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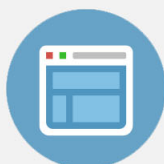
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The Raman Spectra of Ring Compounds. I. Mono-Substituted Benzene Compounds

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An improved apparatus for the study of Raman spectra has been developed. The use of filters including nitrobenzene for removing violet light, sodium nitrite for removing ultraviolet and copper nitrate for the removal of red light, has been discussed. The Raman spectra of

n-butane, chlorobenzene, bromobenzene and iodobenzene have been reinvestigated and several new lines found in each. The Raman spectrum of alpha-chloropyridine has been studied for the first time and found very similar to that of chlorobenzene.

THE problem of the structure of the benzene ring has long been of interest to chemists and has attracted the attention of many investigators in the field of Raman spectra. In the five years since the opening of this field, at least thirty-five papers dealing with the Raman spectrum of benzene have appeared, and although the most careful and painstaking work has been done on this compound, authentic new lines are still being reported. In view of this fact and the importance of the problem of the structure of the benzene ring, it has seemed worth while to apply the best current technique to a repetition of the earlier work on the simpler aromatic derivatives. There seems to be a reasonable hope of obtaining, with the present methods, a series of spectra complete enough for the solving of the major points in the analysis of the modes of internal vibration of these molecules.

With these facts in mind, we have photographed the Raman spectra of a group of aromatic compounds and present, in this and a subsequent article, the results obtained. In addition to the data themselves, there are certain improvements in technique which may also be of interest; especially those designed to facilitate the study of compounds of high melting point and unusual fluorescence.

I. APPARATUS

In connection with this work, an illuminating apparatus of great power has been constructed.

* From the dissertation submitted by John W. Murray to the Board of University Studies of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(Figs. 1 and 2.) The illuminator is built around a Pyrex tube *A* of 48 mm inside diameter. The annular space between this tube and the Raman tube *B*, which is mounted at its axis, may be used for filters and for heating or cooling when necessary. The light is furnished by four quartz capillary mercury arcs *G*, of the type described by Langer and Meggers,¹ operating in running water. The water jacket can *C*, which also serves as a reflector, is of chromium plated brass and has the form of a combination of four ellipses as in the apparatus described by Anand.² This can is supported and held in shape by a set of horizontal plates *D* whose centers are cut out to fit

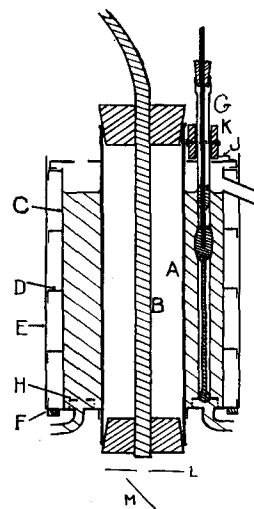


FIG. 1. Raman apparatus.

¹ Langer and Meggers, *Bur. Standards J. Research* **4**, 711 (1930).

² B. Anand, *J. Sci. Inst.* **8**, 258 (1931); **9**, 324 (1932).

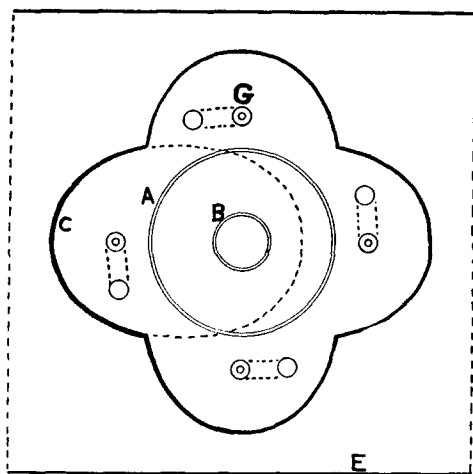


FIG. 2. Diagram of reflectors.

it and these in turn are bolted to two vertical plates *E* and the whole is mounted on a ring by means of the rods *F*. The arcs are aligned at the outer foci of the ellipses by adjustment of the racks *H* and *J* which hold the bases of the arcs and the transite handles *K* in position. A large fraction of the light is thus reflected into the Raman tube which lies at the common focus of the set of ellipses. Scattered light passes downward through the window and the stop *L* and is reflected by the mirror *M* to the spectrograph which is placed at a distance of about 8 feet in order to eliminate reflected light from the walls of the tube. The spectrograph used in this work is a Bausch and Lomb glass prism instrument with *F* 10 lenses and has a dispersion of 17Å per mm at 4000Å and 50 at 5000Å.

For liquids, a tube of the Wood type may be used as shown in Fig. 1. Two types of tubes have been designed for the study of high-melting compounds which must be distilled continuously during the run on account of decomposition. (Fig. 3, I and II.) The first type is simpler but bulkier. The whole tube is of Pyrex glass and is heated with a winding of nichrome wire. The bulb *N* is heated by a separate circuit at a higher temperature so that distillation takes place from *N* to *O*. The bend below *O* is sooted to furnish a black background. In the second type, the two tubes are concentric and the depressed part serves as a condenser while the horn *Q* is sooted to give the black background. The distillate falls into the funnel at the top of the inner tube. When

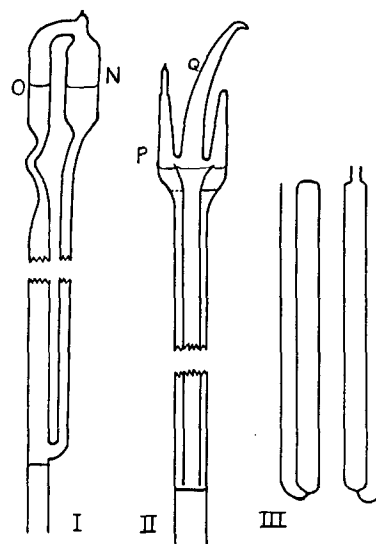


FIG. 3. Raman tubes for continuous distillation (I and II) and cell for use with three liquid filters (III).

distillation is not required, the tube used is like type I with the distilling arm omitted. In either case, the tube is mounted inside of a straight jacket tube which replaces the Raman tube *B* in Fig. 1. The jacket may be lined with mica for thermal insulation.

The filters are arranged in annular layers in the space between *A* and *B*, as in the apparatus described by Dadiou and Kohlrausch.³ The cell shown in Fig. 3, III, permits the use of three layers of liquid filters, two in the cell and one outside. The cell may be simplified in an obvious manner when only two layers are needed. Glass filters may be used with this apparatus either as tubes or as sets of four plates.

The use of filters is practically necessary for the location of the weaker lines of the spectrum. Three distinct purposes are served: simplification of the spectrum, removal of continuous background from the mercury arc, and protection against decomposition and fluorescence from short wave radiation. For excitation with the blue mercury lines, a one mm layer of nitrobenzene will completely suppress the violet lines while transmitting most of the blue. It darkens with use but compares favorably, in this respect,

³ See Kohlrausch, *Der Smekal-Raman-Effekt*, Springer, Berlin (1931).

with quinine sulfate which is in general use for this purpose. A 2 mm layer of a saturated sodium nitrite solution will protect the nitrobenzene against ultraviolet light so that its transmission of the blue light is but slightly reduced by an eight hour exposure. Pfund⁴ has recently recommended the use of sodium nitrite solution for the purpose for which nitrobenzene is used here. It has the advantage of stability but its relative transmission of blue to violet light is far inferior to that of nitrobenzene. It is, however, very useful for the purpose described above and also, in lesser concentrations, for removing ultraviolet when exciting with the violet lines. An excellent combination for excitation with the blue lines is: 2 mm of saturated sodium nitrite solution, 1 mm of nitrobenzene, and 10 mm of saturated praseodymium nitrate solution to remove the continuous background. The nitrobenzene may be diluted with alcohol and crystal violet may be added to remove the blue-green region. For excitation with the violet lines, a 2 mm layer of Corning Red Purple Ultra glass is useful for removing the blue. This compares favorably with iodine in carbon tetrachloride which is often used for this purpose. A layer of sodium nitrite is used

with one of these filters and is more efficient than Noviol glass. When excitation with the green line is necessary, as with some colored or fluorescent substances, a combination of potassium chromate, copper nitrate, and neodymium (or didymium) nitrate gives almost complete isolation of the 5461 mercury line. Excitation by this line is sometimes of value in deciding questions as to the origin of lines of low displacement.

The apparatus described above will record the strong Raman lines of benzene in thirty seconds. Exposures of several hours with strong filters are generally used in order to obtain the weaker lines.

II. RESULTS

The Raman spectrum of *n*-butane was investigated for the purpose of obtaining data for thermal calculations. Since this work was done, results of an earlier investigation by Bhagavantam⁵ have appeared which are in good agreement with those reported here. The material used was 99 percent commercial *n*-butane and was distilled twice before using. Chlorobenzene, bromobenzene and iodobenzene have been re-examined and a number of new lines have been found. These compounds have been studied by

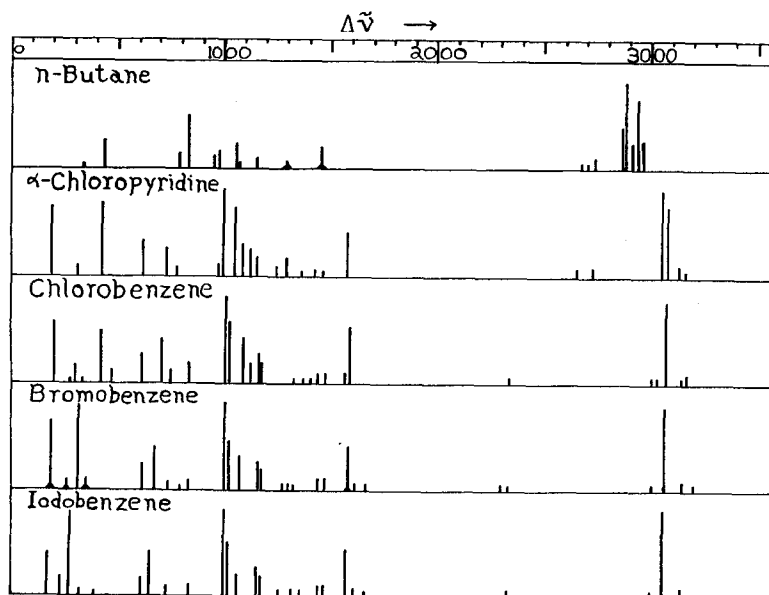


FIG. 4. Raman displacements of compounds studied.

⁴ A. H. Pfund, Phys. Rev. **42**, 581 (1932).

⁵ S. Bhagavantam, Ind. J. Phys. **6**, 595 (1931).

several earlier workers.⁶ The material used was specially purified for specific heat studies by Mr. D. E. Teets of this laboratory. Alpha-chloropyridine has been studied for the first time. This substance was prepared by Dr. Lyman C. Craig of this laboratory. The results obtained are recorded in the following tables and are presented graphically in Fig. 4.

The procedure advocated by R. W. Wood,⁷ of taking two plates of each substance using

different exciting lines, has been employed. The violet and blue mercury lines have been used in all cases and the green line in some. In the cases in which it has not been necessary to remove the ultraviolet to prevent decomposition, Raman lines excited by the 3650 group appear with the lines from the violet. This is very evident in the photograph of *n*-butane shown in Fig. 5. The use of several exciting lines makes it possible to decide questions arising from excitation by the

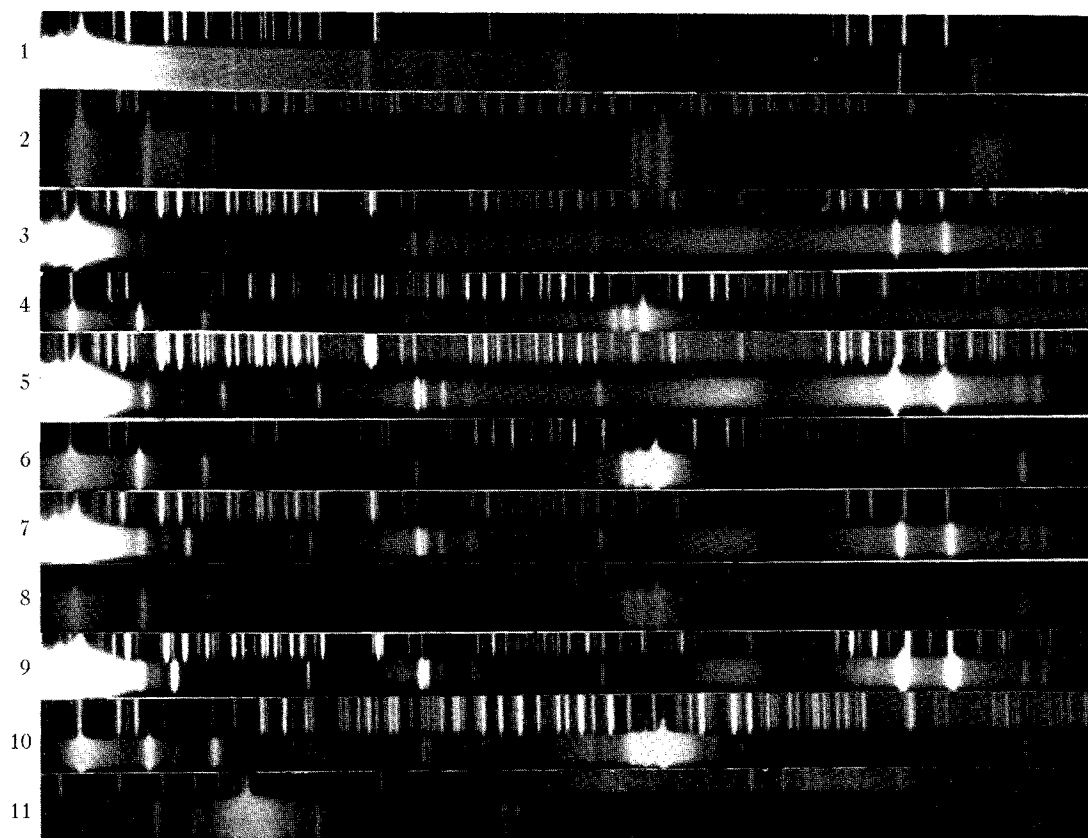


FIG. 5. Raman spectra.

- | | | | |
|-----------------------------|---------------------------|-----------------|---------------------------|
| 1. <i>n</i> -Butane | excited by $\lambda=4358$ | 7. Bromobenzene | excited by $\lambda=4358$ |
| 2. <i>n</i> -Butane | excited by $\lambda=4047$ | 8. Bromobenzene | excited by $\lambda=4047$ |
| 3. α -Chloropyridine | excited by $\lambda=4358$ | 9. Iodobenzene | excited by $\lambda=4358$ |
| 4. α -Chloropyridine | excited by $\lambda=4047$ | 10. Iodobenzene | excited by $\lambda=4047$ |
| 5. Chlorobenzene | excited by $\lambda=4358$ | 11. Iodobenzene | excited by $\lambda=5461$ |
| 6. Chlorobenzene | excited by $\lambda=4047$ | | |

⁶ Pringsheim and Rosen, *Zeits. f. Physik* **50**, 741 (1928); Petrikaln and Hochberg, *Zeits. f. physik. Chemie* **B3**, 217, 405 (1929); Dadiou and Kohlrausch, *Monats. f. Chem.* **52**, 379 (1929); **57**, 488 (1931); Dadiou, Kohlrausch and Pongratz, *Monats. f. Chem.* **61**, 426 (1932); Langseth, *Nature* **124**, 92 (1929); Fujioka, *Sci. Pap. Inst. Phys.*

Chem. Res. Tokyo **11**, 205 (1929); Cleeton and Dufford, *Phys. Rev.* **37**, 362 (1931); Bhagavantam and Venkateswaran, *Proc. Roy. Soc. (London)* **A127**, 360 (1930); Wood, *Phys. Rev.* **38**, 2168 (1931).

⁷ Wood, *Phys. Rev.* **38**, 2168 (1931).

weaker companions of the 4358 and 4046 mercury lines. The fact that the violet mercury lines themselves are not visible in the plates from which the data for the blue excitation are taken removes the possibility of error from this source in assigning origins to the Raman lines. This is of

great importance in the region of 12–1400 cm^{-1} displacement. Fig. 5 shows the photographs obtained.

The values recorded are averages from several plates in most cases. In Tables I–V, the wave numbers of observed lines are given in the first

TABLE I. *n*-butane.

$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$
24479	<i>a</i>	5 <i>b</i>	2909	22557	<i>g</i>	1 <i>b</i>	438	21741	<i>d</i>	4	2964
24457	<i>a</i>	8 <i>b</i>	2931	22510	<i>h</i>	3	428	21645	<i>h</i>	1 <i>b</i>	1293
24422	<i>a</i>	5 <i>b</i>	2966	22150	<i>h</i>	2	788	21640	<i>e</i>	1	2876
24356	$\left\{ \begin{smallmatrix} c \\ d \end{smallmatrix} \right.$	3	$\left. \begin{smallmatrix} 2937 \\ 349 \end{smallmatrix} \right\}$	22105	<i>h</i>	6	833	21609	<i>e</i>	0	2907
24282	<i>d</i>	2	423	22045	<i>d</i>	0	2660	21580	<i>e</i>	2	2936
23916	<i>d</i>	2	789	22002	<i>d</i>	1	2703	21488	<i>h</i>	3 <i>b</i>	1450
23877	<i>d</i>	4	828	21987	<i>h</i>	1	951	20268	<i>h</i>	0	2670
23748	<i>d</i>	0	957	21967	<i>d</i>	1	2738	20236	<i>h</i>	0	2702
23729	$\left\{ \begin{smallmatrix} d \\ e \end{smallmatrix} \right.$	1	$\left. \begin{smallmatrix} 976 \\ 787 \end{smallmatrix} \right\}$	21958	<i>h</i>	2	980	20199	<i>h</i>	1	2739
23689	<i>e</i>	0	827	21880	<i>h</i>	3	1058	20074	<i>h</i>	5	2864
23649	<i>d</i>	2	1056	21868	<i>h</i>	0	(1070)	20059	<i>h</i>	10	2879
23557	<i>d</i>	1	1148	21843	<i>d</i>	5	2862	20026	<i>h</i>	3	2912
23252	<i>d</i>	4 <i>b</i>	1453	21826	<i>d</i>	10	2879	19997	<i>h</i>	8	2941
22600	<i>h</i>	0	(338)	21794	<i>d</i>	4	2911	19975	<i>h</i>	3	2963
				21789	<i>h</i>	1	1149				
				21766	<i>d</i>	10	2939				

(338) (0), 428 (3), 787 (2), 832 (6), 951 (1), 980 (2), 1058 (3), (1070) (0), 1149 (1), 1293 (1*b*), 1450 (3*b*), 2670 (0), 2702 (0), 2739 (1), 2864 (5), 2879 (10), 2912 (3), 2941 (8), 2963 (3).

TABLE II. Chlorobenzene.

$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$
24307	<i>a</i>	1	3081	23235	$\left\{ \begin{smallmatrix} d \\ h \end{smallmatrix} \right.$	0	$\left. \begin{smallmatrix} 1470 \\ -297 \end{smallmatrix} \right\}$	21780	<i>h</i>	3	1158
24287	<i>d</i>	2	418	23119	<i>d</i>	1	1586	21763	<i>h</i>	2	1175
24091	$\left\{ \begin{smallmatrix} d \\ e \end{smallmatrix} \right.$	2 <i>b</i>	$\left. \begin{smallmatrix} 614 \\ 425 \end{smallmatrix} \right\}$	22740	<i>h</i>	7	198	21700	<i>d</i>	0	3005
24001	<i>d</i>	5	704	22663	<i>h</i>	0	275	21678	<i>d</i>	0	3027
23964	<i>d</i>	0	741	22639	<i>h</i>	2	299	21637	<i>d</i>	10 <i>b</i>	3068
23962	<i>h</i>	1	-1024	22607	<i>h</i>	0	331	21614	<i>h</i>	0	1324
23938	<i>h</i>	1	-1000	22580	<i>g</i>	1	415	21572	<i>h</i>	0	1366
23813	<i>e</i>	1	703	22520	<i>h</i>	6	418	21564	<i>d</i>	0	(3141)
23702	<i>d</i>	5	1003	22473	<i>h</i>	1	465	21539	<i>d</i>	0	3166
23680	<i>d</i>	2	1025	22380	<i>g</i>	0	615	21536	<i>h</i>	0	(1402)
23618	<i>d</i>	2	1087	22324	<i>h</i>	3	614	21500	<i>h</i>	1	1438
23581	<i>d</i>	1 <i>b</i>	1124	22294	<i>g</i>	1	701	21459	$\left\{ \begin{smallmatrix} h \\ f \end{smallmatrix} \right.$	1	$\left. \begin{smallmatrix} 1479 \\ 1580 \end{smallmatrix} \right\}$
23549	<i>d</i>	0	1156	22236	<i>h</i>	5	702	21447	<i>e</i>	2	3069
23530	<i>d</i>	0	1175	22196	<i>h</i>	1	742	21410	<i>g</i>	1	1585
23512	<i>e</i>	1	1004	22108	<i>h</i>	2 <i>b</i>	830	21377	<i>h</i>	1	1561
23491	<i>e</i>	1	1025	22035	<i>f</i>	1	1004	21354	<i>h</i>	6	1584
23430	<i>e</i>	1	1086	21993	<i>g</i>	2	1002	20609	<i>h</i>	0	(2329)
23352	$\left\{ \begin{smallmatrix} e \\ h \end{smallmatrix} \right.$	2	$\left. \begin{smallmatrix} 1164 \\ -414 \end{smallmatrix} \right\}$	21973	<i>g</i>	1	1022	19869	<i>h</i>	2	3069
23336	$\left\{ \begin{smallmatrix} d \\ e \end{smallmatrix} \right.$	0	$\left. \begin{smallmatrix} 1369 \\ 1180 \end{smallmatrix} \right\}$	21935	<i>h</i>	10	1003	18110	<i>k</i>	3	198
23260	<i>d</i>	0	1445	21915	<i>h</i>	7	1023	18005	<i>k</i>	1	303
				21854	<i>h</i>	5	1084	17907	<i>k</i>	5	401
				21817	<i>h</i>	2	1121	17697	<i>k</i>	2	611
								17317	<i>k</i>	1	991

198 (7), 275 (0), 299 (2), 331 (0), 419 (6), 465 (1), 614 (3), 703 (5), 743 (1), 832 (2), 1004 (10), 1023 (7), 1084 (5), 1122 (2), 1159 (3), 1174 (2), 1324 (0), 1366 (0), (1402) (0), 1438 (1), 1475 (1), 1561 (1), 1584 (6), (2329) (0), 3005 (0), 3027 (0), 3069 (10), (3141) (0), 3166 (0).

TABLE III. *Bromobenzene.*

$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$
24388	<i>d</i>	3	317	22622	<i>h</i>	10	316	21496	<i>h</i>	1	1442
24286	<i>b</i>	0 <i>b</i>	3067	22585	<i>h</i>	1 <i>b</i>	353	21461	{ <i>h</i> <i>f</i> }	1	1477
24229	{ <i>a</i> <i>c</i> }	1 <i>b</i>	3159 3064	22323	{ <i>h</i> <i>g</i> }	3	615 672	21453	<i>e</i>	3	3063
24199	<i>e</i>	2	317	22265	<i>h</i>	5	673	21415	<i>g</i>	1	1580
24089	<i>d</i>	2	616	22200	<i>h</i>	1	738	21362	<i>e</i>	1	3154
24032	<i>d</i>	3	673	22143	<i>h</i>	0	795	21358	<i>h</i>	5 <i>b</i>	1580
23869	<i>d</i>	0	(836)	22107	<i>h</i>	1	831	21324	<i>h</i>	0	1614
23840	<i>e</i>	1	676	22035	<i>f</i>	1	1004	21271	<i>h</i>	0	1667
23701	<i>d</i>	10	1004	22018	<i>f</i>	0	1021	20645	<i>h</i>	0	2293
23681	<i>d</i>	6	1024	21994	<i>g</i>	3	1001	20605	<i>h</i>	0	2333
23631	<i>d</i>	5	1074	21972	<i>g</i>	1	1023	19876	<i>h</i>	3	3062
23542	<i>d</i>	1 <i>b</i>	1163	21936	<i>h</i>	10	1002	18974	<i>k</i>	0	-666
23527	<i>d</i>	1	1178	21915	<i>h</i>	5	1023	18559	<i>k</i>	1	(-251)
23512	<i>e</i>	2	1004	21866	<i>h</i>	4	1072	18123	<i>k</i>	2	185
23491	<i>e</i>	1	1025	21834	<i>g</i>	0 <i>b</i>	1161	18044	<i>k</i>	0	264
23443	<i>e</i>	1 <i>b</i>	1073	21778	<i>h</i>	3	1160	17989	<i>k</i>	3	319
23253	<i>d</i>	1 <i>b</i>	1452	21761	<i>h</i>	2	1177	17315	<i>k</i>	6	993
23248	<i>h</i>	1 <i>b</i>	-310	21701	<i>d</i>	0	3004	17292	<i>k</i>	1	1016
23124	<i>d</i>	4 <i>b</i>	1581	21664	<i>h</i>	0 <i>b</i>	(1274)	17250	<i>k</i>	1	1058
23113	<i>h</i>	1	-175	21640	<i>d</i>	10 <i>b</i>	3065				
22753	<i>h</i>	8 <i>b</i>	185	21637	<i>h</i>	0	1301				
22719	<i>f</i>	1	320	21616	<i>h</i>	0	1322				
22681	{ <i>h</i> <i>g</i> }	2 <i>b</i>	257 314	21553	<i>d</i>	1	3152				
				21502	<i>d</i>	0	3203				

185 (8*b*), 260 (1*b*), 317 (10), 353 (1*b*), 616 (3), 673 (5), 738 (1), 795 (0), 831 (1), 1002 (10), 1023 (5), 1072 (4), 1160 (3), 1177 (2), (1274) (0), 1301 (0), 1322 (0), 1442 (1), 1477 (1), 1580 (5*b*), 1614 (0), 1667 (0), 2293 (0), 2333 (0), 3004 (0), 3063 (10), 3153 (1), 3203 (0).

TABLE IV. *Iodobenzene.*

$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$
24437	<i>d</i>	2	268	22671	<i>h</i>	10	267	21500	<i>h</i>	1	1438
24247	<i>e</i>	1	269	22623	<i>h</i>	0	315	21469	{ <i>h</i> <i>f</i> }	1	1469
24090	<i>d</i>	0 <i>b</i>	615	22550	<i>h</i>	0 <i>b</i>	(388)	21458	<i>e</i>	1	3058
24048	<i>d</i>	2	657	22383	<i>g</i>	0	612	21425	<i>g</i>	0 <i>b</i>	1570
23966	<i>d</i>	0	739	22324	{ <i>h</i> <i>g</i> }	2 <i>v</i>	614 671	21365	<i>h</i>	5	1573
23904	<i>e</i>	0	612	22282	<i>h</i>	5	656	21323	<i>h</i>	0	1615
23859	<i>e</i>	0 <i>b</i>	657	22210	<i>h</i>	1	728	21278	<i>h</i>	0	1660
23704	<i>d</i>	6	1001	22100	<i>h</i>	1 <i>b</i>	838	20612	<i>h</i>	0	(2326)
23685	<i>d</i>	4	1020	22037	<i>f</i>	2	1002	19943	<i>h</i>	0	(2995)
23640	<i>d</i>	1 <i>b</i>	1065	22028	<i>f</i>	1	(1011)	19878	<i>h</i>	1	3060
23586	<i>h</i>	1	-648	21995	<i>g</i>	3	1000	18565	<i>k</i>	2	-257
23544	<i>d</i>	1 <i>b</i>	1161	21976	<i>g</i>	2	1019	18146	<i>k</i>	3 <i>b</i>	162
23514	<i>e</i>	2 <i>b</i>	1002	21938	<i>h</i>	10	1000	18080	<i>k</i>	1	228
23497	<i>e</i>	1	1019	21919	<i>h</i>	6	1019	18039	<i>k</i>	5	269
23454	<i>e</i>	0	1062	21878	<i>h</i>	2	1060	17693	<i>k</i>	1 <i>b</i>	615
23353	<i>e</i>	1	1163	21845	<i>g</i>	0 <i>b</i>	1150	17652	<i>k</i>	4	656
23329	<i>e</i>	1	1187	21780	<i>h</i>	3	1158	17316	<i>k</i>	7	992
23263	{ <i>d</i> <i>g</i> }	0	1442 -268	21759	<i>h</i>	2	1179	17295	<i>k</i>	3	1013
23231	<i>d</i>	1	1474	21702	<i>d</i>	0 <i>b</i>	3003	17154	<i>k</i>	1 <i>b</i>	1154
23200	<i>h</i>	3	-262	21681	<i>h</i>	0	1257	16735	<i>k</i>	3	1573
23130	<i>d</i>	2	1575	21647	<i>d</i>	10 <i>b</i>	3058	15248	<i>k</i>	8	3060
23103	<i>h</i>	1	-165	21619	<i>h</i>	1	1319	15175	<i>k</i>	1	3163
22770	<i>h</i>	5 <i>b</i>	168	21579	<i>h</i>	0	1359				
22720	<i>h</i>	3 <i>bv</i>	218	21564	<i>d</i>	1	3141				

168 (5), 228 (2), 268 (10), (319) (0), (388) (0), 614 (2), 656 (5), 728 (1), 838 (1), 1001 (10), 1019 (6), 1062 (2), 1158 (3), 1179 (2), 1257 (0), 1319 (0), 1359 (0), 1440 (1), 1472 (1), 1573 (5), 1615 (0), 1660 (0), (2326) (0), (3000) (0), 3059 (10), 3141 (1).

TABLE V. *Alpha-chloropyridine.*

$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$	$\bar{\nu}$	Exc.	<i>I</i>	$\Delta\bar{\nu}$
24388	<i>d</i>	0	(317)	23246	<i>d</i>	0	(1459)	21890	<i>h</i>	8	1048
24272	<i>d</i>	1	433	23130	<i>d</i>	2 <i>b</i>	1575	21852	<i>h</i>	3	1086
24084	<i>d</i>	1	621	23113	<i>h</i>	1	-175	21817	<i>h</i>	3	1121
23976	<i>d</i>	2	729	22744	<i>h</i>	8	194	21784	<i>h</i>	2	1154
23796	<i>e</i>	0	720	22621	<i>h</i>	1	317	21698	<i>h</i>	1	1240
23708	<i>d</i>	4	997	22564	<i>g</i>	1	431	21650	<i>h</i>	2	1288
23655	<i>d</i>	3	1050	22509	<i>h</i>	8	429	21648	<i>d</i>	10	3057
23615	<i>d</i>	1 <i>b</i>	1090	22318	<i>h</i>	4	620	21625	<i>d</i>	6	3080
23582	<i>d</i>	1 <i>b</i>	1123	22270	<i>g</i>	0 <i>b</i>	725	21577	<i>h</i>	0	(1361)
23550	<i>d</i>	1	1155	22210	<i>h</i>	3	728	21573	<i>d</i>	1 <i>b</i>	3132
23519	<i>e</i>	1	997	22160	<i>h</i>	1	778	21544	<i>d</i>	0	(3161)
23466	<i>e</i>	1	1050	22052	<i>d</i>	1	2653	21512	<i>h</i>	0	(1426)
23414	<i>d</i>	0 <i>b</i>	1291	22046	<i>f</i>	1 <i>b</i>	993	21478	<i>h</i>	0	(1460)
23268	<i>h</i>	0	(-330)	22002	<i>g</i>	1	993	21463	<i>e</i>	1	3053
				21981	<i>d</i>	1	2724	21439	<i>e</i>	1	3077
				21967	<i>h</i>	1	971	21366	<i>h</i>	5	1572
				21945	<i>h</i>	10	993	19851	<i>h</i>	2 <i>b</i>	3087

194 (8), 317 (1), 429 (8), 620 (4), 728 (3), 778 (1), 971 (1), 993 (10), 1048 (8), 1086 (3), 1121 (3), 1154 (2), 1240 (1), 1288 (2), (1361) (0), (1426) (0), (1460) (0), 1573 (5), 2653 (1), 2724 (1), 3057 (10), 3080 (6), 3132 (1), (3161) (0).

column, symbols for the exciting line in the second, the intensity and character of the line in the third, and the displacement assigned to it in the fourth. The symbols for the exciting lines are taken from Kohlrausch.³

a 27388 cm⁻¹ *d* 24705 *f* 23039 *k* 18308
b 27353 *e* 24516 *g* 22995
c 27293 *h* 22938

The intensities given are merely visual estimates of the relative blackness of the lines and are not strictly comparable from one substance to another. The letter *b* signifies broad, *v* shaded to the violet, and *r* shaded to the red. The values appearing in parentheses in the body of the tables are uncertain due to extreme weakness or interference of background. Those in parentheses in the summaries are uncertain from the above causes or on account of doubt as to their origin.

The Raman frequencies are summarized at the end of each table and the intensities are given in parentheses after the displacements. The values are probably accurate to within 3 cm⁻¹ or better for the stronger lines but the error for the very weak ones may be as large as 10 cm⁻¹. The plates were measured on a Gaertner comparator and the wave numbers determined from a large dispersion curve constructed from an iron comparison spectrum. The accuracy of the lines excited by the green line is less on account of the low dispersion in that region.

III. DISCUSSION

The results reported here for *n*-butane confirm those of Bhagavantam except that the line he reported at 960 has been resolved into two lines at 951 and 980. The lines at 320 and 1067 were not well substantiated in this work though traces of them were found.

Dadiou and Kohlrausch⁸ reported a line for chlorobenzene at 484 in their first paper on this substance but did not report it in a later paper in which the work was repeated.⁹ A line has been found at 465 which might be the one in question considering the error in measurement of such weak lines. The line at 3133 reported in the latter paper was not substantiated in this work though a trace of it was found. All other previously reported lines have been confirmed. New lines have been found at: 275, 331, 1174, 1324, (1402), 1438, 1475, 1561, (2329), 3005, 3027. The justification for the assignment of a line to 1475 is not apparent from the table and is based on the fact that the observed line at 21459 cm⁻¹ is stronger than the line at 21410 which would not be the case if the former were due to the 1584 line excited by the 4339 line alone. This same reasoning applies to the other compounds in which this line is found.

⁸ Dadiou and Kohlrausch, *Monats. f. Chem.* **52**, 379 (1929).

⁹ Dadiou, Kohlrausch and Pongratz, *Monats. f. Chem.* **61**, 426 (1932).

In the case of bromobenzene, Fujioka⁶ reports a line at 222 which is derived from the observed line at 22716 and is assumed to have been excited by the 4358(*h*) mercury line. A similar line was found in the present work but it was deemed more probable that it was excited by the 4348(*g*) mercury line and is so reported in this paper. The line at 1370 reported by Dadiou and Kohlrausch was not found though several other weak lines were found in this region. The resolution of the strong line at 3063 into two lines reported by Fujioka was not satisfactorily confirmed though a trace of it was found in one plate. In other respects, the previously reported lines have been confirmed. New lines have been found at: 353, 738, 795, 831, 1274, 1301, 1322, 1442, 1477, 1614, 1667, 2293, 2333, 3004, and 3203.

In the case of iodobenzene, a line at 462 was reported by Dadiou and Kohlrausch⁸ in the earlier paper but was not reported by them in a later paper.¹⁰ This line was not found in the present work. All other previously reported lines have been found. New lines have been found at: 228, 319, 388, 728, 838, 1179, 1257, 1319, 1359, 1440, 1472, 1615, 1660, (2326), (3000) and 3141. The line at 228 is not distinguishable from the 268 line excited by 4348(*g*) when excited by the 4358(*h*) line and is masked by the mercury radiation when excited by the violet line. For this reason, its identity has not been established before though the line has been observed. This question has been settled by excitation with the green line. The incompleteness of the previous work on this substance is largely due to the decomposition caused by ultraviolet light. This difficulty has been overcome by protecting it with sodium nitrite.

The marked similarity between the monohalogen derivatives of benzene is very evident from Figs. 4 and 5. Nearly all of the lines which do not correspond throughout the series are so

weak that they may well have been missed in the cases where they are absent. The line at 1122 in chlorobenzene appears to be missing in the bromo and iodo compounds; but this is not certain for it may coincide with the position of the 1159 line excited by 4348(*g*). In this case, however, the intensity must have fallen off sharply. The weak companion of the 1584 line in chlorobenzene is not found in the other compounds but two very weak lines appear on the other side of it at 1615 and 1660.

The lines at 198, 299, 419, 465 and 703 in chlorobenzene move toward the exciting line by very appreciable amounts in passing to the bromo and iodo compounds and thus appear to correspond to motions in which the carbon to halogen bond plays an important part. The lines at 614, 832, 1004, 1023, 1159, 1174, 1438 and 1475 remain nearly constant and hence pertain to motions in which this bond is not very much involved. The lines at 743, 1084, 1584, 3069 and 3166 are very slightly lowered on increasing the mass of the substituent and thus appear to involve this bond to a slight extent. The remainder of the lines are so weak that too much confidence should not be placed in apparent shifts though the lines in the region of 1200 to 1400 appear to have a genuine shift to lower values. It is of interest in connection with the lines at about 2300 that a line at 2291 has recently been found for benzene by Wood and Collins.¹¹

Many of the new lines found for the benzene derivatives are of particular interest in that they were predicted by Mr. D. E. Teets of this laboratory from studies of the vibrating mechanical models which will be published in the near future.

The obvious similarity of the spectra of chlorobenzene and alpha-chloropyridine would appear to indicate that the ring structures of the two compounds are of the same type.

¹⁰ Dadiou and Kohlrausch, *Monats. f. Chem.* **57**, 488 (1931).

¹¹ Wood and Collins, *Phys. Rev.* **42**, 382 (1932).