Raman Spectra of a Series of Normal Alcohols and Other Compounds

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The Raman spectra of benzene, cyclohexane, cyclohexene, carbon disulfide, butyl bromide and the normal alcohols from CH_3OH to $C_{12}H_{25}OH$ were investigated. The technique recently developed by Wood was used in conjunction with a praseodymium filter. New lines were found in all cases and for some compounds the number was nearly doubled. Two new frequencies at 2660 and 2730 cm^{-1} were found in the spectra of essentially all the alcohols and butyl bromide. They appear to be characteristic of the saturated hydrocarbons. The lines which appear in the Raman spectra of the aliphatic hydrocarbons at 1450 and 1300 cm^{-1} have been attributed respectively to the transverse vibrations of the hydrogens of the CH_3 and CH_2 groups. The line appearing in the Raman spectra of the alcohols at 1270 cm^{-1} is attributed to the transverse vibrations of the hydrogens of the CH_2OH groups. It is pointed out that the Raman spectra of $C_{12}H_{25}OH$ is that of an infinitely long normal alcohol. The new lines of benzene reported by Weiler and Krishnamurti were verified with the exception of the 806 cm^{-1} frequency. In addition a new line at 1690 cm^{-1} was found. The two relatively strong lines of CS_2 at 650 and 800 cm^{-1} were each found to be doublet, thus completing the analogy with CO_2. The separation of the components in each case was 10 cm^{-1}. The existence of a line at 391 cm^{-1}, originally reported by Bhagavantam, was verified.

THE Raman spectra of a number or organic compounds were investigated by an experimental arrangement recently developed by Wood.[1] New lines were found in all cases, and in some the number was nearly doubled. This emphasizes the importance of repeating much of the earlier work that was done before the technique of Raman spectra reached its present stage of development. Most of the recent improvements have been in the direction of improved methods of excitation, and it is perhaps well to call attention to the advantages of using spectroscopes of relatively high dispersion. This is shown by the present investigation in which a glass prism spectrograph with dispersion of 22A per mm in the blue was used. It was found that many of the bands reported in the literature actually possess structure. Likewise Langseth[2] using a one meter grating, found that the Raman lines of CCl_4 were double, and in some cases even triple. There is no doubt but that incomplete and inaccurate data have greatly retarded the interpretation of Raman spectra.

We have investigated the Raman spectra of a series of normal alcohols beginning with methyl (CH_3OH) and ending with dodecyl alcohol ($C_{12}H_{25}OH$). This series was loaned to us by Professor E. Emmet Reid of this University, and was complete up to $C_{17}H_{35}OH$. It proved to be unnecessary, however,

[1] R. W. Wood, Phys. Rev. **38**, 2168 (1931).
[2] Langseth, Zeits. f. Physik **72**, 350 (1931).

to investigate those above $C_{12}H_{25}OH$ as the higher members showed no differences in their Raman spectra. Benzene, cyclohexane and cyclohexene were taken since very pure samples of these were available. As they have already been rather extensively investigated, they served to indicate the efficiency of the apparatus. Carbon disulfide was investigated in order to verify the existence of a line at 390 cm^{-1} which is of vital importance in the analysis of the Raman and infrared spectra.

EXPERIMENTAL

All excitation was by Hg 4358. The experimental arrangement was essentially that described by Wood, modified in that two filters were employed in two Pyrex tubes placed one above the other over the mercury arc. The diameters of these tubes were 5 cm and 2.3 cm, the larger being placed below. With this arrangement a large part of the exciting light from the arc was concentrated into a narrow beam passing vertically through the Raman tube. In most cases a 30 percent aqueous solution of praseodymium ammonium
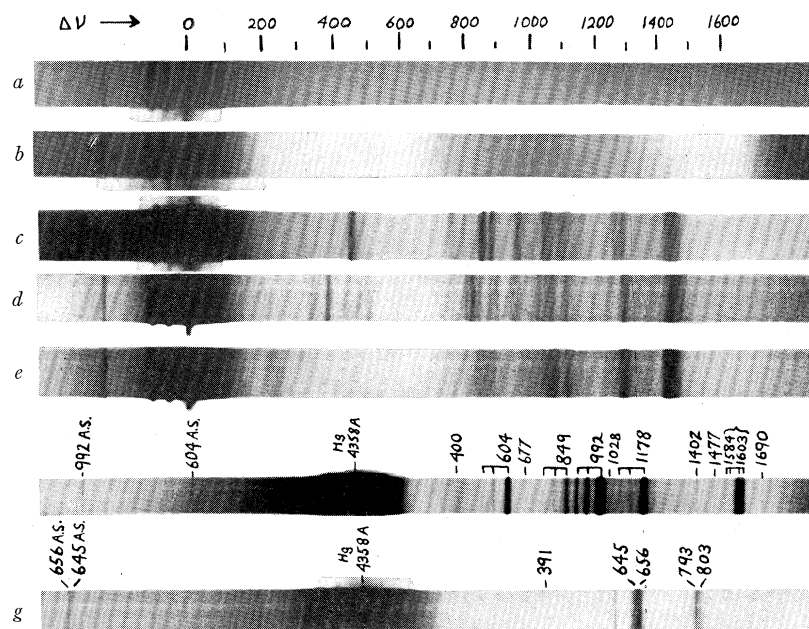

Fig. 1. a, Hg arc; b, Hg arc through praseodymium filter; c, C_3H_7OH (n); d, C_4H_7OH (n); e, $C_{10}H_{21}OH$ (n); f, benzene; g, carbon disulfide.

nitrate was placed in the smaller tube. Praseodymium has a strong and very sharp absorption band on the long wave-length side of, and very close to, Hg 4358, and when used as a filter absorbs the strong continuous spectrum of the mercury arc in this region, leaving a clear background for the Raman lines. Such a filter is particularly advantageous in obtaining Raman lines of low frequency when the excitation is by Hg 4358. Figs. 1a and 1b show the effec-

tiveness with which this filter removes the background. This filter has the disadvantage of reducing the intensity of Hg 4358 to about one-half when used in the above concentration. A rather strong solution of crystal violet was substituted for the praseodymium when investigating Raman lines of frequency greater than 2000 cm^{-1}. The larger tube contained a quinine solution of sufficient concentration to absorb Hg 4047 and Hg 4077 and was protected against photochemical change by a sheet of noviol glass, as previously described. With this arrangement it was possible to make exposures of 70 hours or more before the general background appeared with appreciable intensity.

The wave-lengths of the Raman lines were determined by interpolation on a large dispersion curve obtained from the iron lines of the comparison spectrum. The frequencies given are accurate to about ± 3 cm^{-1} for moderately sharp lines.

The alcohols from $C_8H_{17}OH$ to $C_{12}H_{25}OH$ were prepared by Dr. Jane Meyers of this University. Those from CH_3OH_4 to $C_7H_{25}OH$ were obtained from other reliable sources, and all were carefully purified by distillation. The benzene, cyclohexane, and cyclohexene were from samples especially purified for specific heat and melting point determinations. The remaining liquids investigated were from standard C. P. sources.

RAMAN SPECTRA OF ALCOHOLS

A chart of the Raman lines of the normal alcohols from CH_3OH to $C_{12}H_{25}OH$ is given in Fig. 2. The lines of frequency greater than 1500 cm^{-1} are not included, but may be found in the complete list of Table I. $C_{11}H_{23}OH$ is omitted from this series as it was not obtainable in sufficient quantities. Enlargements of some of the original plates may be found in Fig. 1.
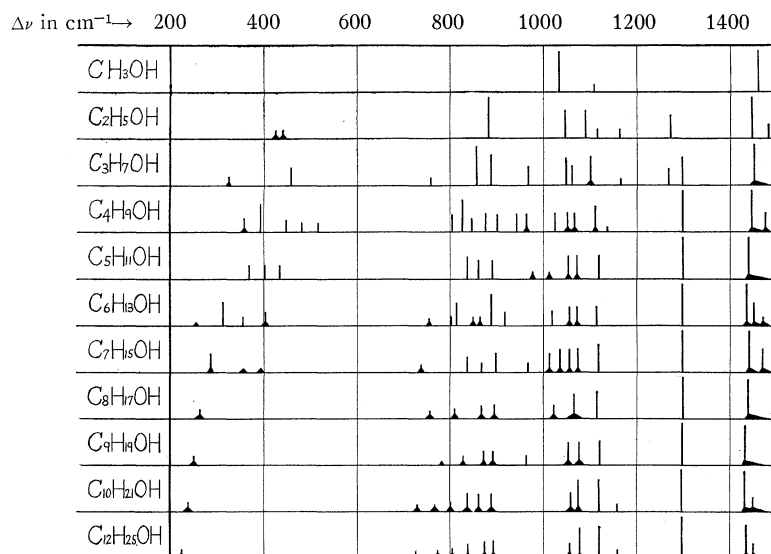

Fig. 2. Diagram of Raman frequencies of alcohols showing relative intensity and breadth of lines.

TABLE I. *Raman frequencies in* cm^{-1}.

CH_3OH	1028(10) 1107(2) 1457(10) 2729(1) 2831(10) 2942(10)
C_2H_5OH	426(5) 443(2) 883(20) 1047(10) 1091(10) 1115(1) (1162)(1) 1273(8) 1449(10) 1481(4) 2637(0) 2714(1) 2823(2) 2783(10) 2925(10) 2972(10)
$C_3H_7OH(n)$	324(2) 458(4) 757(4) 856(10) 887(8) 967(4) 1049(5) 1064(4) 1100(6) 1268(4) 1296(6) 1451(10) 2663(1) 2731(2) 2873(15) 2905(10) 2931(10) 2963(10)
C_4H_9OH	350(3) 394(6) 448(3) 483(2) 514(2) 805(4) 825(8) 845(3) 877(4) 901(4) 944(4) 963(4) 1025(4) 1051(4) 1067(4) 1104(6) 1135(1) 1296(1) 1147(10) 1476(4) 2660(1) 2733(1) 2865(10) 2903(10) 2932(10) 2963(15)
$C_5H_{11}OH$	366(3) 401(3) 434(3) 835(3) 858(4) 889(4) 975(1) 1013(1) 1053(5) 1072(5) 1116(5) 1299(10) 1442(10) 2653(1) 2721(1) 2868(10) 2908(10) 2935(5) 2961(5)
$C_6H_{13}OH$	253(1) 311(5) 355(2) 402(3) 754(2) 802(2) 814(5) 850(2) 864(2) 888(8) 915(3) 1019(3) 1056(4) 1072(4) 1113(4) 1297(10) 1435(10) 1451(5) 1472(2) (Band 2842 to 2932 (10)) 2958(3)
$C_7H_{15}OH$	287(3) 357(1) 392(1) 735(2) 836(3) 866(2) 897(4) 966(2) 1012(4) 1035(5) 1054(5) 1074(5) 1116(6) 1297(10) 1442(10) 1471(5) (Band 2842 to 2952(10))
$C_8H_{17}OH$	263(2) 759(1) 809(2) 867(3) 894(3) 1023(3) 1066(5) 1120(6) 1300(10) 1442(10) (Band 2848 to 2941 (10))
$C_9H_{19}OH$	250(2) 784(1) 830(2) 872(3) 891(3) 963(2) 1055(5) 1078(5) 1118(5) 1297(10) 1432(10) (Band 2842 to 2932(10)) 2958(2)
$C_{10}H_{21}OH$	238(2) 727(1) 768(1) 801(2) 838(3) 863(3) 889(4) 1059(4) 1076(7) 1116(7) 1159(2) 1295(10) 1430(10) 1449(3) 2643(1) 2719(1) (Band 2836 to 2929(10)) 2954(2)
$C_{12}H_{25}OH$	224(2) 722(1) 771(1) 805(2) 838(4) 874(4) 893(4) 1056(4) 1079(7) 1119(7) 1159(2) 1297(10) 1433(10) 1449(10) 2847(10) 2887(10) 2925(8) 2958(3)
Benzene	400(2) 604(10) 677(1) 849(5) 982(2)* 992(20)* 1028(0) 1178(10) 1402(2) 1477(2) 1584(10) 1603(5) 1690(1) 2291(0) 2452(1) 2542(1) 2618(2) 2920(0) 2948(3) 3051(5)* 3065(5)* 3163(2)* 3186(2)*
Cyclohexane	380(2) 422(3) 801(10) 1026(8) 1154(4) 1264(8) 1342(2) 1442(10) 2626(0) 2661(1) 2693(0) 2750(0) 2849(10) 2880(1) 2920(10) 2934(10)
Cyclohexene	171(2) 282(3) 390(5) 445(1) 487(2) 635(1) 715(3) 821(10) 873(2) 904(3) 963(3) 1034(3) 1062(5) 1134(1) 1218(10) 1238(2) 1263(4) 1426(10) 1443(3) 1650(10) 2634(9) 2660(1) 2833(10) 2856(10) 2873(10) 2908(10) 2934(10) 3020(10)
Carbon disulfide	391(1) 645(10) 656(20) 793(8) 803(3)
Butyl bromide	218(3) 235(3) 276(5) 345(1) 387(2) 411(2) 457(5) 559(20) 640(10) 736(5) 796(6) 833(0) 865(5) 893(4) 909(2) 967(1) 993(2) 1011(2) 1048(8) 1097(8) 1214(5) 1260(4) 1294(5) 1441(10) 2660(0) 2733(1) 2833(2) 2868(10) 2902(5) 2934(10) 2963(10) 3008(3)

* Weiler's values.

Two new Raman lines, hitherto unreported, were found in the spectra of C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$ and $C_{10}H_{21}OH$. They lie at about 2660 and 2730 cm^{-1}. CH_3OH shows only the one at 2730 cm^{-1}. To determine whether these frequencies are associated with the OH groups, the Raman spec-

tra of C_4H_9Br were taken. The position of these new lines was found to be the same in C_4H_9Br and C_4H_9OH showing that they are independent of the radical attached to the end of the molecule. This, combined with the fact that these frequencies appear in so many of the alcohols, makes it seem likely that they are characteristic of the saturated hydrocarbons. New lines, in addition to those discussed above, are now considered.

In methyl alcohol a new frequency was found at 1107 cm⁻¹.

In ethyl alcohol the 426 cm⁻¹ frequency as reported in Kolhrausch[3] was resolved into two components, 426 and 443 cm⁻¹, and an additional lines was discovered at 1115 cm⁻¹.

In normal propyl alcohol new lines were found at 324, 757, 1064, 1165 and 1268 cm⁻¹. The frequency 1364 cm⁻¹ reported by Duare[4] and by Gamesan and Venkateswaran[5] was not verified. Trumpy likewise failed to find this line.

Six new lines were found in the spectrum of normal butyl alcohol (C_4H_9OH) and six lines previously considered single were resolved into two components. The Raman spectra of normal alcohols above butyl have not been investigated previously.

Lines whose frequencies remain unchanged, or which change in a systematic way from molecule to molecule, are of course the easiest to interpret. Attention is called to five of this type which occur in the spectrum of the alcohols. There is the broad, often unresolved, line at 1450 cm⁻¹, the strong lines at about 1300 and 1120 cm⁻¹, the double line at 1055 and 1075 cm⁻¹ (unresolved in $C_8H_{17}OH$), and the group of lines below 500 cm⁻¹. Something may be said in regard to these frequencies.

Kohlrausch[3] and Trumpy[6] have attributed the 1450 cm⁻¹ frequency to vibrations of the hydrogens of the

$$\begin{array}{c} H \\ | \\ -C- \\ | \\ H \end{array}$$
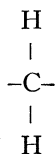
groups (referred to in the future as CH_2 groups). They have at the same time attributed the 1300 cm⁻¹ frequency to vibrations of the end CH_3 groups against the remainder of the molecule. This assignment appears unlikely, since, if the line at 1300 cm⁻¹ were due to vibrations of the CH_3 group against the remainder of the molecule, its frequency should diminish with increasing mass of the molecule. Fig. 2 shows clearly that this is not the case, and another explanation must be looked for. Andrews has pointed out that the line at 1450 cm⁻¹ appears whenever a CH_3 group is present in a molecule, and that the line at 1300 cm⁻¹ is usually associated with the presence of CH_2 groups. These two lines presumably arise from a transverse or bending motion

[3] Kohlrausch, *Der Smekal Raman Effekt,* p. 309.

[4] Duare, Ann. d. Physik **12**, 375 (1929).

[5] Gameson and Venkateswaran, Ind. Jour. Phys. **4**, 196 (1929).

[6] Trumpy, Zeits. f. Physik **62**, 806 (1930).

of the hydrogen atoms with respect to the carbons. The fact that these frequencies are so constant would indicate that the influence of the hydrogen bending motions does not extend to adjacent atoms. The 1270 cm^{-1} line which appears in the spectrum of ethyl and propyl alcohol is then explained as arising from transverse vibrations of the hydrogens of the

$$\begin{array}{c} H \\ | \\ -C-OH \\ | \\ H \end{array}$$
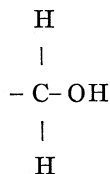
groups (referred to as a CH$_2$OH group). The hydrogens of this group would be expected to have a different frequency from those of the CH$_2$ group as their bond strength should be changed by the presence of the OH radical. In support of this contention, attention may be called to the following.

Methyl alcohol (H$_3$COH) and isopropyl alcohol[3] (H$_3$C·HC·OH) CH$_3$ contain no CH$_2$OH or CH$_2$ groups, and do not show the 1270 and 1300 cm^{-1} frequencies. Ethyl alcohol (H$_3$C·H$_2$COH) contains a CH$_2$OH group, and no CH$_2$ group, and shows only the 1272 cm^{-1} frequency. Normal propyl alcohol (H$_3$C·H$_2$C·H$_2$OH) contains a CH$_2$OH group and shows both the 1270 and the 1300 cm^{-1} frequencies. Butyl (H$_3$C·H$_2$C·H$_2$C·H$_2$COH) and the higher alcohols, however, have both CH$_2$OH and CH$_2$ groups, and show only the 1300 cm^{-1} frequency, indicating a possible discrepancy. The explanation may be, however, that the 1270 cm^{-1} frequency exists in the higher alcohols, and is simply too weak to be recorded. The decreased number of CH$_2$OH groups with respect to the CH$_2$ groups in the higher alcohols makes this explanation plausible.

The double frequency at 1055 and 1070 cm^{-1} probably arises from a sidewise compressional motion of the carbon chain suggested by Collins.[7] These values are close to the calculated one of 1075 cm^{-1}. In calculating this frequency the influence of the hydrogen atoms attached to the carbons was neglected. Their influence may produce two frequencies instead of one, resulting from the hydrogens vibrating with or against the carbon atoms. A compressional vibration of the type considered is optically inactive, and would account for the high intensity of these lines. It is to be noted that the Raman spectra of C$_{10}$H$_{21}$OH and C$_{12}$H$_{25}$OH are identical and these two spectra differ but slightly from that of C$_9$H$_{19}$OH. A further increase in the length of the carbon chain above that of C$_{12}$H$_{25}$OH should then produce no change in the Raman spectra. This being the case the Raman spectra of C$_{12}$H$_{25}$OH may be considered that of an infinitely long hydrocarbon chain with an OH group at one end.

RAMAN SPECTRUM OF BENZENE

The Raman spectrum of benzene has been examined recently by Weiler[8]

[7] Collins, Phys. Rev. **40**, 829 (1932).

[8] Weiler, Zeits. f. Physik **69**, 586 (1931).

and Krishnamurti,[9] who have reported new frequencies at 687, 806, 1407 and 1477 cm^{-1}. The existence of all these frequencies with the exception of 806 cm^{-1} was verified. The position of the latter frequency when excited by Hg 4358 coincides closely with that of the strong 848 cm^{-1} Raman line excited by a weaker line of the mercury triplet (Hg 4347.5), and it was found impossible to distinguish between the two. Inasmuch as Krishnamurti used Hg 4358 as the exciting line, the existence of 806 cm^{-1} is perhaps doubtful. A hitherto unreported frequency was found at 1690 cm^{-1}. This Raman line falls within one of the praseodymium absorption bands, and otherwise would probably be masked by the continuous background of the arc. An enlargement of one of the benzene plates is given in Fig. 1b with the Raman frequencies, both stokes and antistokes marked. The effect of the praseodymium filter in reducing the continuous background is very noticeable.

Raman Spectra of Cyclohexane and Cyclohexene

The samples of cyclohexane and cyclohexene were of extreme purity, and benzene-free. There was no evidence of the cyclohexane line at 992 cm^{-1} reported by Krishnamurti, and since this frequency corresponds to the strong est benzene line, the inference is obvious. The existence of the new lines in cyclohexane reported by Krishnamurti at 2630, 2662, 2889 and 2963 cm^{-1} was verified, with small discrepancies in their exact frequencies.

Cyclohexene, due no doubt to its unsymmetrical ring structure, shows many more Raman lines than either benzene or cyclohexane. In addition to those already reported by Weiler,[8] new lines were found at 445, 715, 1134, 1238, 2634, and 2660 cm^{-1}; the latter not appearing in benzene and having perhaps the same origin as the lines of similar frequency which occur in the Raman spectra of the alcohols.

Raman Spectrum of Carbon Disulfide

A special effort was made to obtain the complete spectrum of CS_2. The lines at 645 and 793 cm^{-1} were resolved into two components, the separation in both cases being 10 cm^{-1}. An enlargement of one of the plates is shown in Fig. 1g. From this is can be seen that the weaker component of the 800 cm^{-1} line is on the long wave-length side while the weaker component of the 650 cm^{-1} line is on the short wave-length side. As is to be expected, this condition is reversed in the antistokes member of the 650 cm^{-1} line. Of the three lines reported by Bhagavantam[10] at 412, 1229 and 1577 cm^{-1} only the first was verified. The observation of 793–803 as a doublet is of especial interest. It has been previously reported single but a doublet is required to make the analogy with the spectrum of CO_2 complete.

[9] P. Krishnamurti, Ind. Jour. Phys. **4,** 543 (1931).
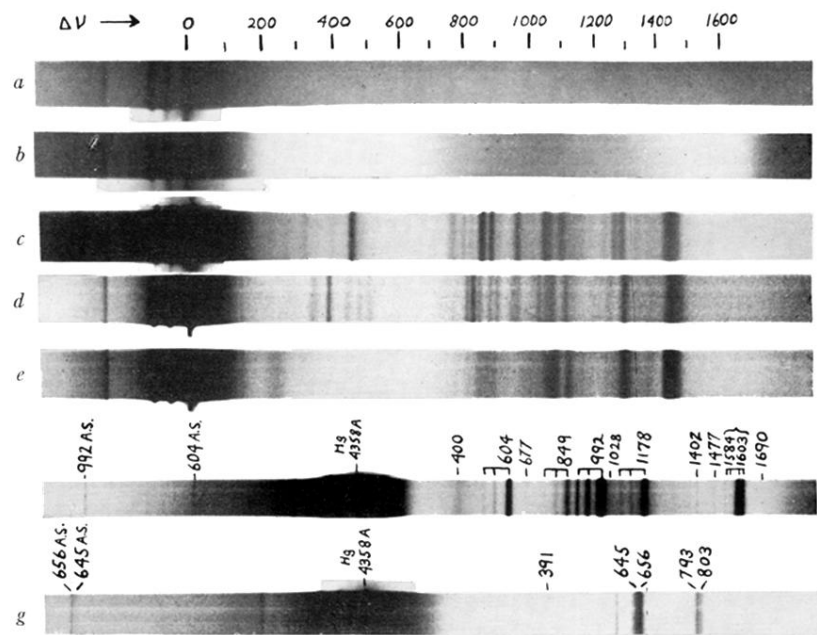[10] Bhagavantam, Nature **126,** 995 (1930).

Fig. 1. a, Hg arc; b, Hg arc through praseodymium filter; c, C_3H_7OH (n); d, C_4H_7OH (n); e, $C_{10}H_{21}OH$ (n); f, benzene; g, carbon disulfide.