker and G. Bosschieter, J. Chem. Phys. 6, 563 (1938).

the C axis, representing the symmetrical stretching and bending of the carbon hydrogen bonds and the carbon-oxygen stretch. They should show the structure of a parallel band with P , Q , and R branches. There are finally three vibrations of the hydroxyl group: the oxygen-hydrogen stretch, the oxygen-hydrogen bending, which because of the nearly rectangular angle of the oxygen hydrogen bond with the C axis of the molecule should give rise to a parallel type band, and the torsion of the hydroxyl against the methyl group, where the hydroxyl hydrogen vibrates perpendicular to the $OH(OD)$ bond and the C axis. At higher energies this vibration changes to a rotation of the hydroxyl group around the CO axis. This frequency is very low and probably undetectable with our instrument.

(a) $C-D$ and $C-H$ Stretches

The assignment of the observed bands to the fundamental frequencies is given in Table V. $\nu(\pi)$ and $\nu(\sigma)$ are easily assigned by comparing with the corresponding frequencies of the ordinary and the deuterio-methyl halides. In these compounds two parallel type bands are found in this region due to resonance of $2^2\delta(\sigma)$ with $\nu(\pi)$. In CH_3OH and CH_3OD only one parallel type band is observed in this range. Because of the impurity band at 2190 in the CD_3 alcohols, the presence of the resonance doublet cannot be ascertained. In the Raman spectrum of CH_3OH and CH_3OD , Halford, Anderson, and Kissin¹ find the resonance doublet $2\delta(\sigma)$, $\nu(\pi)$ at 2837, 2942 and 2882, 2948, respectively. In the Raman spectrum of CD_3OD this doublet occurs at 2082 and 2162 cm^{-1} .

(b) Methyl Group Bendings

From a comparison with the methyl halides and especially with CH_3F , Barker assigns the

TABLE IV. Infra-red frequencies of CH_3OD .

Own measurements	Barker & Bosschieter	Own measurements	Barker & Bosschieter
P 849	863	1427	s
Q 869		1460	s
R 895		1484	s
Q 1019	~1012	Q 2058	m
Q 1040		R 2107	
R 1066	~1060	2735	s
1207		2870	s
1232		2972	s

parallel type bending $\delta(\pi)$ for CH_3OH and CH_3OD as given in Table V. The assignment of the 1120 frequency in CD_3OD and CD_3OH as $\delta(\pi)$ is based on the following considerations: $\delta(\pi)$ increases from 1252 for CH_3I , to 1305 for CH_3Br , 1355 for CH_3Cl , 1455 for CH_3OH , and 1459 for CH_3OD . CD_3Br and CD_3Cl have $\delta(\pi)$ at 987 and 1029 cm^{-1} . From CH_3Cl to CH_3OH the frequency increases by *ca.* 100 cm^{-1} . Expecting a similar change for the deuterio series on the basis

TABLE V. Frequency assignment of the methyl alcohols (in cm^{-1}).

Freq.	Characteristic of band	CH_3OH	CH_3OD	CD_3OH	CD_3OD
$\nu(\pi)$	$C-H$ stretch (\parallel)	2845	2850	2094	2081
$\nu(\sigma)$	$C-H$ stretch (\perp)	2978	2965	2232	2227
$\delta(\pi)$	$H-C-H$ bending (\parallel)	1455	1459	1123	1121
$\delta(\sigma)$	$H-C-H$ bendings (\perp)	~1430	1427	~1055	~1045
$\delta''(\sigma)$		1477	1480	~1080	~1075
		P ~1010	~1012	967	969
		Q 1034	1040	990	987
$\nu C-O(\pi)$	$C-O$ stretch (\parallel)	R ~1058	~1060	1009	1005
$\tau'(\sigma)$	CH_3 -rockings (\perp)	1209	1207	856	?
$\tau''(\sigma)$	$O-H$ stretch (\perp)	1240-60	1232	879	?
$\nu O-H(\sigma)$		3683	2720	3680	2725
$\delta O-H(\sigma)$	Torsion	—	—	—	—
	$O-H$ bending (\parallel)	P 1322*	849	1270	754
$\delta O-H(\pi)$		Q 1340*	869	1289	775
		R 1365*	895	1308	793
$2\nu C-O(\pi)$		2054	2065	1975	1966

* The difference in shape of $\delta OH(\pi)$ for CH_3OH from $\delta O-H(\pi)$ for the other methylalcohols is perhaps due to overlapping by $\tau''(\sigma)$.

of the nearly equal bromide-chloride change in the two series, we obtain the assigned value for $\delta(\pi)$ in CD_3OD and CD_3OH . For the perpendicular type bands in CH_3OH and CH_3OD the bands at 1477 and 1480 can be assigned, but this would assume the molecules to behave like symmetrical top molecules and this band to be doubly degenerate. In CH_3SH , which is probably less asymmetric than CH_3OH , Thompson and Skerrett⁸ find a splitting of about 45 cm^{-1} (1430, 1475 cm^{-1}) for these frequencies. In CH_3OD a band at 1427 and approximately 1480 could account for the splitting. In CH_3OH it is hard to find an exact position for the lower part of this doublet since the 1340 band overlaps very strongly. From comparison with CH_3OD , it could be assumed to be somewhere around 1430, the other part being at 1477 cm^{-1} . In the methyl halides $\delta(\sigma)$ remains nearly constant from CH_3I to CH_3F (1445 to 1476 cm^{-1}).⁹ In CD_3Br

⁸ H. W. Thompson and N. P. Skerrett, Trans. Faraday Soc. **36**, 812 (1940).

⁹ W. H. Bennett and C. F. Meyer, Phys. Rev. **32**, 888 (1928).

and CD_3Cl it is found and calculated from the product rule¹⁰ at 1053 and $\sim 1058\text{ cm}^{-1}$, respectively, and it can be expected at *ca.* 1070 cm^{-1} for the alcohols. Unfortunately, the impurity in CD_3OD and CD_3OH has a strong band at 1060 cm^{-1} , and this makes a definite assignment impossible. The flat part of the absorption curve in this range for nearly pure CD_3OD suggests absorption bands in this region, and also a band is found at 1072 cm^{-1} in the Raman spectrum of CD_3OD which could account for $\delta(\sigma)$. There is some evidence that these vibrations may have the frequencies indicated in Table V. By the ratio rule¹¹ $\delta'(\sigma)$ and $\delta''(\sigma)$ for CD_3OD and CD_3OH are calculated at ~ 1074 and 1036 cm^{-1} . These values are probably not very far from the correct frequencies. The lower part of the doublet may form the shoulder of the strong 990 cm^{-1} band of CD_3OD and CD_3OH or come directly on top of the extremely strong R branch at 1007 and 1009 cm^{-1} , respectively.

The assignment $\delta(\pi) > \delta(\sigma)$ for the CD_3 alcohols is supported by calculations of these frequencies for the CD_3X series with different masses X , using Linnett's¹² set of force constants, which yields the result that for small X $\delta(\pi) > \delta(\sigma)$. Intensity considerations in the methyl halide series where $\delta(\pi)$ is always stronger than $\delta(\sigma)$, polarization measurements on CD_3NO_2 ,¹³ where the higher frequency is polarized, thus proving the assignment and Stitt's¹⁴ assignment of the bendings in C_2D_6 , where the parallel bendings are both higher than the perpendicular bendings, support the deuterio-methyl alcohol assignment of $\delta(\pi) > \delta(\sigma)$.

(c) The Methyl Rocking Frequencies

In the methyl halides the rocking frequencies change from 885 for CH_3I to 957 , 1021 , and 1200 cm^{-1} for the bromide, chloride, and fluoride. The alcohols are very similar to the fluoride, and therefore these fundamentals could be expected somewhat higher than 1200 cm^{-1} . Borden and Barker assign the very strong 1340 band to the methyl rocking in CH_3OH . An objection to this assignment is the fact that the

rocking frequencies are usually not very strong, being at least weaker than the bending frequencies. Furthermore, the 1340 band cannot be found in CH_3OD in spite of its great intensity in CH_3OH . We suggest that the weak bands at 1209 , 1260 in CH_3OH and 1207 and 1230 in CH_3OD be assigned to rocking frequencies. There is considerable uncertainty about the exact position of these bands, at least in the case of CH_3OH , because they are probably strongly overlapped by the 1340 and to a lesser extent by the 1034 bands. It is possible that in CH_3OH the higher frequency of the doublet comes on top of the 1340 band.

A comparison with the rocking frequencies of the halides and deuterio-halides places these motions of the CD_3 alcohols in the neighborhood of 900 cm^{-1} and thus leads to the assignment of $\tau'(\sigma)$ and $\tau''(\sigma)$ for CD_3OH as given in Table V. The rocking frequencies of CD_3OD are probably in the same range, but they cannot be found because of the strong absorption at 775 and 987 cm^{-1} and the impurity band at 833 cm^{-1} .

(d) The C—O Stretch

This band is the strongest band in the alcohol. It is a parallel type band showing P , Q , and R branches. In all four bands, the R branch is the strongest. The first harmonic is found at 2054 , 2065 , 1975 , and 1966 cm^{-1} , respectively. In the Raman spectrum $\nu_{\text{C-O}}(\pi)$ appears at 1029 (CH_3OH), 1032 (CH_3OD), and 989 (CD_3OD).

(e) The Hydroxyl Frequencies

The hydroxyl stretches are easily assigned on comparison with other molecules containing the OH or OD group.

The hydroxyl bendings should show bands of parallel type since the vibration is nearly parallel to the C axis. The assignment of frequencies for hydroxyl bendings is in general quite difficult due to association of molecules with hydroxyl groups and due to the complexity of the spectrum of such molecules in the bending range. For isotopic molecules where only the hydrogen of the hydroxyl group can be exchanged by deuterium, a criterion for a correct hydroxyl bending assignment is the disappearance of this band on exchanging the hydrogen and the

¹⁰ E. B. Wilson, Jr., J. Chem. Phys. **9**, 76 (1941).

¹¹ H. D. Noether, J. Chem. Phys. (to be published).

¹² J. W. Linnett, J. Chem. Phys. **8**, 91 (1940).

¹³ T. P. Wilson, J. Chem. Phys. (to be published).

¹⁴ F. Stitt, J. Chem. Phys. **7**, 297 (1939).

TABLE VI. Doublet spacings for the methyl alcohols (in cm^{-1}).

Freq.	CH_3OH	CH_3OD	CD_3OH	CD_3OD
$\nu_{\text{C-O}}(\pi)$	48	48	43	36
$\delta_{\text{O-H}}(\pi)$	43	46	38	39
Calc.	46.0	45.9	44.6	44.0

appearance of a very similarly shaped band in a lower frequency range. With this rule, it was possible to obtain the hydroxyl bending frequency for the isotopic methyl alcohols. The spacings agree quite well with the spacings of $\nu_{\text{C-O}}(\pi)$ (Table VI). They are calculated, using Dennison and Gerhard's formula,¹⁵ which is strictly correct only for symmetrical top molecules.

$$\Delta\nu = (S/\pi)(kT/A)^{1/2}$$

where $\log_{10} S = 0.72/(\beta + 4)^{1.13}$

$$\beta = [(A/C) - 1]$$

$$\text{C-H} = 1.09\text{\AA}, \quad \text{C-O} = 1.42\text{\AA}, \quad \text{O-H} = 0.96\text{\AA}, \\ \text{C-O-H angle} = 105^\circ.$$

The above discussion leads to an assignment on a purely experimental basis. A theoretical check could be obtained by the application of the product rule, treating the molecules as of symmetry C_s (C-O bond is assumed to be rigid, thus splitting out the torsional motion in the molecule). It is found that the shifts in frequencies observed cannot be accounted for by this rule. Applying the ratio rule, the frequencies responsible for the failure are found to be the hydroxyl bending $\delta_{\text{O-H}}(\pi)$ and the methyl rocking

frequencies $\tau(\sigma)$. It should be noted that the hydroxyl bending frequency is reduced by more than $\sqrt{2}$ on substitution of deuterium. Because of the failure of the product rule a theoretical calculation on the basis of a quadratic potential function becomes impossible, at least in the approximation in which the torsional motion is split out.

It is interesting to note that only frequencies which represent motions influenced by the hydroxyl group show disagreement with the rule. A very strong shift in the hydroxyl stretching motion is usually observed in measurements on liquids. This is due to association. Here, however, in the measurements of the methyl alcohols in the gas phase, the O-H stretch occurs in its normal place, thus excluding association as a basis for the discrepancy. It is possible that the lack of agreement with the product rule can be explained by a difference in the amount of coupling between the hydroxyl bending and the torsional motion for the isotopic species. This would simultaneously explain the failure of the rule in the case of the methyl rocking, because this motion is certainly influenced by the torsional motion. A solution for these questions can be given only when more data on the isotopic hydroxyl groups become available. Unfortunately, heat capacity data for the isotopic methyl alcohols cannot be used for the solution of the problem, because the torsional motion has to be known accurately first, to permit any conclusions concerning the hydroxyl bendings.

In conclusion I should like to thank Professor E. Bright Wilson, Jr. for suggesting this work and for his continued interest and for many discussions during the course of this study.

¹⁵ S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).