on two chemically analyzed samples of engine drainings. Sample 1 was run in a parallel manner while the data presented for sample 2 were obtained on consecutive days and represent the results that can be expected on a day-after-day basis. These data are presented in Table II.

Table II. Replicate Study of Copper Determination

Detn. No.	Copper, P.P.M.					
	Sample 1, Parallel Detn.			Sample 2, Successive Detn.		
	Cu Line			Cu Line		
	3247.5 A.	3274.0 A.	Average	3247.5 A.	3274.0 A.	Average
1	25.8	25.3	25.6	116	113	114
2	23.6	22.6	23.1	110	113	112
3	26.4	26.5	26.5	108	116	112
4	29.2	30.0	29.6	112	113	113
5	30.3	32.0	31.2	124	123	124
6	21.6	23.0	22.3	124	128	126
7	26.0	24.3	25.2	106	107	107
8	26.5	24.9	25.7	106	112	109
9	25.5	23.8	24.7	100	102	101
10	26.4	24.3	25.3	...	...	...
11	24.0	24.3	24.2	...	...	...
Av.			25.8			113
Std. dev., *S*			2.6			7.8
Chemical analysis			25.3			103

To check further the validity of the analytical curves prepared from synthetic standards, a series of drainings of known copper content was analyzed. The gamut of concentrations was covered by making successive dilutions of drainings having a relatively high copper content. These data are shown in Table III.

Table III. Analysis of Successive Dilutions of Used Oil Sample

Dilution Ratio	Copper, P.P.M.	
	Calculated value	Spectrochemical
0	203[a]	218
2	102	102
4	50.8	45
8	25.4	23
16	12.7	12
32	6.4	5.3

[a] By chemical analysis (*1*), Cu p.p.m. 209, 196, 203.

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Infrared and Raman Spectra of a Series of Deuterated Alcohols

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A review of the literature revealed disagreement about the assignment of the OH deformation frequency in alcohols in which the H atom moves in the COH plane and perpendicular to the OH bond. The purpose of this investigation was to assign this hydroxyl deformation frequency and at the same time to obtain information about the OD stretching and bending frequencies in higher alcohols. The OH deformation frequency in the liquid state is assigned to the region of 1010 to 1035 cm.$^{-1}$ by comparison of the infrared and Raman spectra of a series of alcohols with their corresponding OD compounds. The OD deformation frequency appears at 915 to 949 cm.$^{-1}$ in the liquid state. The OH stretching frequency in the associated state gives rise to a broad band at 3330 cm.$^{-1}$ which shifts to a weak band at 3682 cm.$^{-1}$ in the vapor state. The corresponding OD stretching frequency appears as a broad band at 2476 cm.$^{-1}$ in the liquid state and shifts to 2726 cm.$^{-1}$ upon vaporization. The regularity of the OD stretching frequency indicates its value as a group frequency, and the presence of either the free or associated OD stretching frequency can be used to indicate the presence or absence of hydrogen bonding in complex molecules.

THE purpose of this investigation was to characterize the OH bending frequency. It was hoped that this characterization would be helpful in distinguishing between an OH group and a NH group in cases where hydrogen bonding occurs; both groups give rise to a stretching vibration in the region of 2900 cm.$^{-1}$ to 3500 cm.$^{-1}$ However, this investigation subsequently points out that the use of these deformation bands is very limited as a group frequency.

The parallel bending deformation frequency of the NH group has been assigned recently to the region from 1406 to 1460 cm.$^{-1}$ (*11*). The vibrational assignment of the OH deformation frequency of alcohols, in which the hydrogen moves perpendicular to the OH bond and out of the C–OH plane, recently was assigned by Stuart and Sutherland (*19*) to a broad band in the liquid starting at 800 cm.$^{-1}$, reaching a maximum near 670 cm.$^{-1}$ and extending beyond 500 cm.$^{-1}$ In deuterated methanol this was found to shift to 475 cm.$^{-1}$ Koehler and Dennison (*9*) assign a broad band with a maximum at about 270 cm.$^{-1}$ for this vibration in methanol vapor.

The assignment of the in-plane hydroxyl deformation vibration was recently made by the authors in a brief letter (*15*), and this paper represents a more complete report. The purpose of this investigation, therefore, is to characterize the in-plane or parallel deformation frequency of the OH and OD groups.

The position of the OH stretching frequency is well established. Errera (*6*), after studying the infrared spectra of a series of aliphatic alcohols at various dilutions, was the first to assign a value of 3640 cm.$^{-1}$ to the free OH stretching, and a value of 3350 cm.$^{-1}$ to this vibration when the molecules are associated because of hydrogen bonding. In a more recent study, Smith and Creitz (*17*) resolved the broad association band at 3350 cm.$^{-1}$ into components attributed to the dimeric and polymeric forms. The free OH in the vapor has been reported at slightly higher frequencies of 3650 and 3687 cm.$^{-1}$ (*2, 14*).

The only deuterated alcohols reported in the literature to date were methyl and ethyl alcohols (*2, 3, 13*). Halford, Ander-

Table I. Infrared and Raman Spectra of Deuterated Alcohols (Liquid State)

(Frequency, cm.$^{-1}$)

C_3H_7OD		C_4H_9OD		$C_5H_{11}OD$		$C_6H_{13}OD$		$C_8H_{17}OD$		$C_{10}H_{21}OD$		$C_2H_5CHODCH_3$	
Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared
460 (4)	..	355 (4)	..	333 (2)	..	319 (3)	..	..	666 w	..	667 w	384 (2)	..
771 (2)	752 w	409 (7)	..	361 (2)	..	361 (2)	..	..	720 m	..	683 vw	439 (2)	..
850 (8)	..	453 (2)	..	407 (2)	..	406 (2)	..	..	760 w	..	703 vw	505 (3)	..
879 (6)	886 m	492 (2)	..	424 (2)	..	..	726 m	..	766 w	..	715 vw	779 (6)	775 m
961 (3)	968 vs	523 (2)	..	510 (2)	..	..	765 vw	864 (3)	874 w	..	723 m	820 (8)	814 m
..	1017 vs	..	735 w	..	679 w	811 (4)	..	..	932 w	855 b(2)	..	906 (3)	911 s
1048 (4)	1055 vs	808 (4)	..	..	729 m	854 (2)	..	..	944 w	..	877 w	..	947 w
1072 (4)	1071 w	820 (7)	..	..	738 w	889 (7)	890 w	..	954 w	..	944 w	..	968 m
1101 (5)	1101 w	845 (3)	845 m	776 (4)	780 w	927 (2)	918 m	1050 b (4)	1050 s	..	1020 w	..	993 s
..	1232 w	876 (2)	..	830 (5)	832 w	..	949 w	1077	..	..	1052 s	1024 (3)	1034 s
1276 (4)	1266 w	893 (1)	900 w	859 (4)	..	..	964 w	1122 (7)	..	1072 b(7)	..	1110 (2)	1120 s
1299 (4)	..	947 (3)	915 w	881 (5)	889 m	..	991 w	..	1240 w	1115 (7)	..	1158 (2)	1142 s
..	1338 w	957 (3)	951 m	..	938 w	..	1032 m	1299 (8)	1308 w	1299 (9)	..	1205 (1)	1268 w
..	1385 s	1025 (3)	1030 s	1002 (2)	1007 s	..	1057 s	..	1332 w	..	1316 w	1308 (1)	1300 w
1443 (8)	1460 s	1043 (3)	1043 s	1055 (6)	1056 vs	1072 b(4)	..	..	1370 s	..	1338 m	1359 (1)	1332 w
..	2477 sb	1073 (3)	1074 s	1081 (6)	1075 w	1115 (5)	1118 w	..	1417 w	..	1374 s	..	1374 s
..	2726 w	1105 (4)	1114 m	1119 (4)	1121 w	..	1192 w	1448 (9)	1469 s	..	1396 w	..	1419 vw
2884(10)	2879 vs	..	1208 w	..	1217 w	..	1257 vw	..	2160 vw	..	1421 w	1450 (7)	1458 s
2924(10)	2941 vs	..	1236 w	..	1250 w	1299 (9)	1309 w	..	2192 vw	1439 (8)	1437 w	2457 (1)	..
2936(10)	2969 vs	1299 (7)	1299 w	1306 (8)	1300 w	..	1336 m	..	2476 sb	..	1462 s	..	2490 sb
2972(10)	..	..	1340 w	..	1336 w	..	1367 m	..	2740 w	..	2477 sb	2673 (6)	..
		..	1380 s	..	1380 s	1448 b(9)	1465 s	2848 b(10)	2864 vs	..	2736 w	2884(10)	2883 m
		1432 (8)	1440 w	1448 (7)	1467 s	..	2158 vw	2948	2934 vs	2848(10)	2858 vs	2948(10)	2934 s
		1476 (8)	1462 s	..	2025 w	..	2193 vw	2972 (2)	2962 s	2944(10)	2931 vs	2980(10)	2973 s
		..	2476 sb	..	2477 sb	..	2476 sb			2972 (2)	2962 s		
		2673 (6)	..	2681 (5)	2680 w	..	2740 vw						
		..	2740 w	..	2740 w	2864 b(10)	2868 vs						
		2876(10)	2878 vs	2876(10)	2876 s	2952	2935 vs						
		2912(10)	..	2912(10)	..	..	2963 s						
		2944(10)	2939 vs	2944(10)	2939 vs	..	..						
		2972(10)	2967 vs	2972(10)	2965 vs	..	..						

vw = very weak
w = weak
m = moderate
s = strong
vs = very strong
b = broad band

son, and Kissin (*7*) reported a value of 2500 cm.$^{-1}$ in the Raman spectrum for the corresponding OD stretching frequency in liquid deuterated methanol. The OD stretching vibration of deuterated methanol has a broad infrared band at 2500 cm.$^{-1}$ in the associated state which shifts to 2720 cm.$^{-1}$ in the vapor state.

EXPERIMENTAL

The alcohols used in this study were dried over Drierite (anhydrous calcium sulfate) and fractionated over calcium hydride in an all-glass still consisting of a 35-cm. fractionating column packed with glass helices, and equipped with a variable ratio distillation head.

Preparation and Purification of Deuterated Alcohols. The deuterated alcohols were prepared in a dry box from the corresponding magnesium alkoxides. The magnesium alkoxides were prepared by the method of Meerwein and Schmidt (*12*), and then reacted with 99.8 mole % D_2O.

Preliminary Raman spectra of the deuterated alcohols showed a continuous background which obscured many of the Raman shifts. This background was eliminated by heating the alcohol for approximately 0.5 hour at about 10° below its boiling point with Nuchar. The suspension was shaken frequently and the charcoal removed by filtration in a dry box after the suspension was cooled to room temperature.

Infrared Spectra. Infrared spectra were obtained with a Perkin-Elmer, Model 12-B, recording spectrometer using a sodium chloride prism from 650 to 1850 cm.$^{-1}$ and a lithium fluoride prism from 1850 to 4000 cm.$^{-1}$ The spectrometer was maintained in an air-conditioned room at 20° ± 1° C. and at a relative humidity of 40 ± 1%. A 0.025-mm. fixed cell with rock salt windows was used for these spectra, except for the broad bands which were resolved by putting 1 drop of the alcohol between two rock salt windows and fastening them tightly together. Vapor spectra were obtained with a 10-cm. or a 1-meter gas cell with rock salt windows.

The spectra of all the liquid alcohols were also measured on a Baird Associates spectrometer using a sodium chloride prism.

Raman Spectra. Raman spectra were obtained with a Hilger Raman source using a Hilger medium spectrograph equipped with glass optics. The dispersion of this unit was about 25 A. per mm. at 4358 A. A 0.5-hour exposure, using the 4358 A. mercury line for excitation with a sodium nitrite filter was sufficient to give good spectra of the alcohols, which were photographed on Eastman Kodak spectrographic plates 103-0. Intensity values were determined by visual estimation, arbitrarily assigning a value of 10 to the most intense line on each plate.

DISCUSSION AND CONCLUSION

The Raman and infrared spectra of the deuterated alcohols are listed in Table I. The spectra in the liquid state of the un-

Table II. Infrared Spectra of Alcohols (Vapor State)

(Frequency, cm.$^{-1}$)

C_3H_7OH	C_3H_7OD	C_4H_9OH	C_4H_9OD	$C_5H_{11}OH$	$C_5H_{11}OD$	$C_2H_5CH(OH)CH_3$	$C_2H_5CH(OD)CH_3$
667 wb	667 wb	604 wb	604 wb	..	..	..	..
678 wb	680 wb	..	..	676 wb	676 wb	678 wb	678 wb
687 wb	..	698 wb	..	695 wb	695 wb	696 wb	..
707 wb	706 wb	722 wb	..	711 wb	711 wb	...	..
733 wb	719 wb	738 wb	738 wb	734 wb	732 wb	722 w	722 w
..	..	..	..	752 wb	740 wb	..	..
..	..	772 wb	770 wb	762 wb	777 wb	..	..
808 wb	808 wb	799 wb	799 wb	807 wb	799 wb	..	846 w
816 wb	..	..	..	..	..	..	..
827 wb	827 wb	..	..	..	..	..	..
843 wb	..	..	..	..	..	..	..
858 wb	848 wb	853 wb	848 wb	872 wb	872 wb	886 w	856 w
911 wb	911 wb	..	..	897 wb	897 wb	907 m	907 m
962 ⎫	962 ⎫	954 wb	950 wb	938 wb	935 wb	920 m	920 m
971 ⎬ s	971 ⎬ s	..	..	975 wb	975 wb	..	..
980 ⎭	980 ⎭	997 w	983 w	997 wb	..	992 m	992 m
1012 w	1012 w	1021 w	1021 w	1013 w	1013 w	1026 vw	1028 vw
1032 w	1032 w	1043 ⎫	1043 ⎫	..	..	1040 vw	1042 vw
1050 m	1050 m	1057 ⎬ s	1057 ⎬ s	1054 s	1054 s	1076 ⎫ m	1076 ⎫ m
1065 s	1065 s	1070 ⎭	1067 ⎭	..	..	1084 ⎭	1084 ⎭
..	..	..	..	..	..	1128 w	1130 w
..	..	..	..	..	..	1145 w	1145 w
1222 m	1222 m	1210 w	1210 w	..	..	1241 m	1241 m
1393 m	1394 m	1394 m	1394 m	1394 m	1394 m	1394 m	1393 m
1462 m	1462 m	1459 m	1459 m	1459 m	1459 m	1459 m	1459 m
..	2726 w	..	2726 w	..	2726 w	..	2726 w
..	..	2853 w	2853 w	2856 w	2856 w	..	..
2894 s	2894 s	2893 s	2894 s	2889 m	2888 m	2891 s	2892 s
2928 m	2928 m	2926 m	2928 m	..	..	..	..
2949 s	2949 s	2949 s	2949 s	2943 m	2943 m	2943 s	2943 s
2978 s	2978 s	2973 s	2973 s	2973 m	2973 m	2980 s	2980 s
3682 w	..	3682 w	..	3682 w	..	3682 w	..

deuterated alcohols showed excellent agreement with results previously reported (*1, 5, 20*). Spectra in the vapor state are reported in Table II for both types.

The OH stretching frequency in the liquid, or associated state, gives rise to a broad band at about 3332 cm.$^{-1}$ which shifts to a sharp band at 3682 cm.$^{-1}$ in the vapor state as indicated in Table III. The corresponding OD stretching frequency appears as a broad band at 2476 cm.$^{-1}$ in the liquid state. Dilution of the deuterated alcohols with carbon disulfide brought about a decrease in intensity of this 2476 cm.$^{-1}$ band and a corresponding appearance of a band at 2680 cm.$^{-1}$ which is ascribed to the dimeric state of aggregation corresponding to the dimeric band of 3497 cm.$^{-1}$ in alcohols reported by Smith and Creitz (*17*). Extensive dilution with carbon tetrachloride or transition to the vapor state caused the disappearance of the broad association band and the appearance of a weak, sharp band at 2726 cm.$^{-1}$ corresponding to the free OD stretching vibration. The regularity of the OD stretching frequency in this series of alcohols indicates its value as a group frequency in the study of hydroxylic compounds.

Table III. Hydroxyl Stretching Frequencies, for a Series of Alcohols

(Frequency, cm.$^{-1}$)

	OH		OD		
	Free	Associated	Free	Dimer	Associated
1-Propano	3682	3330	2726	2680	2477
1-Butanol	3682	3332	2726	2685	2476
1-Pentanol	3682	3331	2726	2684	2477
1-Hexanol	3682	3332	2726	2683	2476
1-Octanol	..	3329	..	2683	2476
1-Decanol	..	3332	..	2683	2477
2-Butanol	3682	3360	2726	2680	2490

The in-plane OD bending frequency appears at about 940 cm.$^{-1}$ in this series of alcohols as indicated in Table IV. The intensity of this band varies from moderate in methyl and ethyl alcohols to weak in the higher alcohols. In the vapor state this band is shifted to lower frequencies and is found at 860 cm.$^{-1}$ in methanol and 2-butanol. The vapor spectra of the other alcohols show a series of weak bands in this region which obscure this vibration. Dilution with carbon disulfide produces a decrease in intensity of the 940 cm.$^{-1}$ band, characteristic of an associated vibration.

Table IV. Hydroxyl Deformation Frequencies for a Series of Alcohols

(Frequency, cm.$^{-1}$)

	OH	OD
1-Propanol	..	..
1-Butanol	1010	915
1-Pentanol	..	938
1-Hexanol	1021	949
1-Octanol	1020	944
1-Decanol	1035	944
2-Butanol	..	947

The corresponding OH deformation vibration was assigned by various authors (*4, 13*) to two general regions—i.e., 1030 and 1340 cm.$^{-1}$ These assignments are based on the change in intensity of the particular band in transition from liquid to vapor states or else by analogy with the spectra of methanol and deuterated methanol, since this is the only deuterated alcohol previously investigated for structural studies.

The similarity of the infrared spectra of the deuterated and undeuterated higher alcohols in the region 1300 to 1400 cm.$^{-1}$ precludes the assignment of the OH deformation frequency in this region. There is an infrared band at about 1120 cm.$^{-1}$ in the associated state which disappears upon vaporization. This band, however, is present in the deuterated as well as in the undeuterated alcohols, so it is not the OH deformation formation. It disappears from the infrared spectra of 1-octanol and 1-decanol upon deuteration but it is Raman active in both the deuterated and undeuterated alcohols throughout this series. Recent studies of hydrogen bonding in alcohols assign this frequency to a rocking vibration of the molecule (*18*).

The saturated straight-chain alcohols have the hydroxyl deformation vibration from 1010 to 1035 cm.$^{-1}$ This assignment of the symmetrical OH deformation frequency is in agreement with the suggestion of Herzberg (*8*) of a value of 1056 cm.$^{-1}$ Because the CO stretching frequency of these alcohols appears at 1030 to 1060 cm.$^{-1}$ there is considerable overlapping, especially in the lower members of the series where the CO stretching vibration is approximately 1030 to 1050 cm.$^{-1}$ and the deformation band cannot be resolved. In the longer chain alcohols the CO stretching frequency is at 1060 cm.$^{-1}$ and the OH deformation band can be found as a definite band on the low frequency side of the broad 1060 cm.$^{-1}$ band. Dilution with carbon disulfide shifts the OH band to a lower frequency by about ten wave numbers. The shift to lower frequency brought about by unbonding is characteristic of the deformation frequency. The weakness of the OH deformation band and its unfavorable position close to the strong CO stretching frequency and skeletal vibrations of some of the aliphatic groups, limits its usefulness as a group frequency.

A similar problem arises in the assignment of the NH deformation frequency. A strong band at 1560 cm.$^{-1}$ has been assigned to both the CN stretching and NH bending frequency by various investigators (*10, 16*). A recent study (*11*) of the amide group assigns this frequency to the CN stretching vibration and the NH bending, which cannot be found in the infrared spectrum, must therefore be obscured by the strong CH bending group at 1406 to 1460 cm.$^{-1}$ The sensitivity of both the NH and OH deformation frequencies to inter- and intramolecular interactions, and their positions in the region of skeletal frequencies makes the assignment of the hydrogenic deformation modes much more difficult than the corresponding stretching vibrations.

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