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BAND SERIES IN INFRA-RED ABSORPTION SPECTRA OF ORGANIC COMPOUNDS. II

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Abstract

The absorption bands of secondary intensity occurring, in addition to the more pronounced members of the previously described C-H series, in the short wave-length infra-red spectra of methyl iodide, methylene chloride, methylene bromide, methylene iodide, chloroform and bromoform are accounted for on the basis of linear C–Cl, C–Br, and C–I series starting at 16.8μ, 17.2μ and 17.5μ respectively; and on the basis of simple additive combinations between these frequencies and those of the C–H series.

IN PART I of this paper[1] it has been shown that the numerous bands occurring in the nearer infra-red absorption spectra of carbon-hydrogen compounds can be arranged into series of three types: a non-linear series attributed to C-H vibrations, a linear series attributed to C-C vibrations, and combination series resulting from direct addition of frequencies of these two. There have just come to the writer's attention two papers by Bonino[2] which contribute to the identification of the well-known band near 3.4μ as a member of a C-H series. This band, assumed by the author to be the second member of a C-H series, lies in a region of the spectrum which is easily accessible and which is relatively free from overlapping bands due to other molecular sources. Bonino selected this band around which to measure molecular absorption coefficients in homologous series, in particular, four ketones and several compounds formed by successive halogen substitutions into the ethane molecule. In the case of the ketones he found the molecular absorption coefficient to increase regularly with the number of hydrogen atoms present in the molecule; in the case of the halogen compounds the coefficient decreased regularly with additional substitutions of the halogen atoms. Bonino's work contains slightly more convincing evidence of the independent absorption by a C-H group than a similar earlier investigation by Henri[3] in which the latter measured the molecular absorption coefficient of a series of alcohols in this same spectral region. Although this coefficient increased regularly throughout the homologous series, Henri had to assume that part of it

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[1] Ellis, Phys. Rev. **27,** 298 (1926).

[2] G. B. Bonino, Gaz. chim. italiana **55,** 335 and 348 (1925).

[3] V. Henri, Études de Photochimie (1919).

was due to the O-H group and part, following Coblentz, to CH_2 and CH_3 groups.

Further evidence, indicating the absorption by a single group within the molecule, is found in a recent article by Salant[4] in which he identifies bands near 6.1μ and 3μ as the first two members of a N-H series. The evidence is made convincing by the disappearance of the 3μ band characteristic of the di-alkyl amines in the tri-alkyl amines, which lack the N-H bond.

In the present paper an attempt is made to identify and arrange into series bands which arise because of the presence of halogen atoms within the molecule. Only those compounds are considered which result from a substitution of one, two or three halogen atoms into the methane molecule, thus eliminating the possibility of any C-C bands. The six substances used were: methyl iodide, CH_3I; methylene chloride, CH_2Cl_2; methylene bromide, CH_2Br_2; methylene iodide, CH_2I_2; chloroform, $CHCl_3$; bromoform, $CHBr_3$. Since the investigation was limited to liquids, methyl chloride and methyl bromide, which are vapors at ordinary temperatures, and iodoform, which is a solid, were not studied.

TABLE I

Calculated and observed wave-lengths of a C-H series.

n	calc. $\nu_n \times 10^{-12}$	calc. λ_n	methylene chloride CH_2Cl_2	chloroform $CHCl_3$	methylene bromide CH_2Br_2	bromoform $CHBr_3$	methyl iodide CH_3I	methylene iodide CH_2I_2
1	46.6	6.44	‡	6.8 *	‡	‡	*	‡
2	91.6	3.28	‡	3.32	‡	‡	3.4	‡
3	135.2	2.22	2.27	2.22 †	‡	2.27 *	2.23 *	2.32 *
4	177.0	1.695	1.675*	1.66 *	1.68*	1.67 *	1.66 *	1.68 *
5	217.5	1.379	1.36 *	1.385*	1.37*	1.40 *	1.35 *	1.37
6	255.9	1.172	1.15 *	1.145*	1.15*	1.15 *	1.15 *	1.15 *
7	293.4	1.022	1.03 *	1.015*	1.03*	1.015*	......	1.03 *
8	328.8	0.912	0.935*	0.890*	0.89*	0.890*	0.895*	0.895*

* Has another band superposed upon it.
† Occurs as a point of inflection only.
‡ No reliable measurements recorded.

In Table I is shown the agreement between the C-H bands observed in the spectra of the six substances mentioned and the wave-lengths calculated from the formula already given (1):

$$\nu_n \times 10^{-12} = 47.37n - 0.783n^2$$

In Fig. 1 are shown the absorption curves to 2.5μ previously published in this journal.[5] Fig. 2 shows the additional details which are brought

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[4] E. O. Salant, Proc. Nat. Acad. of Sci. **12,** 74 (1926).

[5] Ellis, Phys. Rev. **23,** 48 (1924).

out in the spectrum of chloroform by increasing the thickness of the absorbing cell. Figs. 3 and 4 show the absorption produced in the region 2μ to 3μ by 0.5 mm cells of five of these substances. These curves were obtained with a recording quartz spectrograph previously described.[6]

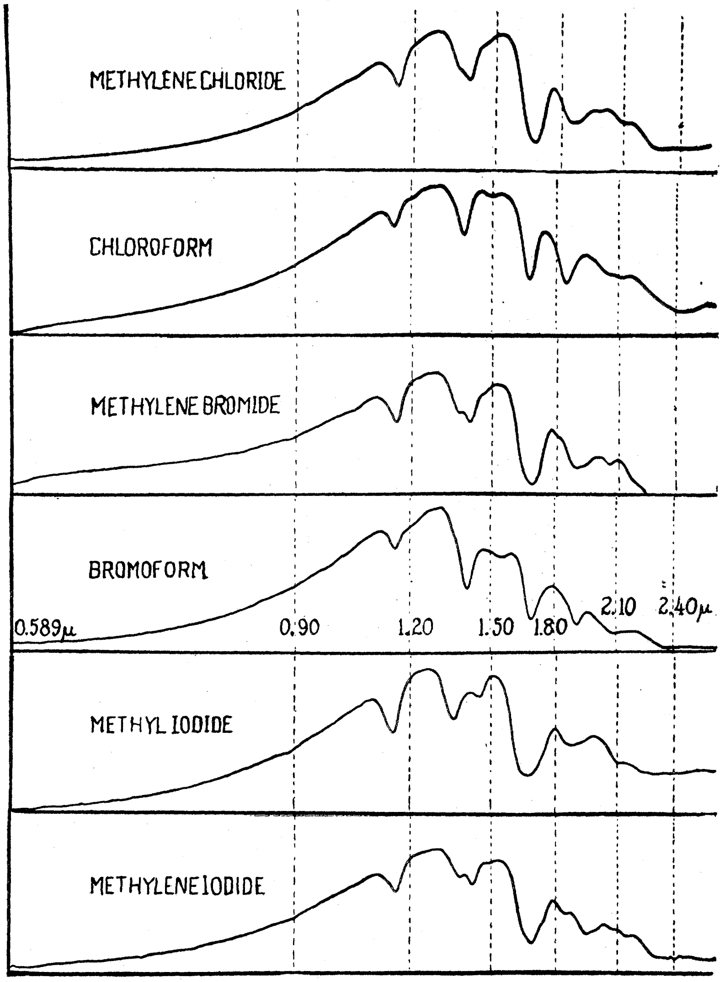

Fig. 1. Absorption spectra obtained with a recording spectrograph with flint glass prisms. Absorbing cell = 11 mm.

It has been pointed out in Part I of this paper that Márton[7] has independently discovered the existence of the non-linear series of

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[6] Ellis, J.O.S.A. & R.S.I. **11**, 647 (1925).

[7] Márton, Zeits. f. Phys. Chem. **117**, 97 (1925).

prominent bands previously attributed by the author to C-H oscillations. In this same report Márton, using data obtained by himself, Coblentz, and the writer, attempts to account for the other bands in the spectrum of chloroform on the basis of a linear series starting at 8.35μ and combinations between this and the above mentioned non-linear series.

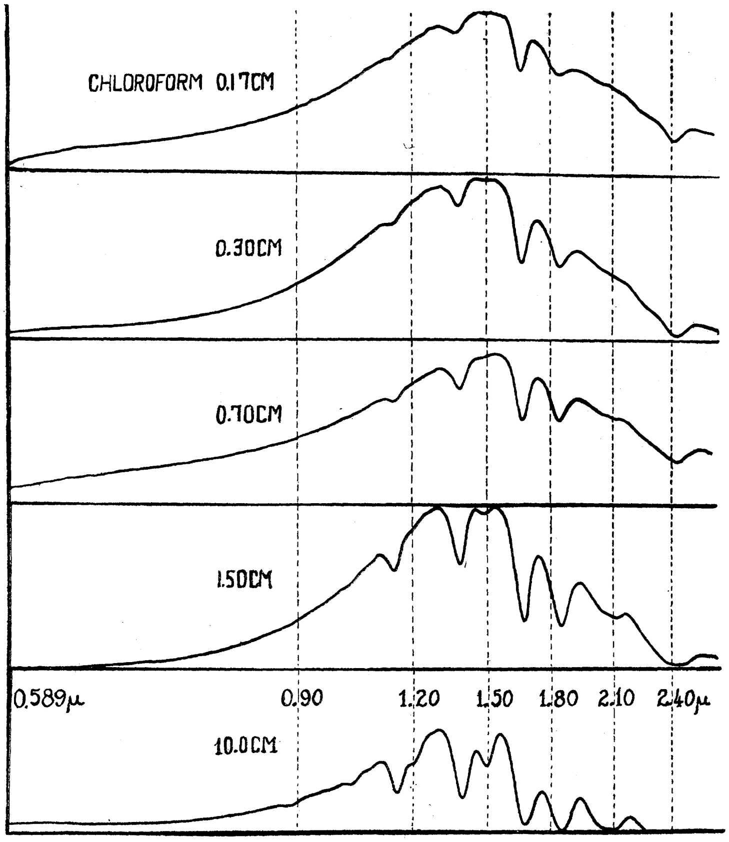

Fig. 2. Effect of increasing thickness of absorbing cell.

The choice of 8.35μ as the wave-length value of the initial member of the series in the spectrum of chloroform is natural, since it is the most outstanding band. However, a series starting at this frequency will not account for the many bands of secondary intensity appearing in Figs. 1, 2 and 3. But by assuming a linear series starting at about twice this value, namely 16.8μ, it is possible to identify all of these bands as members of such a series or of simple combination series of the type already mentioned. Moreover, the spectrum of methylene chloride shows the same absorption maxima, although there are apparent external differences between the spectra of these two substances. Such differences should be anticipated because of different intensity ratios among the bands, since chloroform contains one atom of hydrogen and three atoms of chlorine, while methylene chloride contains two of each.

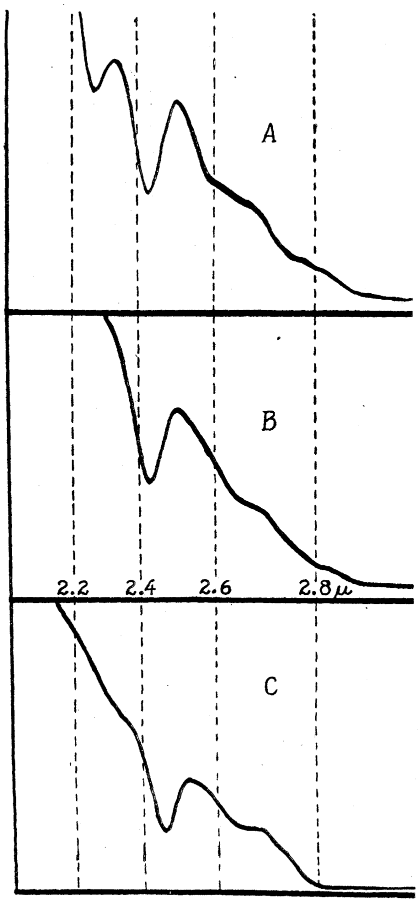

Fig. 3

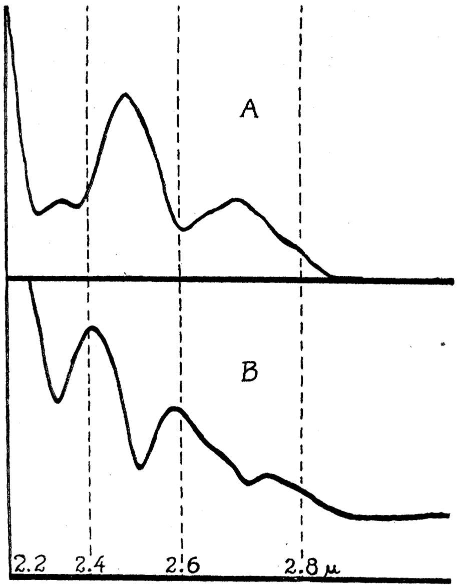

Fig. 4

Fig. 3. Absorption spectra obtained with a recording spectrograph with quartz prisms. $A = 0.5$ mm of methylene chloride; $B = 0.5$ mm of chloroform; $C = 0.5$ mm of bromoform.

Fig. 4. $A = 0.5$ mm of methyl iodide. $B = 0.5$ mm of methylene iodide.

Table II gives the agreement between the calculated and observed wave-length values of a series starting at 16.8μ which is attributed to

TABLE II

Calculated and observed wave-lengths of a C-Cl series.

n	calc. $\nu_n \times 10^{-12}$	calc. λ_n	methylene chloride CH_2Cl_2	chloroform $CHCl_3$
1	17.9	16.8	†	†
2	35.7	8.4	‡	8.35
3	53.6	5.6	‡	5.40 M
4	71.4	4.2	‡	4.15 M 4.4 *
5	89.3	3.34	‡	3.32 *
6	107.1	2.80	2.80	2.80
7	125.0	2.40	2.42	2.42
8	142.8	2.10	2.10 *	2.12
9	160.7	1.865	1.87 *	1.845*
10	178.5	1.68	1.765*	1.66 *
11	196.3	1.525	.....	1.50
12	214.2	1.40	1.39 *	1.385*
13	232.1	1.29	.....	1.28
14	249.9	1.20	1.20	1.20
15	267.8	1.12	1.15 *	1.145*
16	285.6	1.05	1.03 *	1.022*
17	303.5	0.99	.....	0.98
18	321.3	0.933	0.935*	0.935*
19	339.2	0.885	0.890*	0.890*

* Has another band superposed upon it.
‡ No reliable measurements recorded.
† Region never investigated.
M Obtained by Márton.

C-Cl oscillations. Table III gives the agreement between calculated and observed bands of combination series. In this case ν_n and ν'_{n1} refer

TABLE III

Combination bands of C-H and C-Cl series.

	calc. $\nu_c \times 10^{-12}$	calc. λ	methylene chloride	chloroform
$\nu_1+\nu_1'$	64.5	4.68	‡	4.4 *
$\nu_1+\nu_2'$	82.4	3.65	‡	3.75
$\nu_1+\nu_3'$	100.3	2.99	‡	.....
$\nu_1+\nu_4'$	118.2	2.55	2.57	2.55
$\nu_1+\nu_5'$	136.1	2.21	2.27 *	2.22 *
$\nu_1+\nu_6'$	154.0	1.95	1.98 *	.....
$\nu_1+\nu_7'$	171.9	1.75	.....	.....
$\nu_2+\nu_1'$	109.5	2.74	2.76	2.73
$\nu_2+\nu_2'$	127.4	2.36	2.27 *	†
$\nu_2+\nu_3'$	145.3	2.07	2.10 *	2.055*
$\nu_2+\nu_4'$	163.2	1.84	1.84 *	1.845*
$\nu_2+\nu_5'$	181.1	1.66	1.68 *	1.66 *
$\nu_2+\nu_6'$	199.0	1.51	.....	1.50 *
$\nu_2+\nu_7'$	216.9	1.38	1.39 *	1.385*
$\nu_3+\nu_1'$	153.1	1.96	1.98 *	.....
$\nu_3+\nu_2'$	171.0	1.76	.....	.....
$\nu_3+\nu_3'$	188.9	1.59	*	1.58 †
$\nu_3+\nu_4'$	206.8	1.45	1.455	1.385*

* Superposed upon another band.
† Occurs as a point of inflection only.
‡ No reliable measurements recorded.

to members of C-H and C-Cl series respectively. All values above 3μ except as otherwise indicated, are from measurements by Coblentz, while values below 3μ are from the curves of Figs. 1, 2 and 3.

Comparisons among the curves of Fig. 1 indicate that series similar to the one attributed to C-Cl might be found for C-Br and C-I oscillations. The slight shifts toward longer wave-lengths of the halogen bands when chlorine is replaced by bromine, and bromine by iodine, indicate that values slightly greater than 16.8μ must be assumed for the initial members. Tables IV and VI give agreements between observed and calculated wave-lengths on the assumption of a C-Br series starting at 17.2μ and a C-I series starting at 17.5μ. Tables V and VII give values for combination series similar to those of Table III.

TABLE IV

Calculated and observed wave-lengths of a C-Br series.

n	calc. $\nu_n \times 10^{-12}$	calc. λ	methylene bromide CH_2Br_2	bromoform $CHBr_3$
1	17.5	17.2	§	§
2	34.9	8.6	‡	‡
3	52.4	5.73	‡	‡
4	69.8	4.30	‡	‡
5	87.3	3.42	‡	‡
6	104.6	2.87	‡	‡
7	122.0	2.46	‡	2.47
8	139.5	2.15	2.16	2.15
9	156.9	1.91	1.92	1.90
10	174.6	1.72	1.68 †	1.67 *
11	192.0	1.56	.....	1.55
12	209.6	1.43	1.405	1.40 *
13	227.0	1.32	.....	1.285
14	244.5	1.225	1.22	1.22
15	262.0	1.145	1.15*	1.15 *
16	278.5	1.07	.....	1.08
17	297.0	1.01	.....	1.02
18	314.0	0.955	.....	0.97

* Superposed upon another band.
† Occurs as a point of inflection only.
‡ No reliable measurements recorded.
§ Region never investigated.

If the series whose members appear in Table II arises from oscillations of a C-Cl pair of atoms, then one should expect to find a corresponding series of strong bands in the spectrum of carbon tetrachloride, CCl_4. On the contrary, investigators have repeatedly reported perfect transparency of this substance for short infra-red rays. The writer, using a cell thickness of many centimeters, has observed a few very weak bands, which correspond to C-H and C-Cl bands. The substance tested was of an ordinary commercial grade, and it is probable that the bands were due to impurities. A 15 mm cell of tetrachlorethylene, $Cl_2C{:}CCl_2$, from a sample prepared by the Eastman Research Laboratories, showed weak bands similar to those of carbon tetrachloride. If these are due to the compounds themselves they possess but a small fraction of the intensity which would be expected. The anomalous effects in the

TABLE V

Combination bands of C-H and C-Br series.

	calc. $\nu_c \times 10^{-12}$	calc. λ	methylene bromide	bromoform
$\nu_1+\nu_1'$	64.1	4.68	‡	‡
$\nu_1+\nu_2'$	81.6	3.68	‡	‡
$\nu_1+\nu_3'$	99.1	3.015	‡	‡
$\nu_1+\nu_4'$	116.6	2.58	‡	
$\nu_1+\nu_5'$	134.1	2.25	‡	2.29
$\nu_1+\nu_6'$	151.6	1.985	......	.....
$\nu_1+\nu_7'$	169.1	1.78	1.80	1.78
$\nu_2+\nu_1'$	109.1	2.75	‡	2.73
$\nu_2+\nu_2'$	126.6	2.37	‡	2.36
$\nu_2+\nu_3'$	144.1	2.08	2.06	2.08
$\nu_2+\nu_4'$	161.6	1.86	1.88	1.90 *
$\nu_2+\nu_5'$	179.1	1.675	1.695 †	1.67 *
$\nu_2+\nu_6'$	196.6	1.53	.....	1.55 *
$\nu_3+\nu_1'$	152.7	1.97	1.93 *	.....
$\nu_3+\nu_2'$	170.2	1.50	1.47	1.55 *
$\nu_3+\nu_3'$	187.7	1.38	1.405 *	1.40 *
$\nu_3+\nu_4'$	205.2	1.275	1.27	1.285*

* Superposed upon another band.
† Occurs as a point of inflection only.
‡ No reliable measurements recorded.

TABLE VI

Calculated and observed wave-lengths of a C-I series.

n	calc. $\nu_n \times 10^{-12}$	calc. λ	methyl iodide CH_3I	methylene iodide CH_2I_2
1	17.2	17.5	§	§
2	34.4	8.75	8.25 *	‡
3	51.6	5.83	5.8 †	‡
4	68.7	4.38	4.55 *	‡
5	85.8	3.50	3.40 *	‡
6	103.0	2.92	.....	‡
7	120.0	2.50	†	2.52†
8	137.5	2.19	2.23 *	2.15*
9	154.5	1.945	1.94	1.95
10	171.6	1.750	1.74 †	1.73†
11	189.0	1.580	1.59 †	1.63*
12	206.2	1.455	1.455	1.49
13	223.5	1.345	1.35 *	1.37*
14	240.5	1.250	.....	†
15	257.5	1.165	1.15 *	1.15*
16	275.0	1.095	1.15 *	1.15*

* Has another band superposed upon it.
† Occurs as a point of inflection only.
‡ No reliable measurements recorded.
§ Region never investigated.

spectra of these substances may be in some way associated with the symmetry in the molecular structure.

Since there is no observable deviation from linearity in the above series the molecular forces acting must be very nearly linear. The presence of combination frequencies requires a quantum theory interpretation. This means that the first member of the series, due to an energy jump from oscillation state zero to oscillation state one, will be practically equal to the primary rate of vibration. The first member, then, of the series should be approximately expressible by

$$\nu = c/\lambda = 1/2\pi\sqrt{U/M}$$

where U is the force between the two atoms and M the reduced mass. M is determined by $1/M = 1/M_c + 1/M_x$ where M_c and M_x are the masses of the carbon and halogen atoms respectively.

TABLE VII

Combination bands of C-H and C-I series.

	calc.	calc.	methyl iodide	methylene iodide
	$\nu_c \times 10^{-12}$	λ		
$\nu_1+\nu_1'$	63.8	4.71	4.55	‡
$\nu_1+\nu_2'$	77.3	3.88	*	‡
$\nu_1+\nu_3'$	98.1	3.06	*	
$\nu_1+\nu_4'$	114.9	2.61	2.61	2.62
$\nu_1+\nu_5'$	134.0	2.27	2.23 *	2.32*
$\nu_1+\nu_6'$	149.1	2.01	.....	1.98*
$\nu_1+\nu_7'$	167.0	1.795	*	....
$\nu_2+\nu_1'$	108.5	2.76	2.77	2.72
$\nu_2+\nu_2'$	123.5	2.385	2.38	2.32*
$\nu_2+\nu_3'$	143.0	2.095	2.1	2.08
$\nu_2+\nu_4'$	159.5	1.875	1.87	1.84
$\nu_2+\nu_5'$	177.5	1.69	1.66 *	1.68*
$\nu_2+\nu_6'$	194.5	1.54	*	....
$\nu_3+\nu_1'$	152.5	1.97	1.94	1.98
$\nu_3+\nu_2'$	169.5	1.77	*	1.73†
$\nu_3+\nu_3'$	187.0	1.605	1.61 *	1.63*
$\nu_3+\nu_4'$	204.0	1.47	1.455*	1.48
$\nu_3+\nu_5'$	220.5	1.36	1.35 *	1.37*

* Superposed upon another band.
† Occurs as a point of inflection only.
‡ No reliable measurements recorded.

The value of U will be different for every chemical bond; yet the above formula should serve for a qualitative comparison of the frequencies among bonds of a similar character. Thus, it should serve for a comparison among the fundamental frequencies due to C-H, C-Cl, C-Br and C-I, for hydrogen, chlorine, bromine and iodine atoms lack one electron only in the K, M, N and O shells, respectively. The departure from constant proportionality between values of $\sqrt{M}$ and

λ_1 as given in Table VII may be regarded as a measure of the differences in the strengths of the chemical bonds among the four cases cited. The results lead to the conclusion that in this type of bond the iodine atom is held by the carbon atom more tightly than are the chlorine or bromine atoms. This need not be interpreted as in conflict with the fact that bromine and chlorine will replace iodine in the molecule, since this replacement is determined by the heat of dissociation, which in turn depends upon the distance of separation of the atoms as well as upon the bonding forces.

TABLE VIII

Bond	$\sqrt{M}/\sqrt{M_H}$	λ_1	$\sqrt{M}/\lambda_1$
C–H	0.96	6.44μ	0.149
C–Cl	3.00	16.8	0.178
C–Br	3.30	17.2	0.192
C–I	3.45	17.5	0.197

The writer is much indebted to Mr. Edward Condon of Berkeley, California, who has called his attention to an article by Born and Heisenberg[8] on the theory of polyatomic molecules and for his assistance in the interpretation of the bearing of this article upon the present paper. Born and Heisenberg assume a molecule consisting of electrons and nuclei, the nuclei being ordinarily at rest with approximately linear forces acting between them, such forces arising from the motions of the electrons. Higher energy states of the nuclei are also assumed to exist, and the evaluation of these states is obtained by a series of approximations. The first approximation leads to the conclusion that during a change from one state to another a member of a linear, or harmonic, series of frequencies should be emitted or absorbed. A second approximation shows that a linear deviation from a true harmonic relation should occur in the frequency series absorbed or emitted. It should be pointed out, however, that the characteristic frequencies assumed under this theory to occur during energy changes within the molecule are dependent in some manner upon all parts of the molecule. The theory does not deal with the isolation of a portion of the molecule, for example, a pair of atoms. The results of infra-red absorption study, however, make it very apparent that certain fields of force may be considered practically isolated within the molecule. With this interpretation it would seem that C-H series might be regarded as experimental evidence of the existence of the type of frequency series predicted by the second approximation in Born and Heisenberg's solution,

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[8] Born and Heisenberg, Ann. d. Physik **74,** 1 (1924).

while the other four series might be regarded as completely expressed within the limits of experimental error by their first approximation solution.

The bands attributed in this paper to the halogens are not characteristic alone of the simple types of molecule considered here. In another paper numerous molecules of a more complicated nature, many of them containing halogen atoms, will be dealt with. It will be found that many of these bands may be identified in the more complicated spectra which these substances present.

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