RAMAN SPECTRA STUDIES.[1] I. DIPHENYLMETHANE, ALIPHATIC BROMIDES AND MERCAPTANS

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Introduction

During the past five years experimental investigations and theoretical development of the Raman effect have contributed much to our knowledge of the structure and chemical behavior of molecules by identifying Raman lines with the chemical bond.[2] The energy changes represented by Raman lines were early associated with fundamental molecular frequencies,[3] and the relation of Raman frequencies to the vibrational energy of the molecule has recently been presented and discussed by Andrews.[4]

The present work includes a study of the Raman spectra of diphenylmethane, normal butyl and normal hexyl bromides, and normal amyl, normal hexyl, and normal heptyl mercaptans. It was suggested by the important function of Raman data in specific heat determinations and in the calculation of thermal energy associated with the vibrations of the different parts of the molecule.[5]

Apparatus

Light Source and Light Filter.—A helium spiral discharge tube similar to the one described by Wood,[6] and made by the Claude Neon Company of Baltimore, furnished the light for exciting the Raman lines recorded for diphenylmethane. The copper gauze electrodes of this discharge tube were connected to an oil transformer which converted the 220 volts across the alternating circuit to approximately 20,000 volts. The helium line, λ 3888.6, was transmitted by a nickel oxide glass filter.

A Cooper–Hewitt quartz mercury arc, maintained between 35 and 45 volts, was used to excite the Raman lines of all other substances. An aluminum reflector concentrated the mercury light on the Raman tube. In some instances the 4046 mercury group was eliminated by a 0.5% acid quinine sulfate filter.

An iron arc, taking 4 or 5 amperes, furnished comparison spectra for measuring the Raman lines.

Raman Tube.—The Raman tube, similar to those used by Wood, was 2.5 cm. in

[1] From the dissertation submitted by Elizabeth A. Crigler to the Faculty of Philosophy, The Johns Hopkins University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Andrews, *Phys. Rev.*, **36**, 544 (1930); Bhagavantam, *Indian J. Physics*, **5**, 237 (1930); Kohlrausch, "Der Smekal-Raman Effekt." Julius Springer, Berlin.

[3] Raman, *Indian J. Physics*, **2**, 387 (1928); Raman and Krishnan, *Nature*, **122**, 278 (1928); Coblentz, *Phil. Mag.*, **7**, 203 (1929).

[4] Andrews, *Ind. Eng. Chem.*, **23**, 1232 (1931).

[5] Andrews and Southard, *Phys. Rev.*, **35**, 670 (1930); Smith and Andrews, THIS JOURNAL, **53**, 3644 (1931); Smith and Andrews, *ibid.*, **53**, 3661 (1931); McGraw, *ibid.*, **53**, 3683 (1931).

[6] Wood, *Phil. Mag.*, **7**, 859 (1929).

diameter and had a capacity of 60–65 cc. Instead of grinding a plane face on the end of the tube after it was made, a thin piece of glass, plane on both sides, was fused to the end. To prevent stray light from fogging the spectra, the tapered end and all parts of the tube not directly illuminated by the arc were either painted black or wrapped with black tar tape.

Spectroscope.—A Hilger quartz spectroscope was used with the helium discharge tube. A Bausch and Lomb glass prism spectroscope was used to analyze the light from the mercury arc.

Comparator.—The Raman lines were measured with a traveling micrometer by comparison with known iron lines. These readings plotted against the international standard wave lengths for the iron lines enabled one to interpolate with fair accuracy the wave lengths of the Raman lines.

Materials.—Normal butyl and normal hexyl bromides were compounds which have been previously described by R. F. Deese.[7] The mercaptans were pure compounds kindly loaned by Professor E. Emmet Reid and Doctor L. M. Ellis, Jr.[8]

Hammer Press Ultra Rapid plates, Agfa developer, and Eastman "hypo" were used in photographing the Raman spectra.
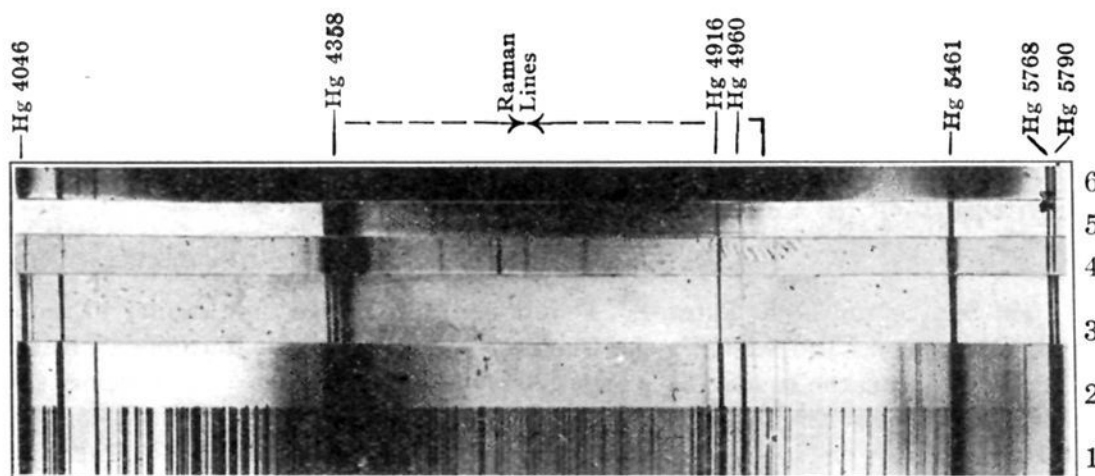

Plate I.—Comparison of spectra: 1, iron arc; 2, Hg arc (slit wide); 3, Hg arc (slit narrow); 4, benzene (quinine sulfate filter); 5, butyl bromide (quinine sulfate filter); 6, butyl bromide (no filter).

Technique and Procedure.—In general, Wood's method for obtaining Raman spectra was followed. In the set-up with the helium discharge tube, the Raman tube containing the diphenylmethane was slipped within the helium spiral, so that the substance under investigation was illuminated only by light passing through the nickel oxide glass filter. Forty-eight hour exposures were made. The photographic plates were backed with Duco enamel to prevent halation around the intense lines.

As the nickel oxide glass transmitted other helium lines, λ 3965 and λ 4045, falling in the same region as the Raman lines excited by the 3888.6 helium line, and since the Raman lines excited by the helium discharge tube were not as intense as those excited by the mercury arc, the latter was adopted as source of excitation for the remaining work.

In the set-up with the mercury arc the distance between the Raman tube and the spectroscope was 84 cm. The light coming from the face of the Raman tube was reflected by a small right angle prism down a long black iron tube to a double convex

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[7] Deese, THIS JOURNAL, **53**, 3673 (1931).

[8] Ellis and Reid, *ibid.*, **54**, 1674 (1932).

lens which concentrated the light and focused a bright image of the prism face on the slit of the spectroscope. The prism was placed in a pasteboard box which fitted over the face of the Raman tube and the end of the iron tube in order to prevent reflection of stray mercury light.

Several preliminary experiments with the mercury arc showed the difficulties encountered in using the complete mercury spectrum. Most of the compounds investigated gave a continuous background in the presence of the 4046 mercury group. To eliminate this background the short-wave length mercury lines were absorbed by an acid quinine sulfate filter. The effect of this filter is shown in Plate I. The solution of quinine sulfate was slowly decomposed by the ultraviolet light from the quartz mercury arc. but by allowing it to circulate through a copper coil surrounded by a jacket containing ice and salt, the rate of decomposition was retarded sufficiently to allow time for an exposure of several hours.

Results

The third column in Table I gives the Raman lines for diphenylmethane. Photographs of these lines excited by the mercury arc were taken also; however, the lines were accompanied by such a dark continuous background that only results obtained with the helium discharge tube have been recorded. The diphenylmethane which was colorless

TABLE I

COMPARISON OF RAMAN LINES OF DIPHENYLMETHANE WITH THE RAMAN LINES OF COMPOUNDS OF SIMILAR STRUCTURE

Values given in wave numbers $\left[\Delta\bar{\nu}\right] = \left[\dfrac{1}{\lambda_{ex}} - \dfrac{1}{\lambda_{Ra}}\right]$ cm.$^{-1}$

Ethylbenzene[a]	Diphenyl ether[b]	Diphenylmethane	Methane[c] (liq.)
153	231	178 (broad)	
482	309	468 (He)	
547		520	
620	615	599	
768	748	722	
962	794	791	
1003	1005	971	
1029	1021		
1157	1153		
		1170	
1203	1195		
1384			
1440		1425	
1604	1590		
		1659 (broad)	
2933		2898	2909
			2953
2962			2999
3002			3023
3052		3038 (broad)	3047
3063	3062		3071

[a] Kohlrausch, "Der Smekal-Raman Effekt," 1931, p. 329, $\left[\Delta\bar{\nu}\right]$ = mean value.
[b] Kohlrausch, ibid., p. 332.
[c] McLennan, Smith and Wilhelm. Trans. Roy. Soc. Canada, 23, 279 (1930).

under ordinary conditions became yellow when exposed to the light of the mercury arc. This color disappeared when the substance was distilled *in vacuo*, but returned again upon exposure to the mercury light.

Results for normal butyl and normal hexyl bromides are recorded in Tables II and III. Plate I shows the rapid decomposition of the bromide under strong illumination both with and without the quinine sulfate filter. By cooling the Raman tube with water passed through a copper coil, a photograph of butyl bromide was obtained which showed a comparatively weak background and, therefore, could be used for measuring the Raman lines excited by both the 4046 and the 4358 mercury groups. A comparison of these lines with the ones given by Kohlrausch[9] is found in Table II. Hexyl bromide, illuminated with the use of a filter, gave the lines recorded in Table III. In Tables IV and V are listed the wave lengths and wave numbers for the Raman lines of normal amyl, normal hexyl and normal heptyl mercaptans together with the frequencies of the Raman lines of isoamyl and normal butyl mercaptans studied by Venkateswaran.[10]

TABLE II

RAMAN LINES OF NORMAL BUTYL BROMIDE

4358.6 λ_{Ra} Å.	Exc. Hg line 4358.6 $\Delta\nu_{Ra}$	4046 $\Delta\nu_{Ra}$	$\Delta\nu_{Ra}$ (K)[a]
4407.5–4411.2	254– 274	271– 291	279 (2)
4431.5	377	394	
4442.0–4447.5	431– 458	448– 475	
4462.3–4468.5	533– 564	550– 581	557 (5)
4479.5–4483.5	619– 639	636– 656	637 (2)
4503	736	753	
			794 (1/2)
4512	780	797	
			853 (1/4)
4524.5	841	858	
			1057 (1/2)
4598.3	1196	1213	1139 (1)
4669 –4674	1526–1548	1543–1565	1257 (1b)
			1440 (2b)
4969.5–4997.5	2819–2933	2836–2950	
			2865 (5)
			2930 (3)
			2962 (4)

[a] (K) = Kohlrausch, "Der Smekal-Raman Effekt," p. 308.

Discussion

Studies of Petrikaln and Hochberg[11] show no Raman lines but continuous spectra for solutions of diphenylmethane in alcohol and triphenylmethane

[9] Kohlrausch, "Der Smekal-Raman Effekt," 1931, p. 329.

[10] Venkateswaran. *Indian J. Physics.* 5, 219 (1930).

[11] Petrikaln and Hochberg. *Z. physik. Chem..* B3, 217 (1929).

TABLE III
RAMAN LINES OF NORMAL HEXYL BROMIDE
Exciting line = Hg 4358.6
w = weak   s = strong

λ_{Rs} Å.	$\Delta\nu$
4387	149 (w)
4409.8	267 (w)
4432	380 (w)
4458	512 (s)
4468.5–4471.8	564–581 (s)
4480.5	626 (w)
4484.8–4489.2	644–668 (s)
4492	682 (w)
4497.5	708 (w)
4503.7	739 (w)
4508.6	764 (w)
4521.5	826 (w)
4529 –4536.7	864–901 (s)
4552	977 (s)
4572.6–4583.5	1074–1126 (s)
4593.5	1173 (w)
4603	1219 (w)
4613	1266 (s)
4623.8	1316 (s)
4630	1345 (w)
4640	1396 (w)
4650.3–4658	1439–1475 (s)
4927	2647 (w)
4937.5	2690 (w)
4877.5–5010.5	2853–2985 (s)
5021	3027 (s)

TABLE IV
RAMAN LINES OF MERCAPTANS
[λ in Ångström Units]

n-Amyl	n-Hexyl	n-Heptyl
4387.6		4409
4424.8	4425.7	4430.5
4456	4457.5	4445.8
4474	4479	4461.5
4484 –4488.5	4485.6–4491.5	4469.6
4496	4497.3	4478.8
4508.3	4505.2	4487.5–4491.7
4520	4517.7	4498.8
4532.6	4521.2	4507
4537.8	4534.6	4517.4
4556.8	4539	4525
4566.8	4553.5	4537
4572.3	4576.3	4576.3
4580.2	4584.3	4585.6
4598.2	4592	4594.3
4606.5	4600.3	4600.3
4612	4613.2	4614.5
		4620.7
4621.7	4624	4624.8
4628.6	4635.4–4643.4	4628
4643		4634
4648.6–4654.5	4650.2–4658.4	4646
4665.6	4672.8	4651.2–4662.3
4896	4903.2	4901
4908.5	4910.8	
4926		
4936.5	4927.5	4910.6
4952	4957.5	4944.5
4970.5	4974.5	4955
4977 –4989	4979 –5002.5	4978 –5014.5
5011.5–5015.5	5010.7	
5024	5019.5	5025

in ether. However, in the present case, when diphenylmethane was illuminated by the helium line, λ3888.6, a continuous background did not accompany the Raman spectrum.

Calculated frequencies for the stretching and bending of non-polar chemical bonds have been identified with known Raman lines.[12] A comparison of the Raman lines for diphenylmethane with those for diphenylether, ethylbenzene and methane, obtained by other investigators, shows definitely that certain frequencies can be attributed to vibrations of particular molecular groups and linkages. The lowest frequency, 178 cm.$^{-1}$ which does not appear in methane, has a corresponding value in ethylbenzene and diphenyl ether. This frequency is attributed to the bending of the

[12] Andrews, *Phys. Rev.*, **36**, 544 (1930).

TABLE V

RAMAN LINES OF MERCAPTANS

$$[\Delta \nu] = \left[\frac{1}{\lambda_{ex.}} - \frac{1}{\lambda_{Ra.}}\right] \text{cm.}^{-1}$$

b = broad. V = Venkateswaran, *Ind. J. of Phys.*, 5, 219 (1930).

n-Amyl	Isoamyl[V]	n-Hexyl	n-Butyl[V]	n-Heptyl
152	279 (5b)	348	298 (1)	262
343	422 (3b)		333 (2)	372
502		509	437 (0)	450
592		617	656 (6)	529
642–664	659 (5)	650–679	707 (0b)	570
701	719 (2)	708		616
761	741 (2)	747	843 (0)	659–680
819	818 (1b)	818		715
881	855 (0)	825	889 (0b)	755
906	929 (0)	891	951 (1)	807
998	955 (1)	912		
1046	1038 (0b)	982	1049 (1b)	844
1072	1114 (0b)	1091	1106 (0)	902
1110		1130		1091
1196	1185 (0b)	1166		1136
1235	1287 (1)	1205	1296 (2b)	
		1266		1177
1261	1300 (1)			1205
		1317		
1306	1337 (2)		1361 (0b)	1282
1338		1370–1407		1300
1405	1470 (6)	1439–1477		1321
1431–1459		1543	1438 (3b)	1336
1510		2548		1364
2519				1420
2570	2574 (10)	2580	2574 (10)	
2643		2649		{1443–1494}
				2539
2686		2772		2579
2749				2718
2824		2841		2762
2851–2899	2870 (10b)	2859–2945	2869 (8b)	
2989–3005	2929 (7b)	2986	2905 (7b)	2855–3001
3039	2962 (10b)	3021	2934 (10b)	3042 .

C–C–C linkage. Vibrational frequencies in the 900–1200 cm.⁻¹ region are associated with the stretching of the C–C bond, and occur in every case except methane. The calculated value for the H–C–H bending motion is 1430 cm.⁻¹. Ethylbenzene and diphenylmethane show Raman lines with frequencies of 1440 cm.⁻¹ and 1425 cm.⁻¹, respectively, whereas diphenyl ether shows no frequency in this region. The frequency 2898 cm.⁻¹ and the broad band at 3038 cm.⁻¹ indicate the difference between the C–H vibration of the aliphatic and aromatic linkages, both of which are present in diphenylmethane.

Differences in the values of corresponding Raman lines of butyl bromide, calculated from the two exciting mercury lines, Table II, are likely due to discrepancy in determining the true micrometer readings for the centers of the exciting mercury lines. The breadth and increased intensity of these lines toward the long wave length side make true readings difficult. This explanation is supported by the fact that practically the same variation occurs for each respective wave number. The wave numbers calculated from the 4046 mercury line agree more closely with the average values listed by Kohlrausch.[13] Greater accuracy is attained in measuring these lines since they fall in the shorter wave length region of higher dispersion than the Raman lines from the 4358 mercury line. Frequencies 1057 cm.$^{-1}$ and 1139 cm.$^{-1}$ recorded by other investigators for butyl bromide[13] were not found; however, hexyl bromide gave a broad line at 1074–1126 cm.$^{-1}$ and a less intense line at 1173 cm.$^{-1}$.

Mercaptans higher in the series than butyl mercaptan give at least twenty Raman lines. There seems to be only a slight increase in the number of lines after the molecule has added the fifth carbon atom to its chain. In Table V each group of values in brackets represents but one characteristic Raman frequency, as all values except the last in each group can be attributed to the 4339 and 4348 mercury lines found in the exciting mercury group. Raman and Krishnan[14] give 15, 30 and 200 as the relative intensities of the mercury lines λ 4339, λ 4347 and λ 4358. Therefore, duplication of weak- and high-frequency Raman lines by the two weak mercury lines seems improbable. Raman frequencies in the 2600 cm.$^{-1}$ region may be false, since there is a strong mercury line, λ 4916, in this region. The lines in the neighborhood of 2900–3000 cm.$^{-1}$ are very diffuse, and in the case of heptyl mercaptan completely overlap each other.

Several interesting relations from the data are noted. The close agreement in corresponding Raman lines for the mercaptans fails in the lower frequency region where the Raman frequencies characteristic of the wave motion of the molecule as a whole depend upon the length and modification of the carbon chain.[12] The C–S linkage has a strong characteristic frequency at approximately 600 cm.$^{-1}$ and two weaker vibrations in the 700 cm.$^{-1}$ region. The C–S linkage in thiophene, mercaptans and alkyl sulfides shows practically the same characteristic oscillations, namely, 607 cm.$^{-1}$ and 754 cm.$^{-1}$ for thiophene,[15] 659 cm.$^{-1}$ and 739 cm.$^{-1}$ for mercaptans,[16] and 651 cm.$^{-1}$ and 746 cm.$^{-1}$ for alkyl sulfides.[17] The single lines in both the 700 cm.$^{-1}$ and 300 cm.$^{-1}$ regions are replaced in the

[13] Kohlrausch. "Der Smekal-Raman Effekt," 1931, p. 308.

[14] Raman and Krishnan, *Indian J. Physics*, **2**, 399 (1928).

[15] Venkateswaran, *Indian J. Physics*. **5**, 145 (1930).

[16] Venkateswaran, *ibid.*, p. 219.

[17] Venkateswaran, *ibid.*. **6**, 51 (1931).

higher members of the mercaptans by two lines in each region. The S–H linkage at approximately 2575 cm.$^{-1}$ is identical with the S–H frequency of 2575 cm.$^{-1}$ for hydrogen sulfide.[18] This indicates that the frequency of vibration between these two atoms is negligibly affected by other atoms in the molecule. The lower frequency of the S–H linkage at 2575 cm.$^{-1}$ compared with the frequencies of the C–H and O–H linkages at 2930 cm.$^{-1}$ and 3388 cm.$^{-1}$, respectively, suggests a weaker binding force and more polar nature for S–H than for either C–H or O–H, and agrees with the fact that hydrogen sulfide and the mercaptans show acid properties not exhibited by water and the corresponding alcohols.

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Summary

The Raman spectra of diphenylmethane, normal butyl and normal hexyl bromides, and normal amyl, normal hexyl and normal heptyl mercaptans have been photographed and the corresponding lines measured. From a comparison of these lines with those of similar compounds several important relations have been noted.

Lines in the Raman spectrum of diphenylmethane exhibit frequencies characteristic of both aliphatic and aromatic linkages.

The number of Raman frequencies in the case of higher member mercaptans increases with the length of the carbon chain.

The respective values for the C–S and S–H vibrations are almost identical in thiophenes, mercaptans and the alkyl sulfides.

The S–H frequency at 2575 cm.$^{-1}$, lower than the corresponding C–H and O–H frequencies, indicates a fairly weak binding force and explains the slightly polar properties of hydrogen sulfide and the mercaptans.

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[18] Bhagavantam. *Nature*, **126**, 502 (1930).