

Raman Spectra under High Dispersion.

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(Plate X)

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ABSTRACT.

Raman spectra of benzene, chloroform and carbon-tetrachloride are studied using a high dispersion spectrograph. The benzene 3μ band is observed to split up into five different components. Two new lines 22516.2 cm^{-1} and 22743.3 cm^{-1} are observed on the benzene plate, their probable assignment is given as 2188 cm^{-1} and 1961 cm^{-1} due to $\lambda 4046$ excitation. A new frequency 3072.4 cm^{-1} is reported for chloroform along with the 3017.3 cm^{-1} already reported by previous workers. Details of the spectral characters of the various Raman lines of these liquids are recorded. A winged nebulosity is observed accompanying the unmodified Hg lines in benzene. This appears with reduced breadth in chloroform, but is hardly noticeable in CCl_4 .

1. Introduction.

Since the discovery of the Raman effect early in 1928, a large mass of data on the subject has been published, but very few workers have so far examined the Raman spectra of

substances under high dispersion. Wood¹ was the first to make a high dispersion study of the Raman spectra of benzene and carbon-tetrachloride by using a 6 inch plane grating with a lens of three metres focus. In a recent investigation Langer and Meggers² have also employed a grating spectrograph to study a few common substances. The only satisfactory examination, however, seems to have been done by Söderqvist³ who used a two-prism spectrograph with a high dispersion, and has observed some interesting results in the case of benzene, the most frequently studied liquid.

The present investigation was undertaken to study the Raman spectra of some typical common substances, under fairly high dispersion. For this purpose a Hilger quartz E₁ spectrograph having a dispersion of 13 A.U. per mm. at $\lambda 4000$ was very kindly placed at the disposal of the author by Prof. Sir C. V. Raman. The instrument was set up for the visible region as only glass containers were used for the liquids studied. Wood's arrangement was followed to get the scattered light. Even with the best conditions of illumination the spectrum observed visually was far too weak to show any thing but the incident Hg line $\lambda 4358$. Consequently prolonged exposures of 24-36 hours had to be given to get fairly well-exposed plates using Isozenith plates. To make the instrument least susceptible to the thermal variations of the atmosphere during such long periods of exposures, all the exposed parts of the instrument were carefully covered by quilt pieces.

A comparison spectrum from an iron arc was recorded on each plate. The plates were measured on a Hilger cross-slide photo-measuring micrometer reading up to 0.001 mm. Wave-lengths were computed by linear interpolation between close iron lines not more than 15-20 A. U. apart, or by Hartmann's interpolation formula, taking suitable iron lines as

¹ Wood, *Phil. Mag.* VI, p. 1282 (1928).

² Langer and Meggers, *Jour. Bur. Stand.*, 4, p. 711, (1930).

³ Söderqvist, *Z. f. Phys.* 59, p. 446 (1930).

standards. Very faint and diffuse lines that could not be seen clearly under the high magnification of the measuring instrument, were visually estimated correct to one Angstrom unit.

2. Results.

The Raman spectra of benzene, chloroform and carbon-tetrachloride are studied and the results are given in tables I-III. The first two columns give the intensities and wave numbers in vacuo per cm. of the Raman lines observed. The third gives the frequency shifts or the Raman-frequencies $\Delta\nu$ in vacuo per cm., the letters *a, b, c, etc.*, denote the various exciting Hg lines according to the lettering given in the following table.

Table IV—Hg arc in vacuo.

	λ in A.U.	ν vac. per cm.		λ in A.U.	ν vac. per cm.
<i>a</i>	3650.14	27388.5	<i>e</i>	4077.84	24515.7
<i>b</i>	3654.83	27353.4	<i>f</i>	4339.25	23088.7
<i>c</i>	3663.27	27290.3	<i>g</i>	4347.50	22994.9
<i>d</i>	4046.80	24703.8	<i>h</i>	4358.34	22937.8

The results of some of the previous workers and of the present investigation are given in the comparative tables V-VII. It will be seen that the agreement between the various values is quite good.

TABLE I. Benzene.

Raman lines.		$\Delta\nu$	Raman lines.		$\Delta\nu$
I.	Wave numbers in vacuo per cm.		I.	Wave numbers in vacuo per cm.	
2	19811.3	<i>g</i> -3183.6	0d	22516.2	?
2	19876.5	<i>h</i> -3061.3	0d	22743.3	?
1B	19894.1	<i>h</i> -3043.7	1	23096.7	<i>d</i> -1607.1
1	19984.3	<i>h</i> -2953.5	1	23120.0	<i>d</i> -1583.8
1	21330.2	{ <i>h</i> -1607.6 <i>e</i> -3185.5	1	23341.1	<i>e</i> -1174.3
1	21354.7	{ <i>h</i> -1583.1 <i>e</i> -3161.0	5	23523.5	{ <i>d</i> -1180.3 <i>e</i> -992.2
0	21456.2	<i>e</i> -3059.5	10	23713.3	<i>d</i> -990.5
0B	21463.3	<i>e</i> -3052.4	0	23859.1	<i>d</i> -844.7
0	21521.7	<i>d</i> -3182.1	0	23927.7	<i>h</i> +989.9
0	21543.2	<i>d</i> -3160.6	2	24100.4	<i>d</i> -603.4
0	21561.8	<i>e</i> -2953.9	0	24126.6	<i>e</i> -3163.8
5B	21641.7	<i>d</i> -3062.1	2	24169.1	<i>b</i> -3184.0
2B	21656.1	<i>d</i> -3047.7	2	24203.6	<i>a</i> -3184.9
3	21758.2	{ <i>h</i> -1179.6 <i>d</i> -2945.6	4	24226.5	{ <i>a</i> -3158.0 <i>e</i> -3063.8
10	21945.1	<i>h</i> -982.7	4	24289.4	<i>b</i> -3064.0
1	22002.5	<i>g</i> -992.4	0	24304.3	<i>b</i> -3049.1
0	22049.0	<i>f</i> -989.7	1	24323.7	<i>a</i> -3064.8
1	22065.1	<i>h</i> -862.7	1	24403.2	<i>b</i> -2950.2
3	22382.3	<i>h</i> -605.5	1	24437.8	<i>a</i> -2950.7

Raman-frequencies of benzene.—

{ $\Delta\nu$ —3184.0 (2), 3160.5 (0), 3062.8 (4), 3048.5 (1B), 2950.8 (2).
 λ in μ —3.140, 3.163, 3.265, 3.279, 3.388.

{ $\Delta\nu$ —1607.4 (1), 1583.4 (1), 1178.1 (1), 991.2 (8), 848.7 (0), 603.9 (2).
 λ in μ —6.219, 6.314, 8.486, 10.09, 11.88, 16.55.

TABLE II. Chloroform.

Raman lines.		$\Delta\nu$	Raman lines.		$\Delta\nu$
I.	Wave No. in vacuo per cm.		I.	Wave No. in vacuo per cm.	
1	19920.5	$h-3017.3$	0	23260	$\left\{ \begin{array}{l} g+265 \\ d-1444 \end{array} \right.$
Od	21445.5	$e-3070.2$			
1	21499.8	$\left\{ \begin{array}{l} e-3015.9 \\ h-1438.0 \end{array} \right.$	1	23302.4	$\left\{ \begin{array}{l} h+364.6 \\ e-1213.3 \end{array} \right.$
Od	21628.7	$d-3075.1$	0	23492.0	$d-1211.8$
4	21685.8	$d-3018.0$	1	23609.9	$h+673.1$
2	21723.0	$h-1214.8$	OB	23749.5	$e-766.2$
0	21780	$g-1214$	1	23848.5	$e-666.2$
3V.B	22179.1	$h-758.7$	2V.B	23944.5	$d-759.3$
0V.B	22231	$g-763$	5	24039.1	$d-664.7$
8	22269.3	$h-663.5$	2	24148.3	$e-367.4$
1	22332.3	$g-662.6$	Od	24218	$c-3072$
0	22374.3	$f-664.1$	1B	24254.4	$e-261.3$
6	22571.1	$h-366.7$	1B	24274.4	$c-3015.9$
1	22628.6	$g-366.3$	3	24369.1	$a-3019.4$
5	22677.5	$h-260.3$	3	24966.4	$d+262.6$
0	22730.1	$g-264.8$	2	25073.5	$d+369.7$
2	23203.3	$h+264.6$	1	25376.1	$d+672.3$

Raman frequencies of chloroform:—

 $\left\{ \begin{array}{l} \Delta\lambda \text{---} 3072.4 \text{ (Od), } 3017.3 \text{ (2), } 1441.0 \text{ (1), } 1213.5 \text{ (2),} \\ \lambda_{in} \mu \text{---} 3.254, \quad 3.313, \quad 6.937, \quad 8.233. \end{array} \right.$
 $\left\{ \begin{array}{l} \Delta\nu \text{---} 761.8 \text{ (3B), } 667.2 \text{ (6), } 366.9 \text{ (5), } 263.3 \text{ (4),} \\ \lambda_{in} \mu \text{---} 13.12, \quad 14.98, \quad 27.25, \quad 38.11. \end{array} \right.$

TABLE III. Carbon tetrachloride.

Raman Lines		$\Delta\nu$	I	Raman Lines		$\Delta\nu$
I	Wave No in vacuo per cm.			Wave No in vacuo per cm.	I	
0d	21408	$h-1535$	0	23314	$g+319?$	
2d	23147.9	$h-789.9$	1	23307.1	$h+459.3$	
2d	22177.6	$h-760.2$	2d	23012.3	$d-791.5$	
10	22476.1	$h-461.7$	2d	23944.2	$d-759.6$	
0	22539.8	$g-455.1$	2	24051.7	$e-494.0$	
8	22621.2	$h-316.6$	0	24200.5	$e-315.2$	
0	22676.0	$g-318.9$	5	24244.1	$d-459.7$	
6	22718.4	$h-219.4$	0	24297.5	$e-218.2$	
0	22775.9	$g-219.4$	3	24387.8	$d-316.0$	
1	23119.2	?	3	24486.0	$d-217.8$	
4	23154.6	$h+216.8$	1	24931.0	$d+219.2$	
1	23208	$g+213$	0	25016.6	$d+312.7$	
2	23252.0	$h+314.2$	0	25162.5	$d+468.7$	

Raman frequencies of Carbontetrachloride—

{ $\Delta\nu=1535$ (0d), 790.7 (2d), 759.9 (2d), 459.7 (6), 315.6 (4), 317.7 (4).
 λ in $\mu=6.513, 12.64, 13.16, 21.75, 31.68, 45.92$.

TABLE V. Raman frequencies of benzene.

Raman* and Krishnan	Wood*	Pringsheim and Rosen	Dadiou* and Kohlrausch	Soderqvist	Langer and Meggers	Author.
...	286.2
605 (1)	606.3	615 (3)	604 (4)	604.6 (2)	605.7	603.9 (2)
849 (0)	847.9	867 (2)	846 (2)	849.1 (0)	848.6	848.7 (0)
991 (10)	989.7	995 (4)	994 (10)	991.3 (5)	992.1	991.2 (8)
1176 (2)	1170.2	1183 (3)	1174 (3)	1179.0 (1)	1177.3	1178.1 (1)
...	1363 (0)
...	...	1479 (2)
...	1581.1	1591 (2)	...	1583.6 (1)	1585.2	1583.4 (1)
1592 (1)	1588 (3)
...	1604.9	1605 (2)	...	1604.1 (1)	1604.5	1607.4 (1)
...	2946 (5)	2946.8 (2)	2946.9	2950.8 (2)
...	3046.9 (1)	3045.4	3048.5 (1B)
8061 (10)	8056.4	8059 (3)	8058 (8)	8061.3 (4)	8060.1	8062.3 (4)
...	8162.9 (1)	...	8160.5 (0)
...	8184.8 (2)	8185.0	8184.0 (2)

* Raman and Krishnan, Proc. Roy. Soc., 122, p. 23 (1929).

* Wood, Phil. Mag. VI, p. 729, (1928).

* Pringsheim and Rosen, Zs. f. Phy. 50, p. 741 (1928).

* Dadiou and Kohlrausch., Phys. Zs. 30, p. 384 (1929).

TABLE VI: Raman frequencies of chloroform.

Wood	Pringsheim and Rosen	Ganesan and Venkateswaran*	Langer and Meggers	Author.
262.1	257 (4)	261 (5)	261.1	262.3 (4)
365.5	368 (4)	367 (6)	365.8	366.9 (5)
668.2	666 (4)	669 (6)	668.4	667.3 (6)
757.1	766 (3)	762 (8)	760.1	761.8 (3B)
...	1214 (2)	1218 (2)	1215.0	1213.5 (2)
...	...	1441 (1)	...	1441.0 (1)
...	3009 (2)	3019 (4)	3018.7	3017.3 (3)
...	3072.4 (0d)

TABLE VII, Raman frequencies of carbon tetrachloride.

Raman and Krishnan	Wood	Pringsheim and Rosen	Ganesan and Venkateswaran	Langer and Meggers	Author.
219	216.3	217 (4)	216 (5)	218.8	217.7 (4)
312	313.0	315 (5)	313 (7)	313.9	315.6 (4)
457	456.9	458 (5)	459 (8)	459.3	459.7 (6)
768	757.1	757 (5)	762 (2)	758.1	759.9 (2d)
791	787.4	793 (5)	791 (2)	789.3	790.7 (2d)
...	...	1539 (2)	1535 (0)	1539.0	1535 (0d)

3. Discussion of the Results.

Benzene.—This liquid has been thoroughly studied by Söderqvist and also by Langer and Meggers. The present investigation confirms the result of Söderqvist that the single band at 3μ found by earlier workers is in reality a group of five different bands of Raman-frequencies 3184.0 cm^{-1} .

* Ganesan and Venkateswaran—Ind. Journ. Phys. 4, p. 195 (1929).

3160.5 cm^{-1} . 3062.3 cm^{-1} . 3048.5 cm^{-1} . and 2950.8 cm^{-1} . The mean 3080 cm^{-1} of these five is in remarkable agreement with the infra-red frequency 3076 cm^{-1} of the single broad band at 3.25μ obtained by Coblentz. The frequency 3062.3 cm^{-1} is the most prominent one in this group, almost as intense as the 991.2 cm^{-1} . The corresponding Raman-lines are considerably broad, the estimated width of the 3048.5 cm^{-1} line is nearly 3 A.U, and that of the 3062.3 cm^{-1} line is 1.6 A. U. for $\lambda 4046$ excitation.

The most prominent frequency is 991.2 cm^{-1} , the intensity and sharpness of the corresponding lines being comparable to some of the incident Hg lines. Other frequencies of benzene are weak except the 603.9 cm^{-1} .

In the present investigation two new feeble and diffuse lines with frequencies 22516.2 cm^{-1} and 22743.3 cm^{-1} are observed which have not been previously reported. The possible assignments of these lines are 422 cm^{-1} and 195 cm^{-1} due to $\lambda 4358$, or 2188 cm^{-1} and 1961 cm^{-1} due to $\lambda 4046$. The former frequencies are too low to be admitted in the case of a compact molecule like benzene. The latter assignment appears to be more likely as the frequencies correspond to infra-red bands 4.6μ and 5.1μ which fall very nearly in the same position as some bands which Daugherty⁹ gets in a recent infra-red study of benzene. No definite choice of the assignment can however be made until a single-line excitation picture is taken. Söderqvist also reported a feeble line 22792.7 cm^{-1} of uncertain assignment in this region.

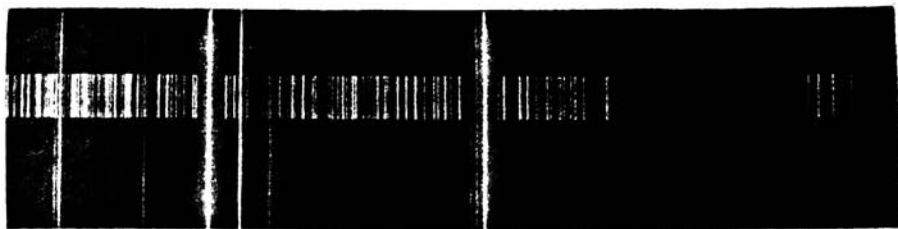
One very interesting and remarkable thing that the author finds in the Raman spectrum of benzene is the presence of a winged nebulosity with fairly definite edges, accompanying the unmodified Hg lines. Similar nebulosities were observed by Raman and Krishnan, and Cabannes and Daure in their earliest studies. It has been explained as due to the

⁹ Daugherty, *Phy. Rev.* 34, p.1549 (1929).

-4046.8

-4358.3

-4916.1



Raman Spectra

1. Benzene 2. Chloroform 3. Carbon tetrachloride

rotation of the molecules under the action of the incident light.¹⁰ This nebulosity however does not show any structure under the fairly high dispersion employed in the present investigation. An interferometric study is in progress to study the nature of the origin of this nebulosity which is a general phenomenon observed in case of liquids with a fairly high degree of anisotropy.

Chloroform.—From table VI it will be seen that a new weak frequency 3072.4 cm^{-1} has been obtained for chloroform by the author. This shift is observed by three different excitations which gives this new frequency a definite footing. The band at 3μ is thus seen to be in reality a double one and not a single one as reported by Bhagavantam and Venkateswaran.¹¹ This band, assigned to the C—H vibrations is usually found to consist of a number of close components in case of aliphatic and also aromatic compounds, and it is not at all surprising that chloroform also shows the same splitting. In fact these two frequencies 3017.3 cm^{-1} and 3072.4 cm^{-1} are in close agreement with two frequencies 3022.1 cm^{-1} and 3071.5 cm^{-1} which Rasetti¹² and others get in their study of the Raman spectrum of gaseous methane (the parent substance of chloroform). It is however very surprising that the most intense frequency 2914.8 cm^{-1} of methane is absent in chloroform.

A glance at the chloroform plate shows that each Raman line has a distinct character of its own, supporting the view that the observed Raman frequencies are none other than the fundamental frequencies of the chloroform molecule arising out of primary oscillations within the molecule. The three prominent frequencies 262.8 cm^{-1} , 367.5 cm^{-1} and 666.5 cm^{-1} give a first impression that they are all alike, but a careful examination of the lines shows that the first is distinctly the widest and the third decidedly the most intense and the sharpest.

¹⁰ Raman and Krishnan, *Nature* 122, pp. 278 and 882 (1928).

¹¹ Bhagavantam and Venkateswaran, *Proc. Roy. Soc.*, p. 360 (1930).

¹² Dickinson, Dillon and Rasetti, *Phy. Rev* 31, p. 582 (1939).

Quite different in appearance from these three is the frequency 761.8 cm^{-1} , assigned to the C-Cl vibrations. The lines corresponding to this frequency have huge breadths, as much as 6 A. U. for the $\lambda 4358$, 4 A. U. for the $\lambda 4347$ and 5 A. U. for the $\lambda 4046$ excitations. This breadth may be the result of the coupling of the rotation of the entire molecule with the C-Cl vibrations, superimposed on the small broadening due to the presence of the other isotope of chlorine.

Compared to the above the Raman lines corresponding to the frequencies 3017.3 cm^{-1} and 3072.4 cm^{-1} are much sharper. It may be noted here that the line corresponding to 3017.3 cm^{-1} due to $\lambda 4046$ appears to be diffuse towards the red, the other lines show a slight shading towards the violet. As in benzene, the winged nebulosity makes its appearance here also, but it is very much narrower, as is expected due to its higher molecular weight and lower anisotropy.

Carbon tetrachloride.—Of the six observed frequencies the first three, *viz.*, 217.7 cm^{-1} , 315.6 cm^{-1} and 459.7 cm^{-1} can be placed in a distinctive group by themselves, the corresponding lines being intense and fairly sharp—although amongst themselves they differ from each other as regards their intensities and sharpness. The last one is the sharpest and the most intense, the other two being comparatively broader.

The lines corresponding to the doublet frequency 759.9 cm^{-1} and 790.7 cm^{-1} are rather diffuse, but much sharper than the 761.8 cm^{-1} band of chloroform. There is a remarkable resemblance between these two lines as regards their intensity and diffuseness.

An important feature of all the Raman lines of this substance is that they are all slightly shaded off towards the violet, probably due to the presence of the chlorine isotope. The nebulosity observed in the previous two liquids has almost completely disappeared in this case. This gives a

strong support to the view that this nebulosity is intimately connected with the molecular anisotropy.

4. *Conclusion.*

It will be seen from the above investigation that apart from accurate measurements, a high dispersion study of the Raman spectra helps to bring out valuable information as regards the spectral nature of the various Raman lines. Further work is in progress and will be communicated in due course of time.

In conclusion the author desires to express his sincere thanks to Professor Sir C. V. Raman for his inspiring guidance and interest in the progress of the work. The author is also thankful to the Nagpur University for the award of a Research Scholarship.
