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# RAMAN SPECTRA OF SOME ORGANIC HALIDES

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## ABSTRACT

Raman spectra obtained by helium excitation from nineteen organic compounds, $CHCl_3$, $CH_3Br$, $CH_3MgBr$, $CH_3I$, $CH_3MgI$, $C_2H_5Cl$, $C_2H_5Br$, $C_2H_5I$, $ClCH_2CH_2Cl$, $BrCH_2CH_2Br$, $CH_3CHCl_2$, $CH_3CHBr_2$, $C_2H_2Cl_4$, $C_2H_2Br_4$, $C_6H_6$, $C_5H_5N$, $C_6H_5CH_2Cl$, $C_6H_5Cl$, $C_6H_5Br$, five of which have not been reported on before, are described and discussed. It is shown that in many cases the observed frequencies can be expressed in terms of four assumed fundamentals (five in the cyclic compounds), two of which are not observed, and which may prove to be illusory. The bearing of such theory as is available is discussed.

THE Raman* spectra of a number of simple organic compounds containing carbon, hydrogen, and halogen (chlorine, bromine, or iodine) atoms are described and discussed in this paper. The work was begun as part of a systematic study of a number of physical properties of the class of compounds known as Grignard reagents, which are formed in anhydrous ether solution when the halogen compounds just mentioned react with magnesium to form compounds of the type R-Mg-X. Raman spectra from two such compounds are described below. At the time the work was started, only a few of the organic halides had been reported on; but since then, various workers have reported the Raman spectra of a great many of them, as will be noted below, and some steps have been made toward theoretical interpretation of the spectra.

## EXPERIMENTAL ARRANGEMENTS

In almost every case, the results reported by others have been obtained using light from a mercury arc, usually unfiltered, following an early scheme suggested by Wood.[1] The advantage of intense exciting light, which this method possesses, is compensated to a large extent by the serious overlapping of the Raman patterns from the numerous exciting lines, which leads to difficulty and error in identifying the exciting line responsible for certain displaced lines. Matters can be improved somewhat by using appropriate filters, as Wood has shown. The results in the present paper are free from such uncertainty, since they were obtained by helium excitation, using a helium spiral surrounding the "resonance" tube, and a tube of Corning red ultra

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* No attempt is made to give here a complete bibliography of all the hundreds of papers that have appeared on the subject since the discovery of the effect was announced by C. V. Raman, Indian Jour. of Physics **2**, 387 (1928). Such bibliographies are available elsewhere; e.g., S. Bhagavantam, Ind. Jour. Phys. **5**, 237 (1930), A. S. Ganesan, Ind. Jour. Phys. **4**, 281 (1929), and the Symposium on Molecular Spectra, Trans. Faraday Soc. **25**, 611–949 (1929).

[1] R. W. Wood, Phil. Mag. (7) **6**, 729 (1928).

glass as a filter. This method is also due to Wood.[2] While the method has not the advantage of the high intensity obtainable from the newer helium arc,[3,4] it does have, in common with this apparatus, the great advantage that there is only one exciting line, λ3889, and almost no helium lines coming through the filter to confuse the Raman pattern. Further, this exciting line has a shorter wave-length than many of the mercury lines used. As shown by Ornstein and Rekveld,[5] the intensity of the Raman lines increases at least approximately with the fourth power of the exciting frequency. Besides the consequent gain in strength of the Raman lines, there is the added advantage that the displaced lines occur at wave-lengths near the sensitivity maximum of the photographic plates.

The first exposures were made using a "resonance" tube about an inch in diameter and twelve inches long. It was soon found that better results were obtained with a smaller tube, about 1 cm in diameter and 10 cm long, with a smaller filter and helium spiral; less power was required, too, and smaller quantities of the substances to be investigated. The spectra were photographed with a specially reconstructed single prism glass spectrograph of considerable speed, which has been described elsewhere.[6] For measurement, images of the spectra were projected, using a magnification of about forty diameters, on a screen on which a scale of wave-numbers had been worked out, using a large number of reference lines. With this scale, wave-number differences could be read off with an accuracy of about 5 $cm^{-1}$ in the case of the sharpest lines. Many of the Raman lines are too broad, however, to permit reading as accurately as this.

## Discussion of Results

In discussing Raman spectra, the quantity of primary interest is the amount by which a given line differs in frequency (or more usually, in wave-number) from the exciting line. Since the arrangements used permitted this quantity to be read directly, it is recorded in the tables that follow. In the tables, compounds of similar structures are grouped, for convenience in comparing their spectra. Intensities are indicated by numbers in parentheses following the observed wave-number shifts.

While measurements could be checked to about 5 $cm^{-1}$, it by no means follows that the results obtained by different observers will check as closely as this. In some cases the agreement is better, but in a considerable number, the disagreement is several times as large. There is very great need now for more accurate results than have been given in most of the investigations so far published. A single table is included to show the extent to which agreement is found in typical cases. In many cases the agreement is worse, owing to difficulty in identifying lines. Beyond this, it has seemed unnecessary to

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[2] R. W. Wood, Phil. Mag. (7) **7**, 744 (1929).

[3] Reynolds and Benford, Rev. of Sci. Insts. **1**, 413 (1930).

[4] R. W. Wood, Phys. Rev. **36**, 1421 (1930).

[5] Ornstein and Rekveld, Zeits. f. Physik **61**, 593 (1930).

[6] R. T. Dufford, J. Opt. Soc. Am. **9**, 405 (1924).

TABLE I. (*a*) *Raman spectrum of chloroform, $CHCl_3$.*

| Cleeton and Dufford | Dadieu and Kohlrausch 8, V | Ganesan and Venkateswaran 13 | Pringsheim and Rosen 10 | Bhagavantam and Venkateswaran 14 |
|---|---|---|---|---|
| 269 (3) | 259 (6) | 261 (5) | 257 (4) | 261 (4) |
| 376 (3) | 364 (5) | 367 (6) | 368 (4) | 367 (5) |
| 671 (3) | 664 (5) | 669 (6) | 666 (4) | 669 (4) |
| 775 (3) | 756 (4) | 762 (3) | 766 (3) | 762 (3) |
| | 1214 (2) | 1218 (2) | 1214 (2) | 1218 (2) |
| | | 1441 (1) | | 1441 (1) |
| 3015 (5) | 3016 (3) | 3019 (4) | 3009 (2) | 3019 (3) |

(*b*) *Raman spectrum of benzene, $C_6H_6$.*

| Daure 7 | Cleeton and Dufford | Dadieu and Kohlrausch 8, I | Dadieu and Kohlrausch 8, II | Fujioka 9 | Pringsheim and Rosen 10 | Wood 12 | Dadieu and Kohlrausch 8, IV | Soderqvist 11 |
|---|---|---|---|---|---|---|---|---|
| 610 | 621 (1) | 605 (4) | 607 (4) | 607 | 615 (3) | 606 | 602 (3) | 604.6 (2) |
| 842 | | 848 (2) | 846 (2) | 849 | 867 (2) | 849 | 844 (1) | 849.1 (0) |
| 991 | 1003 (20) | 995 (10) | 993 (10) | 993 | 995 (4) | 992 | 991 (10) | 991.3 (5) |
| 1178 | 1203 (3) | 1183 (3) | 1180 (3) | 1182 | 1183 (3) | 1178 | 1178 (3) | 1179.0 (1) |
| | | | 1363 (1/2) | | | | 1362 (1/2) | |
| | | 1481 (3) | | | 1479 (2) | | | |
| 1584 | 1619 (5) | 1596 (3) | 1588 (3) | 1585 | 1591 (2) | 1584 | 1586 (3) | 1583.6 (1) |
| | | | | 1612 | 1605 (2) | 1603 | 1603 (1) | 1604.1 (1) |
| | | | | | | 2460 | | |
| | | | | | | 2542 | | |
| | | | | | | 2597 | | |
| | | | | | | 2617 | | |
| | | | | | | 2784 | | |
| | | | | | | 2928 | | |
| | | 2944 (5) | 2947 (3) | | | 2947 | 2945 (4) | 2946.8 (2) |
| | | | | 3050 | | {3046 | | 3046.9 (1) |
| 3060 | 3078 (50) | 3058 (8) | 3057 (5) | 3060 | 3059 (3) | 3060 | 3056 (8) | 3061.3 (4) |
| | | | | | | 3164 | | 3162.9 (1) |
| | | | | | | 3183 | | 3184.8 (2) |

republish all the results of other investigators; but references are given to all such work as is known to the writers.

In studying the Raman spectra of organic halides, one of the writers (C. E.C.), who made the wave-number measurements, discovered the existence of certain apparent regularities, the more important of which are indicated in the tables that follow. It would appear from these that it is possible to express the frequencies found in the Raman spectra of each of the aliphatic halides as combinations or overtones of four fundamental frequencies, of which usually two must be assumed to exist without being observed in the spectra themselves. In the tables, beginning with Table II, there is given for each substance the observed frequency differences in one column, and the

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[7] P. Daure, An. d. Physique **12**, 375 (1929); C. R. **186**, 1833 (1928); **188**, 1492 (1929).

[8] Dadieu and Kohlrausch, Phys. Zeits. **30**, 384 (1929); Ber. **63** B, 251 (1930); Naturwiss. **17**, 366, 625 (1929);

[i] Monatsh. f. Chemie **52**, 220 (1929); Sitzb. Akad. Wiss. Wien (IIa) **138**, 41 (1929).

[ii] Monatsh. f. Chemie **52**, 379 (1929); Sitzb. Akad. Wiss. Wien (IIa) **138**, 335 (1929).

[iii] Monatsh. f. Chemie **52**, 396 (1929); Sitzb. Akad. Wiss. Wien (IIa) **138**, 419 (1929).

[iv] Monatsh. f. Chemie **53–54**, 282 (1929); Sitzb. Akad. Wiss. Wien (IIa) **138**, 607 (1929).

[v] Monatsh. f. Chemie **55**, 58 (1930); Sitzb. Akad. Wiss. Wien (IIa) **138**, 651 (1929).

[vi] Monatsh. f. Chemie **55**, 201 (1930); Sitzb. Akad. Wiss. Wien (IIa) **138**, 799, (1930).

[vii] Monatsh. f. Chemie **55**, 379 (1930).

[9] Fujioka, Sci. Papers Inst. Phys. and Chem. Res. Japan **II**, 205 (1929).

[10] Pringsheim and Rosen, Zeits. f. Physik **50**, 741 (1928).

[11] J. Soderqvist, Zeits. f. Physik **59**, 446 (1929–30).

[12] R. W. Wood, Phys. Rev. **36**, 1431 (1930).

[13] Ganesan and Venkateswaran, Ind. Jour. Phys. **4**, 195 (1929).

[14] Bhagavantam and Venkateswaran, Proc. Roy. Soc. **A127**, 360 (1930).

TABLE II. *Raman spectra of methyl halides.*

| Methyl bromide $CH_3Br$ | Methyl iodide $CH_3I$ | Methyl magnesium bromide $CH_3MgBr$ | Methyl magnesium iodide $CH_3MgI$ | Assumed combinations |
|---|---|---|---|---|
| 603 (10) | 534 (10) | | | $V_3$ |
| | | 1131 (1) | 1076 (1) | |
| | 1254 (3) | | | |
| | 2589 (1) | | | $V_4-4V_1$ |
| | 2771 (1) | | | $V_4-2V_1$ |
| | | | ±2875 (10) | $V_4-V_1$ |
| | 2946 (6) | | ±2928 (10) | $V_4$ |
| | 3036 (1) | | ±2983 (10) | $V_4+V_1$ |
| | | | ± Due to ether | |
| (8VII) | (8VII) | — | — | References to other work. |

computed differences on the assumed scheme in the next column; the last column of each table indicates the nature of the assumed combination or overtone. The fundamentals assumed behave so similarly in different compounds, that it is possible to number corresponding fundamental frequencies in different compounds with the same symbol; the symbols used are $V_1$, $V_2$, $V_3$, $V_4$. The way in which these fundamentals vary from group to group of compounds is regular and interesting. A fifth fundamental appears in the aromatic compounds.

The Raman spectrum of diethyl ether was studied, since Grignard compounds are prepared in ether solution; and for comparison with it, the Raman spectrum of ethyl alcohol was obtained. The wave-number shifts observed for ether are: 443 (1), 844 (2), 1159 (2), 1286 (2), 1466 (10), 2683 (2), 2793 (2), 2806 (5), 2873 (40), 2928 (30), 2983 (30) $\mathrm{cm}^{-1}$. Nearly all these lines, except that at 2806, are broad. Other workers[7,8V,8VII,13]) list a few faint lines which we did not observe; but our list contains three lines not previously observed. Part of the difference may be due to wrong assignment of lines in the mercury arc spectra, and part may be due to the fact that our plates, while often underexposed, show the most-shifted Raman lines with greater relative intensity than reported by other workers. For alcohol, the observed shifts are: 1059 (3), 1108 (3), 1294 (3), 1461 (5), 2683 (1), 2880 (20), 2923 (20), 2976 (20). This list includes one new line, and fails to show one or two lines which are probably real, reported by other workers[7,8V,8VII,13,16]. The only regularity of structure to point out, is that in each case the last three lines can be represented by the formula $V_4 \pm V_1$, with $V_4 = 2928$, and $V_1 = 55\ \mathrm{cm}^{-1}$ for ether and 47 $\mathrm{cm}^{-1}$ for alcohol. This regularity, while similar to that found in many other compounds, may prove to be illusory, as will be pointed out below.

In Table II are given the results from methyl bromide and methyl iodide, and from the Grignard reagents made from them. The plates were all underexposed, except for methyl iodide. Dadieu and Kohlrausch[8VII] have recorded

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[16] Venkateswaran and Karl, Zeits. f. phys. Chem. **B1**, 466 (1928).

data on the first two of these compounds, including lines at 2956 and 3050 $cm^{-1}$ for methyl bromide. No other work on the latter two compounds appears to have been published. The interesting result is the disappearance of the frequency marked $V_3$ in the table, and the appearance of a higher frequency, when the C-Br or C-I linkage changes to C-Mg-Br or C-Mg-I. This seems to indicate that the $V_3$ frequency is associated with the carbon-halogen bond. The group of frequencies around 3000 $cm^{-1}$ is generally assumed to be associated with the C—H bond, since such lines always occur in both Raman and infrared spectra of compounds which possess this bond. In assigning the structure to these lines in the methyl iodide spectrum, a fundamental frequency at 88 $cm^{-1}$ was assumed.

In the case of the mono-halogen derivatives of ethane, Table III, it is found possible to make every observed line on our plates fit into a scheme based on four fundamentals, the lower two being assumed but not observed. The plate for ethyl iodide was underexposed; this substance liberates iodine on exposure to light, and in spite of redistillation of the sample several times during the exposure, the absorption due to the iodine made the exposure time insufficient. This table is perhaps the most satisfactory of all those given.

TABLE III. *Raman spectra of ethyl halides.*

| Ethyl chloride $C_2H_5Cl$ | | Ethyl bromide $C_2H_5Br$ | | Ethyl iodide $C_2H_5I$ | | Assumed combinations |
|---|---|---|---|---|---|---|
| Obs. | Comp. | Obs. | Comp. | Obs. | Comp. | |
| | 41 | | 48 | | 53 | $V_1$ |
| | 84 | | 77 | | 65 | $V_2$ |
| 251 (1) | 252 | | | | | $3V_2$ |
| 341 (1) | 336 | 308 (2) | 308 | 261 (3) | 260 | $4V_2$ |
| 668 (10) | 668 | 566 (15) | 561 | | 527 | $V_3$ |
| | | 968 (1) | 978 | | | $2V_3-2V_2$ |
| 1076 (1) | 1084 | | | | | $2V_3-3V_2$ |
| 1286 (1) | 1295 | 1079 (1) | 1084 | | | $2V_3-V_1$ |
| | | 1254 (5) | 1255 | 1213 (6) | 1213 | $2V_3+3V_1$ |
| | | 1456 (5) | 1458 | | | $3V_3-5V_1$ |
| 2716 (1) | 2716 | | | | | $V_4-5V_1$ |
| 2756 (1) | 2757 | 2736 (1) | 2731 | | | $V_4-4V_1$ |
| 2866 (10) | 2880 | 2875 (10) | 2875 | | | $V_4-V_1$ |
| 2921 (30) | 2921 | 2923 (30) | 2923 | 2915 (30) | 2915 | $V_4$ |
| 2961 (15) | 2962 | 2976 (15) | 2971 | 2968 (10) | 2968 | $V_4+V_1$ |
| 8V, 11 | | 8V, 14, 11 | | 8VII | | References to other work |

The corresponding Grignard compounds gave no lines which could not have been attributed to the ether used as solvent. Moreover, most of these compounds are somewhat fluorescent; this difficulty prevented obtaining any other Raman spectra from Grignard reagents.

The results for dihalogen derivatives of ethane are given in the next two tables; Table IV deals with symmetrical derivatives, Table V with unsymmetrical derivatives. No other results appear to have been published on the latter group of compounds. The four-fundamental scheme works out similarly to the preceding cases, but less satisfactorily.

TABLE IV. *Raman spectra of symmetrical ethyl dihalides.*

| Ethylene chloride $ClCH_2CH_2Cl$ | | Ethylene bromide $BrCH_2CH_2Br$ | | Assumed combination |
|---|---|---|---|---|
| Obs. | Comp. | Obs. | Comp. | |
| | 44 | | 52 | $V_1$ |
| | 105 | | 100 | $V_2$ |
| 129 (1) | 132 | | | $3V_1$ |
| | | 201 (5) | 200 | $2V_2$ |
| 311 (2) | 315 | | | $3V_2$ |
| 420 (1) | 420 | | | $4V_2$ |
| 658 (6) | 654 | 558 (1) | 563 | $V_3-V_2$ |
| 759 (10) | 759 | 663 (30) | 663 | $V_3$ |
| 1049 (1) | | | | (?) |
| | | 1061 (4) | 1063 | $V_3+4V_2$ |
| 1211 (1) | | | | (?) |
| | | 1264 (10) | 1274 | $2V_3-V_1$ |
| 1326 (2) | | | | (?) |
| 1451 (3) | | | | (?) |
| 2816 (1) | 2829 | | | $V_4-3V_1$ |
| 2866 (2) | 2873 | 2874 (3) | 2866 | $V_4-2V_1$ |
| 2961 (30) | 2961 | 2966 (30) | 2970 | $V_4$ |
| 3014 (3) | 3005 | 3020 (8) | 3022 | $V_4+V_1$ |
| 8V, 14 | | 8V, 14 | | References to other work |

The results for tetrahalogen derivatives of ethane are given in Table VI. The spectra contain many lines, several of which do not fit well into the scheme of combinations assumed. The scheme seems forced and unconvincing, but it serves to point out interesting similarities with the Raman spectra of other compounds.

TABLE V. *Raman spectra of unsymmetrical ethyl dihalides.*

| Ethylidene chloride $CH_3CHCl_2$ | | Ethylidene bromide $CH_3CHBr_2$ | | Assumed combination |
|---|---|---|---|---|
| Obs. | Comp. | Obs. | Comp. | |
| | 60 | | 55 | $V_1$ |
| | 133 | 176 (1) | 176 | $V_2$ |
| 266 (2) | 266 | 344 (1) | 352 | $2V_2$ |
| 401 (1) | 399 | 551 (2) | 528 | $3V_2$ |
| 641 (10) | 641 | 608 (2) | 608 | $V_3$ |
| 691 (1) | 701 | | | $V_3+V_1$ |
| 2946 (20) | 2946 | 2921 (15) | 2921 | $V_4$ |
| 3006 (15) | 3006 | 2976 (10) | 2976 | $V_4+V_1$ |

It is interesting to collect the values of the fundamentals used in the spectra of the various compounds described, as is done in Table VII. It will be seen that $V_1$ increases in frequency with increasing molecular weight (or increasing atomic weight of the halogen substituent) in all except the unsymmetrical compounds. The $V_2$ fundamental decreases with increase of molecular weight except in the unsymmetrical compounds, while $V_3$ decreases consistently in all the compounds. The $V_4$ fundamental is less variable, but it is thought that its variation can be explained better by an alternative method.

In addition to the foregoing data, results are here given for several compounds of cyclic structure. The plates for the first three do not show so many

TABLE VI. *Raman spectra of symmetrical ethyl tetrahalides.*

| S-Tetrachloroethane $Cl_2HC \cdot CHCl_2$ |  | S-Tetrabromoethane $Br_2HC \cdot CHBr_2$ |  | Assumed combination |
|---|---|---|---|---|
| Obs. | Comp. | Obs. | Comp. |  |
|  | 50 |  | 73 | $V_1$ |
|  | 139 |  | 99 | $V_2$ |
|  |  | 121 (3) | 120 | $3V_1-V_2$ |
| 101 (2) | 100 | 156 (3) | 146 | $2V_1$ |
| 189 (2) | 189 | *186 | 172 | $V_1+V_2$ |
|  |  | *219 (10) | 219 | $3V_1$ |
| 248 (2) | 250 |  |  | $5V_1$ |
| 299 (2) | 300 |  |  | $6V_1$ |
| 359 (10) |  |  |  | (?) |
| 558 (1) | 550 |  |  | $11V_1$ |
| 656 (8) | 666 |  |  | $V_3-3V_1$ |
|  |  | 541 (3) |  | (?) |
|  |  | 628 (1) | 617 | $V_3-V_2$ |
|  |  | 666 (2) |  | (?) |
| 816 (5) | 816 | 716 (30) | 716 | $V_3$ |
|  |  | 779 (2) |  | (?) |
| 999 (4) | 1005 |  |  | $V_1+V_2+V_3$ |
| 1244 (3) | 1233 | 1014 (5) | 1013 | $V_3+3V_2$ |
|  |  | 1153 (5) | 1140 | $2V_3-4V_1$ |
|  |  | 1206 (5) | 1213 | $2V_3-3V_1$ |
|  |  | 2776 (2) | 2777 | $V_4-2V_1$ |
| 2931 (20) | 2931 | 2923 (40) | 2923 | $V_4$ |
| 2996 (20) | 2981 | 2996 (20) | 2996 | $V_4+V_1$ |
| 8V, 10 |  | 8V |  | References to other work |

*These frequencies apper as "antistokes" lines also.

lines as have been reported by other observers; they are probably underexposed. The results on these are simply listed here without any attempt to point out possible structure, beyond noting that the frequency at about 1000 $cm^{-1}$ is apparently a new fundamental, $V_5$, and that the $V_4$ fundamental at

TABLE VII. *Collected values of fundamentals.*

|  | $V_1$ | $V_2$ | $V_3$ | $V_4$ | $V_5$ |
|---|---|---|---|---|---|
| Diethyl ether $(C_2H_5)_2O$ | 55 |  |  | 2928 |  |
| Ethyl alcohol $C_2H_5OH$ | 47 |  |  | 2928 |  |
| Methyl bromide, $CH_3Br$ |  |  | 603 |  |  |
| Methyl iodide, $CH_3I$ |  |  | 534 | 2946 |  |
| Ethyl chloride, $C_2H_5Cl$ | 41 | 84 | 668 | 2921 |  |
| Ethyl bromide, $C_2H_5Br$ | 48 | 77 | 561 | 2923 |  |
| Ethyl iodide, $C_2H_5I$ | 53 | 65 | 527 | 2915 |  |
| Ethylene chloride, $ClCH_2CH_2Cl$ | 44 | 105 | 759 | 2961 |  |
| Ethylene bromide, $BrCH_2CH_2Br$ | 52 | 100 | 663 | 2966 |  |
| Ethylidene chloride, $CH_3CHCl_2$ | 60 | 133 | 641 | 2946 |  |
| Ethylidene bromide, $CH_3CHBr_2$ | 55 | 176 | 608 | 2921 |  |
| S-Tetrachloroethane, $Cl_2CHCHCl_2$ | 50 | 139 | 816 | 2931 |  |
| S-Tetrabromoethane, $Br_2CHCHBr_2$ | 73 | 99 | 716 | 2923 |  |
| Chlorobenzene, $C_6H_5Cl$ | 90 | 106 | 626 | 3076 | 1009 |
| Bromobenzene, $C_6H_5Br$ | 75 | 104 | 606 | 3071 | 1006 |

about 3050 $cm^{-1}$ has a somewhat higher frequency in the cyclic than in the aliphatic compounds.

Benzene, $C_6H_6$[8I, 8II, 8IV, 9, 7, 10, 11, 12]; 621 (1), 1003 (20), 1203 (3), 1619 (5), 3078 (50) $cm^{-1}$.

Pyridine, $C_6H_5N$[15, 13, 17]; 991 (10), 1033 (10), 1226 (3), 1586 (5), 3046 (50) $cm^{-1}$.

Benzyl chloride, $C_6H_5CH_2Cl$[8IV, 15]; 681 (1), 991 (3), 1601 (3), 2951 (3), 3046 (20) $cm^{-1}$.

In the case of chlorobenzene and bromobenzene, the kind of scheme of analysis attempted above succeeds rather better, all but one of the lines of each substance being representable as either a fundamental or as a combination line of some sort. The results are given in Table VIII.

TABLE VIII. *Raman spectra of phenyl halides.*

| Chlorobenzene $C_6H_5Cl$ | | Bromobenzene $C_6H_5Br$ | | Assumed Combination |
|---|---|---|---|---|
| Obs. | Comp. | Obs. | Comp. | |
| | 90 | | 75 | $V_1$ |
| | 106 | | 104 | $V_2$ |
| | | 176 (3) | 179 | $V_1+V_2$ |
| 213 (3) | 212 | | | $2V_2$ |
| 316 (1) | 318 | 313 (2) | 312 | $3V_2$ |
| 426 (3) | 424 | | | $4V_2$ |
| 626 (3) | 626 | 608 (1) | 606 | $V_3$ |
| 716 (3) | 716 | 678 (1) | 681 | $V_3+V_1$ |
| 789 (3) | 787 | | | $V_5-2V_2$ |
| 1011 (10) | 1009 | 1006 (10) | 1006 | $V_5$ |
| 1098 (5) | 1099 | 1073 (3) | 1081 | $V_5+V_1$ |
| 1183 (2) | 1189 | 1171 (3) | 1156 | $V_5+2V_1$ |
| | | 1586 (6) | | (?) |
| 2140 (1) | 2148 | | | $3V_3+3V_1$ |
| 2736 (1) | | | | (?) |
| 3076 (50) | 3076 | 3071 (50) | 3071 | $V_4$ |
| 3188 (5) | 3182 | | | $V_4+V_2$ |
| (8II, 10, 14) | | (8II, 9, 14, 15) | | |

In attempting to discover some sort of system in Raman spectra, one should proceed with careful attention to the probable sources of error. These may be mentioned in three groups, in the present work. First, the data are too inaccurate to warrant any very great assurance that the apparent regularities found are significant. The wave-number shifts here reported were obtained with dispersion too small to yield exact values for the differences, and it is probable further that a number of the fainter lines were overlooked. The accuracy might be improved by using results from other observers, at least for the stronger lines; but on the other hand, the results reported from mercury arc excitation apparently contain so many spurious lines, due to the difficulty of deciding which of the various mercury lines really was the exciting line, that it seems clear that much of the work done using unfiltered mercury radiation will have to be repeated, in spite of the evident care with which

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[16] Petrikaln and Hochberg, Zeits. f. phys. Chem. **B3**, 217 and 405 (1929); **B4**, 299 (1929).

[17] S. Venkateswaran, J. Phys. Chem. **34**, 145–152 (1930).

much of this work has been done. It is, of course, pointless to try to explain lines which in fact do not exist, just as it is discouraging to try to explain a spectrum from which the fainter lines are lacking.

Second, the lack of a theoretical basis for assuming the lower fundamentals used above is against the suggested scheme, as is the almost complete absence of these lower fundamentals. At first sight it might seem safe to assume fundamental frequencies so low in frequency as to be unobservable in the Raman spectra, and so low as to lie in the region of reststrahlen, so that infrared data would be lacking. But some of them at least are high enough in frequency so that they should not be covered up by the broad exciting line. Many of the combinations that would be expected from these fundamentals are not observed; and in a few cases, the intensities do not seem to fit in well. As will be pointed out below, most of such theory as is available seems to indicate that all the stronger Raman lines are fundamentals. On the other hand, overtones and combinations occur very frequently in infrared spectra; and in many Raman spectra the number of lines is so great that it seems impossible that all of them should be fundamentals. The absence of the lower frequencies is not a fatal objection; the reststrahlen frequencies of sodium chloride, for instance, do not appear in the Raman spectrum. But it will be interesting if liquids prove to have such low characteristic frequencies.

Third, it is frequently possible to find several ways of arranging a spectrum, which appear equally probable. If three frequencies $A$, $B$, and $C$, are found, such that $A+B=C$, it may be that $C$ is a combination tone, or that either $A$ or $B$ is a difference-tone, or that the apparent relation is simply accidental. Again, it was found, for example, that all but four of the lines in the Raman spectrum of chlorobenzene could be set equal to integral multiples of a certain assumed fundamental. No reason could be given for the high intensity of some of the multiples and the absence of many of the others. Bromobenzene showed no analogous relation. Evidently the case was just another illusory relation. One more example may be pointed out; this is the case of carbon tetrachloride, which shows well the different ways in which a spectrum may be explained. On one hand, Langer[18] shows that the Raman frequencies of $CCl_4$ may all be explained as being due to *differences* between fundamental frequencies in the infrared spectrum, and even suggests a wave-mechanics theory to support the argument. On the other hand, Marvin[19] shows that the Raman frequencies of this compound can be explained, and the infrared spectrum as well, in terms of six fundamentals and their overtones and combinations; and the spectra of $SiCl_4$ are explained similarly. Next, Schaefer[20] shows that one of Marvin's fundamentals is unnecessary, as it is the octave of another; and by assuming that two of the remaining frequencies are a doublet, he is able to bring the whole scheme into good agreement with the theoretical results of Dennison[21] as necessarily modified to ap-

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[18] R. Langer, Nature **123**, 345 (1929).

[19] H. H. Marvin, Phys. Rev. **33**, 952 (1929).

[20] C. Schaefer, Zeits. f. Physik **60**, 586 (1930).

[21] D. M. Dennison, Astrophys. J. **62**, 84 (1925).

ply to $CCl_4$ instead of to $CH_4$ (methane). The same is done for $SiCl_4$, and the possibility of similar treatment of $TiCl_4$ and $SnCl_4$ is pointed out, as well as certain similarities with compounds containing the $SO_4$ group. The arguments presented, and the manner in which the scheme fits the observed spectra, are extremely convincing, and there seems to be no reason to doubt the essential correctness of Schaefer's analysis. But if this is conceded, then it seems necessary to admit that overtone frequencies do appear in Raman spectra, as both Daure[7] and Pringsheim and Rosen[10] have observed Raman frequencies in the spectrum of $CCl_4$ which on Schaefer's scheme must be the overtone of one of the fundamentals.

In view of such facts, the writers do not present the suggested arrangements tabulated above as anything more than an interesting set of numerical approximations which it is hoped may be of use to some one in extending the theory of the Raman effect, as Marvin's suggested plan probably helped in analyzing the spectrum of $CCl_4$.

An attack on the problem from a quite different angle is made by Dadieu and Kohlrausch.[8] It is assumed that the chemical bonds in a molecule may be treated as a first approximation as if they behaved like elastic springs; so that when two atoms of masses $m_1$ and $m_2$ vibrate with respect to each other, the restoring force $F$ is proportional to the displacement, $x$,

$$F = fx; \tag{1}$$

and the frequency of the oscillation is given by the equation

$$W_0 = 1/2\pi(f/\mu)^{1/2}, \tag{2}$$

in which $\mu$, the "reduced mass" of the oscillating system, is given by

$$1/\mu = 1/m_1 + 1/m_2. \tag{3}$$

The theory has been extended to the case of anharmonic oscillations, and to the case of coupled vibrations, in which three bodies participate; but these parts of the theory are not immediately essential to the purpose of this paper. Dadieu and Kohlrausch have considered only longitudinal vibrations; but the case of transverse vibrations has been treated briefly in similar fashion by Andrews.[22] Following the theory outlined, the constant $f$ is taken to be approximately proportional to the energy of dissociation $A$ of the chemical bond between the vibrating atoms, this energy being known at least roughly from thermochemical data. Hence if one frequency due to a given pair of atoms is known, the frequency due to any other pair of atoms may be computed if the $A$'s and the $\mu$'s are known. In this way, starting with the aromatic C-H frequency at 3050 $cm^{-1}$ as a reference frequency, Dadieu and Kohlrausch have computed the frequencies to be expected from a large number of types of chemical bond, the computed values being usually somewhat lower than the observed values. In this way, and by comparison of similar compounds in a list of more than a hundred compounds studied, Dadieu and Kohlrausch have

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[22] D. H. Andrews, Phys. Rev. **36**, 544 (1930).

been able to identify the characteristic frequencies of a considerable number of chemical bonds. The theory explains at once why in Raman spectra there is such a noticeable lack of lines between the C-H group, from 2850 $\text{cm}^{-1}$ to 3100 $\text{cm}^{-1}$, and the lines due to the heavier atoms, most of which occur with shifts below 1700 $\text{cm}^{-1}$. The computations show that in cases where similar atoms are joined by single, double, and triple bonds, the average restoring forces are in the approximate ratio 1:2:3. As in infrared spectra, "internal" frequencies characteristic of vibrations within recurring groups, and "external" frequencies, associated with the vibrations of a group against the rest of the molecule, are distinguished. The theory checks with observation in so many ways that it seems impossible to doubt its essential correctness. Further evidence in this direction is afforded by the interesting experiments of Kettering, Shutts, and Andrews,[23] who constructed molecular models and, by noting resonance frequencies by stroboscopic methods when the models were vibrated, found sets of characteristic frequencies in good agreement with this theory.

So far as the theory has been applied to the compounds considered in the present article, frequencies for the carbon-halogen bonds are predicted which are in qualitative agreement with the frequencies marked $V_3$ in the tables; but no frequencies as low as the $V_1$ and $V_2$ assumed are predicted, and these may prove to be illusory. The $V_4$ frequency is clearly the C-H frequency; but if it is assumed that neighboring substituents can alter either the effective mass of the vibrating groups or the strength of the chemical bond between them, and Dadieu and Kohlrausch have presented abundant evidence that both these things occur, then it seems more probable that the occurrence of several lines in the C-H group is due to the existence of several modifications of the C-H bond in the molecules, rather than to combination with a hypothetical $V_1$ or $V_2$ frequency. The approximately equal frequency-differences observed are likely to prove not due to combinations. In all probability, more than four fundamentals will be required to explain the structure of most of the compounds discussed. This is especially likely to be true of the cyclic compounds. The fundamental $V_5$ is probably real, and characteristic of the benzene-ring structure. But Dadieu and Kohlrausch, Soderqvist,[11] and others have pointed out that there are three or four other frequencies which also seem to be characteristic of the ring structure. Whether these are all fundamentals, it is at present impossible to say. Dadieu and Kohlrausch have expressed the opinion that only fundamentals appear in Raman spectra; but an apparently valid exception to this statement has been pointed out above in the case of $CCl_4$.

It is hoped that further considerations may be presented in another paper in preparation by one of the writers.

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[23] Kettering, Shutts, and Andrews, Phys. Rev. **36**, 531 (1930).