STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES. PART I. RAMAN EFFECT OF A SERIES OF ESTERS OF BENZOIC ACID AND PHENYL ESTERS OF FATTY ACIDS.

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Introduction.

Since the Raman effect was discovered in 1928, the investigations of this line have made a rapid progress especially in the field of organic chemistry. Studies of the effect of the length of an organic molecule and of a splitting of the hydrocarbon chain upon the vibration of an atom or atom group attached at the end of the molecule have been a matter of interest. Harkins and his coworkers(1), Dadieu and Kohlrausch(2) have been published several papers on this subject. Alkyl habides(3), fatty acids(4), some of esters of the fatty acids(5), fatty alcohols(6) have been already studied by the investigators above mentioned and others. The present authors carried out the experiment on esters of the aromatic carboxylic acid and fatty acids in view of the standpoint to ascertain the free rotation of the alkyl groups and to confirm the inner and outer vibration of the valency frequencies between the alkyl groups and other atom groups. The materials used in the present research have been synthesized carefully and purified by repeated distillations. Some of the physical constants of the samples used have also been studied.

Experimental.

The investigation was carried out by an arrangement similar to that described by Dadieu-Kohlrausch.(7) A quartz mercury vapour lamp working at 100 volts, 2.7–3.2 amperes, D.C., was used as the source of illumination.

The spectrum of the scattered light was taken by means of an Adam Hilger glass prism spectrograph. The photographic plates APEM, 5000 H. and D. were used. The dispersion obtained was 15 Å. per m.m. at 4050 Å. and 40 Å. per m.m. at 5040 Å, which was the range over which the experiments were conducted. The exposure was required from four to fourteen hours for different substances. The spectra were taken several times for each sample, least the accidental errors should occur, and the repurifications were carried out every time.

The wave lengths were measured by means of the micrometer. The iron comparison spectrum was recorded on each plate. But, as most of the Ramen lines were so weak and diffuse, that we could not measure it without the error of ±0.5 Å., especially, as to the very weak lines, such as those having 0,½ and 1 in their relative intensities, we could scarcely measure them with the assistance of the fine ink-marks which were corrected by the "Mess-Lupe" before measuring under the micrometer.

The intensities were visually estimated, taking that of the strongest line as 10, and that was scarcely visible in the suitable direction of light as 0.

For recording the state of the line, the following abbreviations were used:— *s*: sharp, *d*: diffuse, *b*: broad, *bb*: very broad, *dd*: very diffuse, *ss*: very sharp, *dv*: diffuse towards the violet, *dr*: diffuse towards the red.

Apparatus. The Raman tube containing the liquid is about 35 cm. in length and 1.5 cm. in diameter. About three fourths of its length is enveloped by a cooler through which the cooling water passes continuously to keep the temperature constant during the experiment.

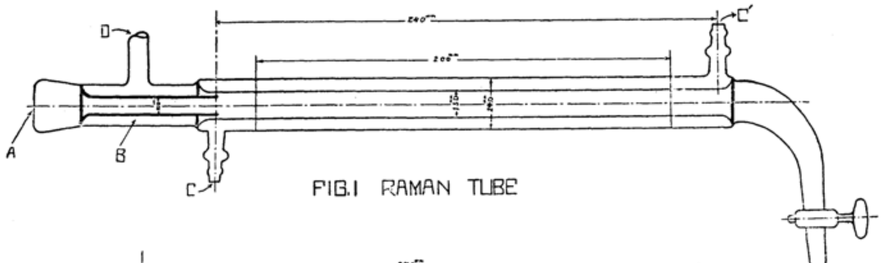


FIG. 1 RAMAN TUBE

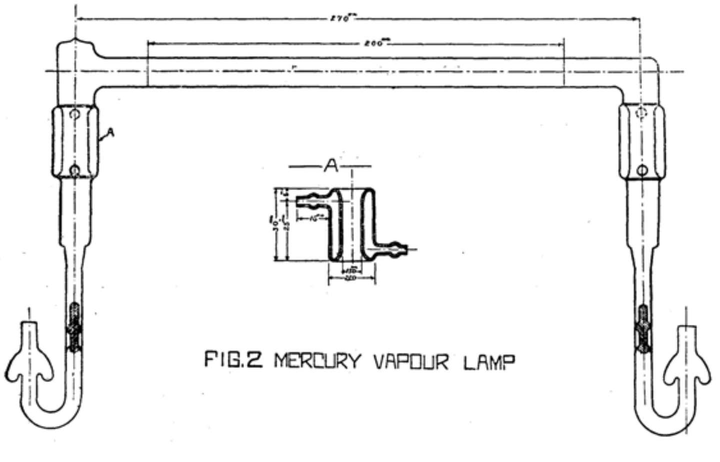


FIG. 2 MERCURY VAPOUR LAMP

In Fig. 1, A is a flat glass plate perpendicular to the beam of light. The part, B, of the tube is made of the brown glass to prevent the light scattered from the outside. A side tube, D, is provided for pouring the sample in and inserting the thermometer for measuring the temperature of the sample. For small quantity of sample, the tube of about 10 c.c. in capacity, made in our laboratory, was used.

The two electrodes of the quartz mercury vapour lamp are cooled by the water jackets fixed to the two sides to protect them from superheating (Fig. 2).

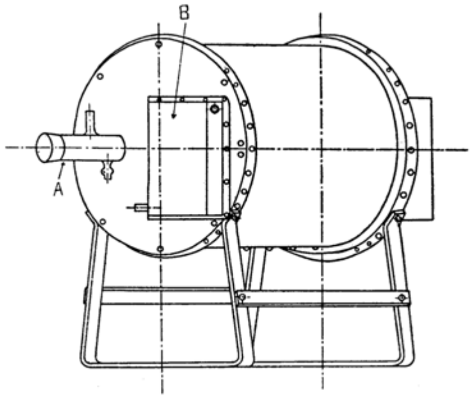


FIG.3 EXTERNAL APPEARANCE

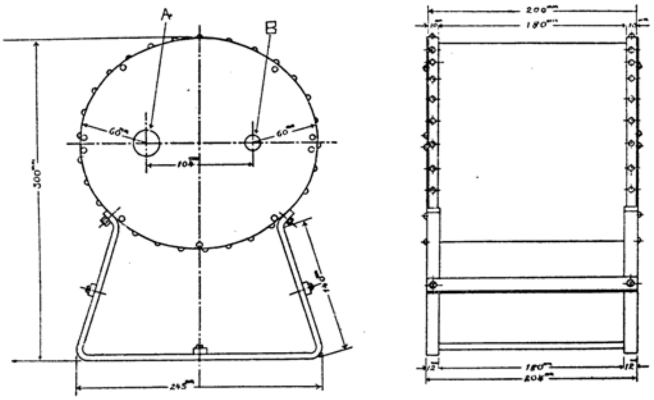


FIG.4 SECTION OF THE APPARATUS

The tube of the light-source and the Raman tube are so enclosed in an elliptical cylinder that the axes of the tube and that of the body of the light fall at the two foci. The cylinder is made of metal which has been well polished and plated with nickel. These tubes and the wall of cylinder are in parallel to each other (Fig. 3).

The quartz mercury vapour lamp and the set of the Raman tube, constructed by Prof. Asada of the Osaka Imp. Univ., were obtained from the Central Trading and M.F.G. Co. Ltd., Osaka.

Preparation and Purification of the Substances. All the alkyl esters(8) of benzoic acid were made from the dehydrated alcohols and the acid by the action of conc. sulphuric acid or dry hydrochloric acid gas.

Cyclohexyl benzoate(9) was prepared by warming the mixture of cyclohexanol and benzoyl chloride in presence of pyridine.

o-Kresyl benzoate(10) was prepared from *o*-kresol and benzoyl chloride. Acetate of phenol(11) and *o*-kresol were synthesized from acetic acid anhydride and phenol and *o*-kresol respectively, in presence of anhydrous sodium acetate.

Penol ester(12) of butyric acid was prepared from butyric acid chloride and phenol.

All the samples used were purified by repeated vacuum distillation (10-6 mm. Hg.), after dehydrated over calcium chloride. For testing the purities of the samples, the physical constants, namely, density (D^{15}) at 15°C., refractive index (n^{15}) at 15°C. and boiling point were measured.

The Experiment. For the sake of simplicity, the number of the substance observed (the 1st column), the name of the substances (the 2nd), the number of the table (Tb. No.) (the 3rd), the numbers of the Raman lines (n) (the 4th), the number of the plate (pl. No.) (the 5th), and the conditions under which the spectra were taken, viz., breadth of the slit (St.) (the 6th), electric current (C) working the mercury vapour lamp (the 7th), temperature (T) of the sample during the experiment (the 8th) and the time of exposure (t) (the 9th), have been tabulated in the following:

Table A.

No.	Substance	Tb. No.	n	Pl. No.	St 10^{-2}mm.	C (amp)	T° (C)	t (hours)
1	Methyl benzoate	I	40	1	7	2.7	24	7
				10	6	,,	23	9
				14	6	,,	22	13
2	Ethyl benzoate	II	37	2	6	2.7	23	8
				11	6	,,	22	4
				15	8	2.8	22	13
3	*n*-Propyl benzoate	III	39	3	7	2.8	24	8
				4	6	,,	23	12
				16	5	3.0	21	13
4	*n*-Butyl benzoate	IV	42	8	7	2.8	23	8
				17	6	,,	21	13
5	*i*-Propyl benzoate	V	39	5	7	2.7	23	9
				6	7	3.2	24	10
				12	6	2.8	21	10
				13	5	2.8	21	14
6	*i*-Butyl benzoate	VI	44	7	7	2.8	23	12
				18	6	2.8	21	14
7	*i*-Amyl benzoate	VII	40	9	6	3.2	23	14
				19	7	2.8	21	13
8	Cyclohexyl benzoate	VIII	29	20	8	2.8	20	8
				21	7	3.2	20	13
				22	6	2.8	20	13
9	*o*-Kresyl benzoate	IX	37	76	7	3.2	19	8
				77	6	3.2	19	12
10	*n*-Octyl	X	30	23	6	3.2	20	10
				26	6	3.2	20	14
11	Benzoyl chloride	XI	26	24	6	3.2	20	4
				25	6	3.2	20	3
12	Acetyl phenol	XII	29	82	6	3.2	20	9
13	Phenyl butyrate	XIII	29	91	6	3.2	20	12
14	Acetyl *o*-kresol	XIV	33	87	8	3.2	20	10

The Notations of the unmodified mercury lines are shown below:—

Table B.

Notation	Wave length (in A)	Wave number (in cm^{-1})
q	3650	27388
p	3655	27353
o	3663	27293
k	4047	24705
i	4078	24518
g	4339	23039
f	4348	22995
e	4358	22938

The physical constants of the substances studied are tabulated:

Table C.

No.	Substance	b.p. (in reduced pressure mm. (Hg))	b.p. (at 1 atm.)	D^{15}	n^{15}
1	Methyl benzoate	77°/ 8	199°	1.0929	1.5177
2	Ethyl benzoate	82 /10	212	1.0510	1.5068
3	*n*-Propyl benzoate	105 /10	231	1.0248	1.5013
4	*n*-Butyl benzoate	108 /10	249	1.0101	1.4989
5	*i*-Propyl benzoate	92 /10	219	1.0150	1.4962
6	*i*-Butyl benzoate	109 / 8	242	1.0026	1.4956
7	*i*-Amyl benzoate	122 / 8		0.9923	1.4950
8	Cyclo-hexyl benzoate	144 / 8		1.0567	1.5223
9	*o*-Kresyl benzoate	153 /10		1.1170	1.5719
10	*n*-Octyl benzoate	164 / 7		0.9658	1.4913
11	Benzoyl chloride	—	197	1.2187	1.5579
12	Phenyl acetate	83 /10		1.0831	1.5047
13	Phenyl butyrate	85 / 8		1.0382	—
14	*o*-Kresyl acetate	89 /10		1.0533	1.5003

Ten kinds of esters of benzoic acid, benzoyl chloride, phenyl acetate, butyrate and *o*-kresyl acetate have been studied. Among them, methyl, ethyl benzoate and benzoyl chloride have been studied by Dadieu-Kohlrauchs(13). Their results are cited for comparison.

Table D.

Methyl benzoate		Ethyl benzoate		Benzoyl chloride	
D. K.	Ours	D. K.	Ours	D. K.	Ours
212(3)	211(3)	184(4)	191(4)	161(3*b*)	158(4*d*)
353(3)	351(3)	334(4)	333(3)	314(3)	314(3)
613(3)	612(3)	614(4)	615(5)	412(1)	414(2*d*)
670(1*d*)	670(1*d*)	670(1)	668(1*d*)	505(3)	505(4)
812(3)	814(4)	775(1)	780($^1/_2$)	615(3)	615(4)
1000(7)	999(8)	1000(10)	1000(8)	670(3)	669(5)
1023(1)	1023(2)	1029(2)	1026(2)	771($^1/_2$)	769($^1/_2$*b*, *d*)
1082(1)	1078(2)	1106(3)	1107(2)	1000(6)	998(4)
1110(2)	1114(2)	(1162)(2)	1164(4*d*)	1028(2)	1027(4)
1160(1)	1161(2*b*)	1276(5)	1268(8)	1168(3*b*)	1166(6)
1278(4)	1268(4)	1310(1)	1305($^1/_2$)	1206(3*b*)	1200(8)
(1302)(1)	(1310)($^1/_2$)	1368(1*b*) 1394($^1/_2$)	(1366)(0) (1395)($^1/_2$*d*)		
1452(1*b*)	1454(2*d*)	1454(2*b*)	1451(2*d*)		
1602(10)	1601(10)	1602(10)	1600(10)	1592(6)	1591(10)
1723(8)	1720(8)	1720(9) 2929(5*b*)	1719(8) 2930(2)	1774(4)	1776(6*b*, *d*)
2950(4)	2948(3*d*)	2981(3)	2980(2*d*)		
3070(5)	3069(8)	3072(6*b*)	3072(8)	3067(4*b*)	3067(7*b*)

Table I.

Methyl benzoate, $C_6H_5.CO.O.CH_3$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0 - \Delta\nu$
1	24437	0(*d*)	*q*-2951	11	23544	2(*b*)	*k*-1161
2	24405	0(*d*)	*p*-2948	12	23517	0(*d*)	*i*- 999
3	24319	$^1/_2$(*d*)	*q*-3069	13	23438	5	*k*-1267
4	24285	2	*p*-3068	14	23395	$^1/_2$(*d*)	(*k*-1310)
5	24220	2(*b*, *d*)	*o*-3073	15	23254	$^1/_2$(*d*)	*k*-1451
6	24093	3	*k*- 612	16	23148	1	*e*+210 ?
7	23891	3	*k*- 814	17	23106	6	*k*-1599
8	23705	6	*k*-1000	18	22797	1(*d*)	*i*-1719
9	23680	2	*k*-1025	19	22727	3	*e*- 211
10	23599	2(*d*)	*k*-1106	20	22587	3	*e*- 612

Table I.—(*Concluded*)

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
21	22326	3	*e*- 612	31	21669	8(*d*)	*e*-1269
22	22268	1	*e*- 670	32	21638	8(*d*)	*k*-3067
23	22124	4	*e*- 814	33	21570	0	*i*-2947
24	21971	$^1/_2$	*f*-1024	34	21489	2(*b*)	*e*-1449
25	21940	8(*s*)	*e*- 998	35	21446	2	*i*-3070
26	21917	2(*s*)	*e*-1021	36	21393	$^1/_2$	*f*-1602
27	21860	2	*e*-1078	37	21335	10(*s*)	*e*-1602
28	21825	2	*e*-1113	38	21218	8	*e*-1720
29	21777	2	*e*-1161	39	19991	3	*e*-2947
30	21757	3(*d*)	*k*-2948	40	19868	5	*e*-3070

$\overline{\Delta\nu}$: 211 (3); 351 (3); 612 (3); 670 (1); 814 (4); 999 (8); 1023 (2); 1078 (2); 1108 (2); 1161 (2*b*); 1268 (8); 1310 (½*d*); 1450 (2*d*); 1601 (10); 1720 (8); 2948 (3*d*); 3069 (8).

Table II.

Ethyl benzoate $C_6H_5.CO.O.C_2H_5$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	24422	0	*p*-2931	16	22751	4(*b*)	*k*- 187
2	24377	0	*p*-2976	17	22605	3	*e*- 333
3	24220	$^1/_2$	*o*-3073	18	22323	5	*e*- 615(*f*- 672)
4	24090	2	*k*- 615	19	22270	1(*d*)	*e*- 668
5	23861	2	*k*- 844	20	22158	$^1/_2$(*d*)	*e*- 780
6	23705	4	*k*-1000	21	22091	5	*e*- 847
7	23680	$^1/_2$	*k*-1025(*i*-836)	22	21999	8	*e*- 999
8	23599	1(*d*)	*k*-1106	23	21911	2	*e*-1027
9	23543	2(*d*)	*k*-1162	24	21830	3(*d*)	*e*-1108
10	23515	$^1/_2$	*i*-1001	25	21774	4(*d*)	*e*-1164(*k*-2931)
11	23438	3	*k*-1267	26	21726	2(*d*)	*k*-2979(*f*-1269)
12	23399	$^1/_2$	*k*-1305	27	21675	8	*e*-1268
13	23339	$^1/_2$	*k*-1366	28	21635	8	*k*-3070(*e*-1303)
14	23252	$^1/_2$(*d*)	*k*-1453(*i*-1264)	29	21585	1(*d*)	*i*-2931(*e*-1353)
15	23106	5	*k*-1599	30	21538	$^1/_2$(*d*)	*e*-1395(*i*-2978)

Table II.—(*Concluded*)

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
31	21489	2(*d*)	*e*-1449	36	19957	1	*e*-2981
32	21446	1	*i*-3070	37	19866	5	*e*-3072
33	21338	10	*e*-1600				
34	21219	8	*e*-1719				
35	20010	2	*e*-2928				

$\overline{\Delta\nu}$: 187 (4); 333 (3); 615 (5); 668 (1*d*); 780 (½*d*); 846 (5); 1000 (8); 1026 (2); 1107 (3*d*); 1163 (4*d*); 1268 (8); 1305 (½); (1366) (½); (1395) (½*d*); 1451 (2*d*); 1600 (10); 1719 (8); 2930 (2); 2980 (2*d*); 3071 (8).

Table III.

n-Propyl benzoate $C_6H_5.CO.O.C_3H_7$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	24423	$^1/_2$(*b*)	*p*-2930	21	22127	3(*d*)	*e*- 811
2	24318	$^1/_2$(*d*)	*q*-3070(*o*-2975)	22	22093	0	*e*- 845
3	24283	$^1/_2$(*b*)	*p*-3070	23	22028	3(*d*)	*e*- 910
4	24221	1(*b*)	*o*-3072	24	21939	8	*e*- 999
5	24086	3	*k*- 619	25	21917	2	*e*-1021
6	24036	$^1/_2$(*d*)	*k*- 669	26	21823	4(*d*)	*e*-1115(*k*-2882)
7	23895	2(*d*)	*k*- 810(*i*- 619)	27	21772	5(*d*)	*e*-1166
8	23707	6	*k*- 998(*i*- 809)	28	21726	3	*k*-2979(*f*-1269)
9	23684	2(*d*)	*k*-1021	29	21669	8	*e*-1269
10	23599	2(*b, d*)	*k*-1106(*i*- 917)	30	21637	8	*k*-3068(*e*-1301)
11	23542	2(*bb*)	*k*-1163	31	21535	2	*i*-2981
12	23435	4	*k*-1270	32	21487	3(*b*)	*e*-1451
13	23402	1(*d*)	*k*-1303(*i*-1114)	33	21441	2(*d*)	*i*-3075
14	23251	3(*d*)	*k*-1454(*i*-1265)	34	21339	10	*e*-1599
15	23103	5	*k*-1602	35	21217	8	*e*-1721
16	22749	0(*d*)	*e*- 189	36	20058	3(*d*)	*e*-2880(Hg)
17	22631	1(*d*)	*e*- 307	37	20024	3(*b*)	*e*-2914(*f*-2972)
18	22600	0(*d*)	*e*- 338	38	19959	3(*b*)	*e*-2972
19	22321	4	*e*- 617	39	19869	5	*e*-3069
20	22271	1(*d*)	*e*- 667				

$\overline{\Delta\nu}$: 189 (0*d*)?; 307 (1*d*); 618 (4); 668 (1*d*); 811 (3*b*); 845 (0); 910 (1*d*); 999 (8); 1021 (2); 1110 (4*d*); 1165 (5*d*); 1270 (8); 1303 (1*d*); 1452 (3*b*); 1601 (10); 1721 (8); (2881) (3*b*); (2914) (2*b*); 2979 (3*d*); 3070 (8).

Table IV.

n-Butyl benzoate $C_6H_5.CO.O.(CH_2)_3.CH_3$.

No.	ν in cm.⁻¹	*I*	ν₀—Δν	No.	ν in cm.⁻¹	*I*	ν₀—Δν
1	24318	½	*q*-3070	26	21939	10	*e*- 999
2	24284	½ *d*)	*p*-3069	27	21915	3	*e*-1023
3	24223	½	*o*-3070	28	21857 ?	0(*d*)	*e*-1081
4	24086	2(*b*)	*k*- 619	29	21817	5(*d*)	*e*-1121
5	24034	½(*b*)	*k*- 671	30	21779	6(*bb*, *dd*	*e*-1159
6	23896	½	*k*- 809	31	21745	2(*d*)	*k*-2960
7	23861	½(*d*)	*k*- 844	32	21666	7	*e*-1272
8	23708	6	*k*- 997	33	21637	8(*b*, *d*)	*k*-3068(*e*-1301)
9	23679	2	*k*-1026	34	21487	5(*b*)	*e*-1451
10	23592	1	*k*-1113	35	21543	3	*e*-1395(*f*-1452)
11	23537	2(*bb*)	*k*-1168	36	21444	3(*d*)	*i*-3072
12	23436	4	*k*-1269	37	21340	10	*e*-1598
13	23399	2	*k*-1306(*i*-1117)	38	21216	8	*e*-1722
14	23314	1(*d*)	*k*-1391	39	20070	2(*d*)	*e*-2868
15	23244	3(*b*, *d*)	*k*-1461(*i*-1272)	40	20044	2(*b*, *d*)	*e*-2894(*f*-2951)
16	23105	8	*k*-1600	41	19980	2(*b*, *d*)	*e*-2958
17	22796	2(*b*)	*i*-1720	42	19868	5	*e*-3070
18	22736	2(*b*, *d*)	*e*- 202				
19	22640	2(*d*) ?	*e*- 298				
20	22600 ?	½(*b*)	*e*- 338				
21	22320	5	*e*- 618(*f*- 675)				
22	22268	3	*e*- 670				
23	22126	2(*d*)	*e*- 812				
24	22097	3(*b*)	*e*- 841				
25	21981	1	*e*- 957				

$\overline{\Delta\nu}$: 202 (2*b*, *d*); 298 (2*d*); 338 (½*d*)?; 619 (5); 670 (3); 810 (2*d*); 843 (3*b*); 957 (1); 998 (10); 1025 (2); (1081) (0)?; 1117 (5); 1164 (6*d*); 1271 (7*d*); 1304 (1*d*); 1393 (3*b*, *d*); 1455 (5*d*); 1599 (10); 1722 (8); 2868 (2); 2894 (2*b*, *d*); 2959 (2*b*, *d*); 3070 (8).

Table V.

Iso-propyl benzoate $C_6H_5.CO.O.CH(CH_3)_2$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	24422	$^1/_2$(*b*)	*p*-2931 (*k*-283, *o*-2871)	21	22270	3	*e*- 668
2	24319	$^1/_2$	*q*-3069 (*k*-386, *o*-2974)	22	22092	5	*e*- 846
3	24287	1	*p*-3068	23	22021	3(*d*)	*e*- 917
4	24222	$^1/_2$	*o*-3071	24	21940	10	*e*- 998
5	24093	1	*k*- 612	25	21916	2	*e*-1022
6	24039	0	*k*- 666	26	21824	3(*b*, *d*)	*e*-1114(*f*-1171)
7	23861	2	*k*- 844	27	21775	5(*b*)	*e*-1163(*k*-2930)
8	23792	$^1/_2$(*d*)	*k*- 913	28	21726	4	*k*-2979(*f*-1269)
9	23707	6	*k*- 998	29	21670	8	*e*-1268
10	23683	1	*k*-1022	30	21639	8(*d*)	*k*-3066(*f*-1356)
11	23598	2(*b*)	*k*-1107(*i*- 918)	31	21588	2	*e*-1350
12	23544	2(*b*)	*k*-1161	32	21489	3	*e*-1449
13	23436	5	*k*-1269	33	21447	2	*i*-3069
14	23355	2	*k*-1350(*i*-1161)	34	21341	10	*e*-1597
15	23251	3(*b*)	*k*-1454(*i*-1265)	35	21222	8	*e*-1716
16	23106	6	*k*-1599	36	20066	1	*e*-2872(*f*-2929)
17	22755	5	*e*- 183	37	20008	3	*e*-2930(*f*-2987)
18	22654	3(*b*)	*e*- 284	38	19960	2	*e*-2978
19	22560	$^1/_2$	*e*- 378	39	19871	4	*e*-3067
20	22325	4	*e*- 613(*f*- 670)				

$\overline{\Delta\nu}$: 183 (4); 284 (3*b*); 378 (½); 613 (4); 668 (3); 846 (5); 916 (3*d*); 998 (8); 1022 (2); 1110 (3*b*); 1162 (5*b*); 1269 (8); 1350 (2); 1451 (4*d*); 1598 (10); 1716 (8); (2872) (1); 2930 (3); 2979 (2); 3068 (8).

Table VI.

Iso-butyl benzoate $C_6H_5.CO.O.CH_2.CH(CH_3)_2$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	24419 ?	0	*q*-2969	6	24032	$^1/_2$(*d*)	*k*- 673
2	24319	$^1/_2$	*q*-3069	7	23902	1(*d*)	*k*- 803
3	24282	$^1/_2$	*p*-3071	8	23840	$^1/_2$(*d*)	*k*- 865(*i*-676)
4	24220	$^1/_2$	*o*-3073	9	23705	5	*k*-1000
5	24089	1	*k*- 616	10	23679	2	*k*-1026

Table VI.—(*Concluded*)

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
11	23602	1(*d*)	k-1103	31	21820	5(*bb*)	*e*-1116(*f*-1173, *k*-2883)
12	23537	2(*b*, *d*)	*k*-1168	32	21775	6(*bb*)	*e*-1163
13	23436	4(*d*)	*k*-1269	33	21732	5(*bb*)	*k*-2973(*f*-1263)
14	23392	$^1/_2$	*k*-1313	34	21670	6	*e*-1268
15	23313	$^1/_2$(*d*)	*k*-1392	35	21639	8	*k*-3066(*f*-1356)
16	23247	3(*d*)	*k*-1458(*i*-1269)	36	21589	1	*e*-1349
17	23107	6	*k*-1598	37	21553	2(*b*)	*e*-1385(*i*-2963)
18	22797	3(*d*)	*i*-1719	38	21486	4(*b*)	*e*-1452
19	22770	2(*b*, *d*)	*e*- 168	39	21445	2	*i*-3071
20	22676	2(*b*)	*e*- 262	40	21333	10	*e*-1605
21	22560	1(*b*)	*e*- 378	41	21220	8	*e*-1718
22	22324	4	*e*- 614(*f*- 671)	42	20065	3(*b*)	*e*-2873
23	22268	2(*d*)	*e*- 670	43	19969	3(*b*)	*e*-2969
24	22161	$^1/_2$	*e*- 777	44	19869	4	*e*-3069
25	22133	3(*b*)	*e*- 805				
26	22075	3(*b*)	*e*- 863				
27	22037	$^1/_2$	*e*- 901				
28	21979	1(*d*)	*e*- 959 ?				
29	21940	8	*e*- 998				
30	21914	2	*e*-1024				

$\overline{\Delta\nu}$: 168 (2*b*, *d*); 262 (2*b*); 378 (1*b*); 615 (4); 671 (2*d*); 804 (3*b*); 863 (3*b*); 901 (½); 959 (1*d*) ?; 999 (8); 1024 (2); 1110 (1*d*); (1165) (5*b*); 1269 (8); (1313) (1*d*); 1349 (1); 1392 (½*d*); 1455 (4*b*); 1601 (10); 1718 (8); 2873 (3*b*); 2968 (3*b*); 3068 (8).

Table VII.

Iso-amyl benzoate $C_6H_5.CO.O.CH_2.CH_2.CH(CH_3)_2$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	24280	$^1/_2$	*p*-3073	6	23833	1(*b*)	*k*- 862(*i*-678)
2	24222	$^1/_2$(*d*)	*o*-3073	7	24707	5	*k*- 998
3	24087	2	*k*- 618	8	23677	1	*k*-1028(*i*-839)
4	24029	0	*k*- 676	9	23600	1(*d*)	*k*-1105(*i*-916)
5	23898	1(*b*)	*k*- 807(*i*-618)	10	23537	2(*b*, *d*)	*k*-1168

Table VII.—(*Concluded*)

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
11	23435	4	*k*-1270	26	21938	10	*e*-1000
12	23399	1	*k*-1306(*i*-1117)	27	21915	2(*s*)	*e*-1023
13	23246	3(*d*)	*k*-1459(*i*-1270)	28	21835	4(*b*)	*e*-1103(*f*-1160)
14	23106	5	*k*-1599	29	21776	5(*d*)	*e*-1162
15	22791	2(*d*)	*i*-1725	30	21734	4(*d*)	*k*-2971
16	22760 ?	0(*d*)	*e*- 178	31	21666	8	*e*-1272
17	22656 ?	0	*e*- 282	32	21632	8(*d*)	*k*-3073(*e*-1306)
18	22582 ?	$^1/_2$	*e*- 356	33	21541	3(*d*)	*f*-1454(*i*-2975)
19	22318	4	*e*- 620(*f*- 672)	34	21479	5(*d*)	*e*-1459
20	22265	2(*b*)	*e*- 673	35	21445	1(*d*)	*i*-3071
21	22157	2(*b*)	*e*- 781(*f*- 838)	36	21336	10	*e*-1602
22	22102	3(*b, d*)	*e*- 836	37	21216	8	*e*-1722
23	22078	3(*b, d*)	*e*- 860	38	20058	3	*e*-2880
24	22025	$^1/_2$(*d*)	*e*- 913	39	19968	3(*b*)	*e*-2970
25	21983	1	*e*- 955	40	19863	4	*e*-3075

$\overline{\Delta\nu}$: 178 (½)?; 282 (0)?; 356 (½)?; 619 (4); 673 (2*b*); (781) (2*b*)?; 836 (3*b, d*); 861 (3*b, d*); 915 (½*d*); (955) (1*d*); 999 (8); 1026 (2); 1104 (4*b*); 1165 (5*b*); 1271 (8); 1306 (1); 1459 (5*d*); 1601 (10); 1722 (8); (2880) (3); 2971 (8); 3073 (8).

Table VIII.

Cyclo-hexyl benzoate $C_6H_5.CO.O.C_6H_{11}$.

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
1	24323	0	*q*-3065	11	22712	$^1/_2$(*d*)	*e*- 226
2	23859	1	*k*- 846	12	22319	2(*d*)	*e*- 619
3	23701	5	*k*-1004	13	22268	$^1/_2$	*e*- 670
4	23676	1	*k*-1029(*i*- 846)	14	22094	1	*e*- 844
5	23541	1(*d*)	*k*-1164	15	21937	7	*e*-1001
6	23436	3(*b, d*)	*k*-1269	16	21910	2	*e*-1028
7	23344	$^1/_2$	*k*-1361(*i*-1172)	17	21843	4	*k*-2862
8	23260	$^1/_2$(*b, d*)	*k*-1445	18	21768	5(*b, d*)	*e*-1170(*k*-2937)
9	23096	5	*k*-1609	19	21670	5(*b, d*)	*e*-1268
10	22760	2(*d*)	*e*- 178	20	21629	5	*k*-3076

Table VIII.—(*Concluded*)

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
21	21585	1(*d*)	*e*-1353(*i*-2931)	26	20148	2	*e*-2790(*f*-2848)
22	21488	1	*e*-1450	27	20075	3(*d*)	*e*-2863
23	21442	½	*i*-3074	28	19997	3(*b*, *d*)	*e*-2941
24	21332	8	*e*-1606	29	19868	3	*e*-3070
25	21216	6	*e*-1722				

$\overline{\Delta\nu}$: 178 (2*d*); 226 (½*d*); 619 (2); 670 (½); 845 (1); 1003 (7); 1028 (2); 1168 (5*d*); 1269 (5*b*, *d*); 1357 (1*d*); 1450 (2); 1607 (8); 1722 (6); (2790) (2); 2863 (4); 2937 (5*b*, *d*); 3073 (5).

Table IX.

o-Kresyl benzoate $C_6H_5.CO.O.C_6H_4.CH_3$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	23710	1	*k*- 995	21	21942	8	*e*- 996
2	23546	½(*d*)	*k*-1159	22	21920	2(*d*)	*e*-1018
3	23495	3	*k*-1210	23	21902	4	*e*-1036
4	23442	3(*d*)	*k*-1263	24	21830	½(*d*)	*e*-1108
5	23257	½(*d*)	*k*-1448	25	21788	6	*k*-2917
6	23107	5	*k*-1598	26	21772	5	*e*-1160
7	22776	4(*b*, *d*)	*e*- 162	27	21720	7	*e*-1218
8	22741	1(*d*)	*e*- 196	28	21679	6(*d*)	*e*-1259
9	22667	2(*d*)	*e*- 271	29	21641	6(*b*, *d*)	*k*-3064
10	22620	1(*b*, *d*)	*e*- 318	30	21561	2(*b*, *d*)	*e*-1377
11	22491	0(*b*)	*e*- 447 ?	31	21491	2	*k*-1447
12	22393	3(*d*)	*e*- 545	32	21452	4	*i*-3064
13	22352	2	*e*- 586	33	21391	½	*f*-1604
14	22322	5	*e*- 616	34	21343	10	*e*-1595
15	22265	3	*e*- 673	35	21208	8	*e*-1730
16	22235	4	*e*- 703	36	20022	2(*d*)	*e*-2916
17	22187	5(*b*, *d*)	*e*- 751	37	19874	6(*b*)	*e*-3064
18	22137	½	*f*- 858				
19	22095	4	*e*- 843				
20	22068	5	*e*- 870				

$\overline{\Delta\nu}$: 162 (4*b*, *d*); 196 (1*d*); 271 (2*d*); 318 (1*b*, *d*); (447) (0*b*)?; 545 (3*d*); 586 (2); 675 (3); 703 (4); 751 (5*b*, *d*); 843 (4); 870 (5); 996 (8); 1036 (4); 1108 (½*d*); 1160 (5); 1214 (7); 1261 (6*d*); (1377) (2*b*, *d*); 1447 (2); 1596 (10); 1730 (8); 2917 (6); 3064 (6*b*).

Table X.

n-Octyl benzoate $C_6H_5.CO.O.C_8H_{17}$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	23704	4	*k*-1001	16	22090 ?	½	*e*- 848
2	23680	½	*k*-1025	17	21938	7	*e*-1000
3	23632 ?	0	*k*-1073 ?	18	21918	1	*e*-1020
4	23603	½(*d*)	*k*-1102	19	21864	5(*d*)	*k*-2841(*e*-1074)
5	23542	0(*d*)	*k*-1163	20	21774	5(*d*)	*k*-2931(*e*-1164)
6	23515	½(*d*)	*i*-1001	21	21671	5(*d*)	*e*-1267
7	23437	3	*k*-1268	22	21638	6(*d*)	*k*-3067(*e*-1300)
8	23402 ?	0(*d*)	*k*-1303	23	21555	½(*dd*)	*f*-1440
9	23255	½(*b*)	*k*-1450	24	21484	2(*b*)	*e*-1444
10	23104	5	*k*-1601	25	21391	½	*f*-1604
11	22753	1(*b*, *d*)	*e*- 185	26	21340	8	*e*-1598
12	22674	1(*b*, *d*)	*e*- 264	27	21221	6(*d*)	*e*-1717
13	22318	4	*e*- 620	28	20097	1	*e*-2841
14	22264	1	*e*- 674	29	20012	1	*e*-2926
15	22140 ?	0	*f*- 855 ?	30	19869	1	*e*-3069

$\overline{\Delta\nu}$: 185 (1*b*, *d*) ; 264 (1*b*, *d*) ?; 620 (4) ; 674 (1) ; 848 (½) ?; 1000 (7) ; 1023 (1) ; (1074) (5*d*) ; 1102 (½*d*) ; 1164 (5*d*) ; 1268 (5*d*) ; 1303 (0*b*) ; 1450 (2*b*) ; 1600 (8) ; 1717 (6*d*) ; 2841 B (2928) (5*b*) ; 3068 (6*b*).

Table XI.

Benzoyl chloride $C_6H_5.CO.Cl$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	23937 ?	0	*k*- 768	16	21939	4	*e*- 999
2	23708	4	*k*- 997	17	21910	4	*e*-1028
3	23678	1	*k*-1027	18	21773	6	*e*-1165
4	23539	3	*k*-1166	19	21740	6	*e*-1198
5	23503	3	*k*-1202	20	21639	7(*b*)	*k*-3066
6	23113	8	*k*-1592	21	21447	1	*i*-3069
7	22780	4(*d*)	*e*- 158	22	21394	½	*f*-1601
8	22688	½(*d*)	*f*- 307	23	21349	10	*e*-1589
9	22624	4	*e*- 314	24	21211	4(*b*, *d*)	*f*-1784
10	22524	3(*d*)	*e*- 414	25	21170	6(*b*, *d*)	*e*-1868
11	22433	4	*e*- 505	26	19871	3	*e*-3067
12	22323	4	*e*- 615				
13	22271	5	*e*- 667				
14	22169	½(*b*, *d*)	*e*- 769				
15	21969	0	*f*-1026				

$\overline{\Delta\nu}$: 158 (4*d*) ; 314 (2*d*) ; 414 (2*d*) ; 505 (4) ; 615 (4) ; 669 (5) ; 769 (½*b*, *d*) ; 998 (4) ; 1027 (4) ; 1166 (6) ; 1200 (8) ; 1591 (10) ; 1776 (6*b*, *d*) ; 3067 (7*b*).

Table XII.

Phenyl acetate $C_6H_5.O.OC.CH_3$.

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
1	24053	½	*k*- 652	16	22048 ?	½(*b*, *d*)	*e*- 890 ?
2	23703	5	*k*-1002	17	21938	8	*e*-1000
3	23687	0 ?	*k*-1018	18	21920	½	*e*-1018
4	23511	4	*k*-1194	19	21860 ?	½(*b*, *d*)	*e*-1078 ?
5	23214	0(*d*)	*k*-1491	20	21779	7(*b*, *d*)	*k*-2926(*e*-1159)
6	23116	5	*k*-1589	21	21746	4(*b*, *d*)	*e*-1192
7	22816 ?	3(*b*, *d*)	*e*- 122	22	21636	8(*b*)	*k*-3069
8	22676	5	*e*- 262	23	21581	0(*d*)	*e*-1358(*i*-1358)
9	22602	5	*e*- 336	24	21517 ?	½	*f*-1488
10	22413	4	*e*- 525	25	21451	2(*d*)	*e*-1487(*i*-3065)
11	22326	4	*e*- 612	26	21347	5	*e*-1591
12	22277	3	*e*- 661	27	21163	2(*d*)	*e*-1760
13	22243	½	*f*- 752	28	20008	3	*e*-2930
14	22192	5	*e*- 746(*f*-803)	29	19872	3(*b*, *d*)	*e*-3066
15	22128	5	*e*- 810				

$\overline{\Delta\nu}$: (122) (3,*d*) ?; 262 (5) ; 336 (5) ; 525 (4) ; 612 (4) ; 661 (3) ; (746) (5) ; 810 (5) ; (890) (½*b*, *d*) ; 1001 (8) ; 1018 (1) ; 1078 (½*b*, *d*) ?; (1159) (7*b*, *d*) ; 1193 (4*b*, *d*) : (1358) (½) ; 1487 (2*d*) ?; 1590 (5) ; 1760 (2*d*) ; 2928 (7*b*, *d*) ; 3068 (8*b*, *d*).

Table XIII.

Phenyl butyrate $C_6H_5.O.CO.C_3H_7$.

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$		$\nu_0-\Delta\nu$
1	23705	4	*k*-1000(*i*-811)	16	22332	3	*e*- 606
2	23608	2	*k*-1097	17	22259 ?	½(*d*) ?	*e*- 679
3	23559 ?	½ ?	*k*-1146	18	22128	3	*e*- 810
4	23513	1(*d*)	*k*-1192	19	22023 ?	½(*d*) ?	*e*- 915
5	23340 ?	½ ?	*k*-1365	20	21939	6	*e*- 999
6	23303	½	*i*-1213	21	21923	½	*e*-1015
7	23246	0(*d*)	*k*-1459	22	21847	1	*e*-1091
8	23188	4(*b*, *d*)	*e*- 250	23	21774	3(*d*)	*e*-1164(*k*-2931)
9	23128	2(*d*)	*e*- 191	24	21742	1(*d*)	*e*-1196(*k*-2963)
10	23070 ?	2(*d*)	*k*-1635	25	21644	6(*d*)	*k*-3061(*e*-1347)
11	22747	1	*e*- 191	26	21488	½	*e*-1450
12	22698	5(*d*)	*e*- 240	27	21345	3(*d*)	*e*-1593
13	22610 ?	0	*e*- 328	28	21185	2(*b*, *d*)	*e*-1753
14	22544	½	*e*- 398	29	19875	1	*e*-3063
15	22406	2	*e*- 532				

$\overline{\Delta\nu}$: 191 (1) ; 245 (5*d*) ; 328 (½) ?; 394 (1*d*) ; 532 (2) ; 606 (3) ; 679 (½*d*) ; 810 (3) ; 915 (½*d*?) ; 1000 (6) ; 1015 (½) ; 1094) (1) ; (1164) (3*d*) ; 1194 (1*d*) ; (1365) (½) ?; 1455 (½) ?; 1593 (3*d*) ; (1632) (2*d*) ?; 1753 (2*b*, *d*) ; (2931) (3*d*) ; (2963) (1*d*) ; 3062 (6*b*, *d*).

Table XIV.

o-Kresyl acetate $CH_3.CO.O.C_6H_4.CH_3$.

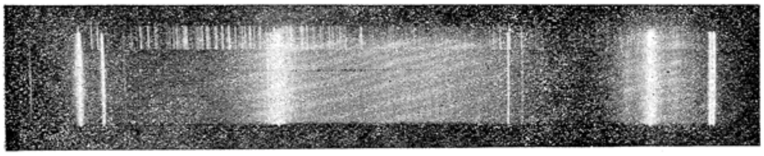
No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
1	23948	½	*k*- 757	21	21900	5	*e*-1038
2	23663	1(*b*)	*k*-1042	22	21814	½(*b*, *d*)	*e*-1124
3	23542 ?	0(*b*, *d*)	*k*-1163 ?	23	21773	8(*b*, *d*)	*e*-1165(*k*-2932)
4	23486	3(*b*)	*k*-1219	24	21720	7	*e*-1218
5	23133	2(*b*)	*k*-1572	25	21651	6(*d*)	*k*-3054
6	23095	1	*k*-1610	26	21562	1(*b*, *d*)	*e*-1376
7	23061	1	*e*- 123	27	21503	1(*d*)	*e*-1435
8	22822	5(*b*)	*e*- 116	28	21461	½(*d*)	*e*-1477
9	22741	4	*e*- 197	29	21363	1	*e*-1575
10	22637	3	*e*- 301	30	21330	4(*s*)	*e*-1608
11	22596	2(*d*)	*e*- 342	31	21174	2	*e*-1764
12	22414	2	*e*- 524	32	19996	2(*d*)	*e*-2942
13	22376	5	*e*- 562	33	19886	1	*e*-3052
14	22282	4	*e*- 656(*f*-713)				
15	22229	4	*e*- 709(*f*-766)				
16	22194	4	*e*- 744				
17	22166	4	*e*- 772				
18	22116	½(*d*)	*e*- 822				
19	22078	0(*d*)	*e*- 860				
20	22024	2(*d*)	*e*- 914				

$\overline{\Delta\nu}$: 120 (5*b*); 197(4); 301 (3); 342 (2*d*); 524 (2); 562 (5); 656 (4); 709 (4); 744 (4); 772 (4); (822) (½)?; (860) (0)?; 914 (2*d*); 1040 (5); (1124) (1*b*, *d*); 1165 (8); 1218 (7); 1376 (2*b*, *d*); 1435 (½*d*)?; 1477 (½*d*)?; 1574(1*b*); 1609 (4*s*); 1764 (2); 2942 (2*d*); 3053 (6*b*, *d*).

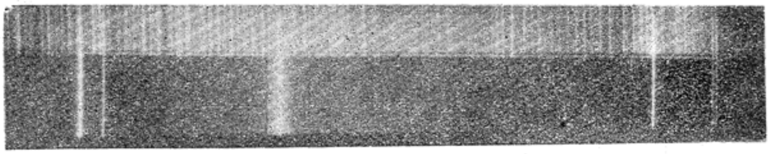
Discussion of the Results.

1. Frequencies Associated with the Benzene Ring. In all the benzoates studied, the frequencies of $\Delta\nu = 615$, 670, 1000, 1025, 1106, 1164, 1269, (1303), 1452, 1600, 1720 and 3070 cm.$^{-1}$ have been observed in good constance, of which those of $\Delta\nu = 615$, 1000, 1164, 1600 and 3070 cm.$^{-1}$ have been known to be associated with the vibrations of C-C, C: C and C-H linkage in the benzene ring. These frequencies are little

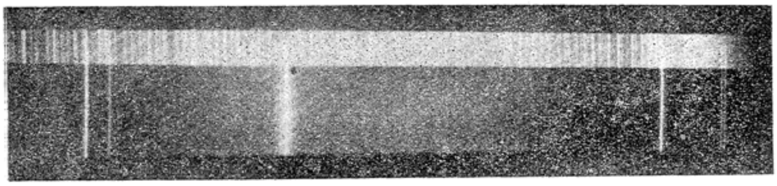
The mercury spectrum



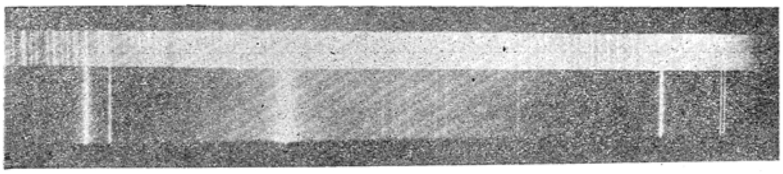
(1) Methyl Benzoate $C_6H_5 \cdot CO \cdot O \cdot CH_3$



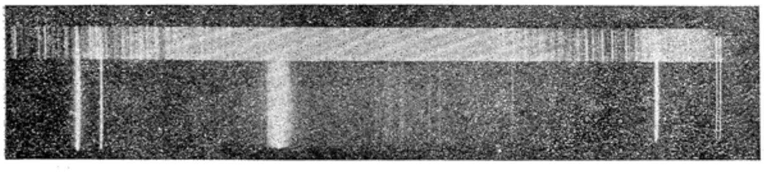
(2) Ethyl Benzoate $C_6H_5 \cdot CO \cdot O \cdot CH_2CH_3$



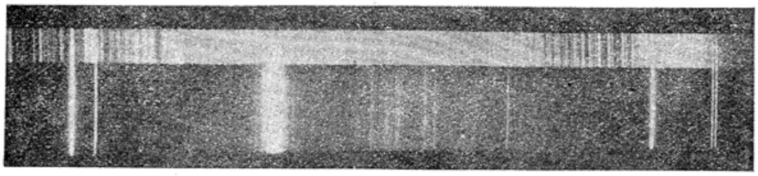
(3) n-Propyl Benzoate $C_6H_5 \cdot CO \cdot O \cdot CH_2CH_2CH_3$



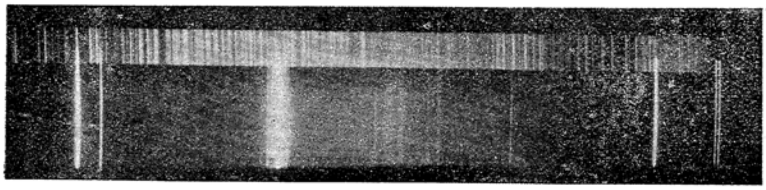
(4) n-Butyl Benzoate $C_6H_5 \cdot CO \cdot O \cdot CH_2CH_2CH_2CH_3$



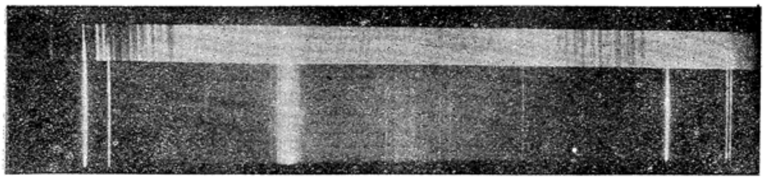
(5) *i*-Propyl Benzoate $C_6H_5CO \cdot O \cdot CH(CH_3)_2$



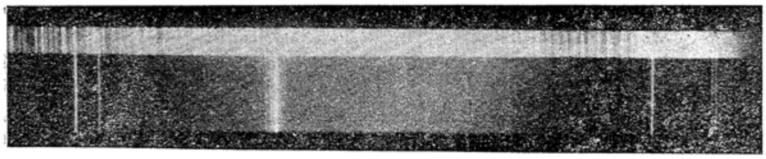
(6) *i*-Butyl Benzoate $C_6H_5CO \cdot O \cdot CH_2CH(CH_3)_2$



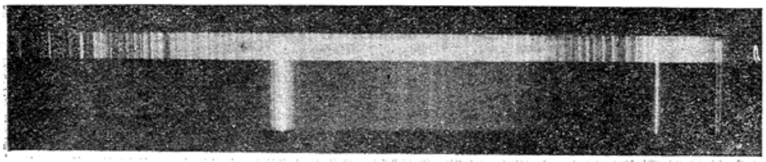
(7) *i*-Amyl Benzoate $C_6H_5CO \cdot O \cdot CH_2CH_2CH(CH_3)_2$



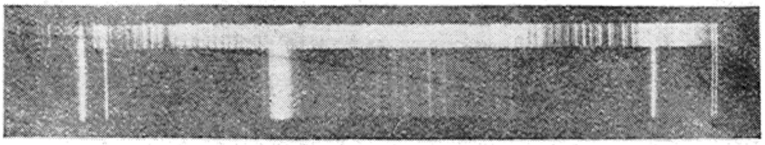
(8) Cyclo-hexyl Benzoate $C_6H_5CO \cdot O \cdot C_6H_{11}$



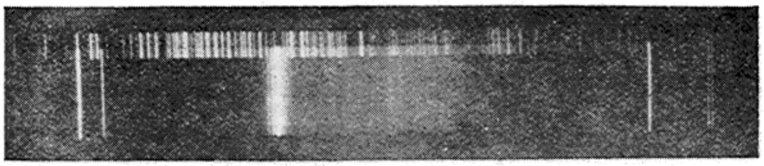
(9) *o*-Kresyl Benzoate $C_6H_5CO \cdot O \cdot C_6H_4 \cdot CH_3$



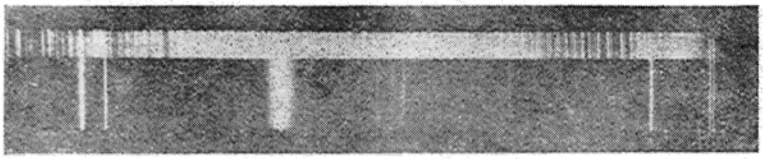
(10) *n*-Octyl Benzoate $C_6H_5CO·O·O_8H_{17}$



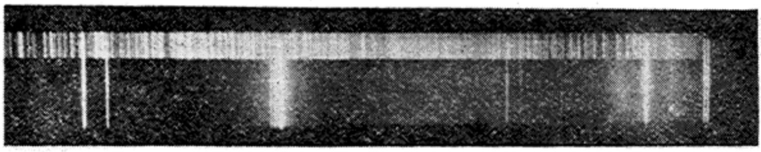
(11) Benzoyl Chloride $C_6H_5CO·Cl$



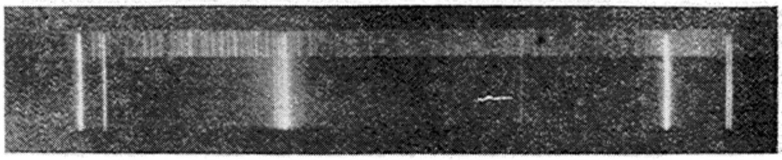
(12) Phenyl Acetate $CH_3CO·O·C_6H_5$



(13) Phenyl Butyrate $C_3H_7CO·O·C_6H_5$



(14) *o*-Kresyl Acetate $CH_3·CO·O·C_6H_4·CH_3$



influenced by increasing carbon atoms of the chain of alkyl radicals in the benzoates, and show little variation in phenyl acetate, butyrate and *o*-kresyl acetate. The absence of $\Delta\nu = 615$ cm.$^{-1}$ in *o*-kresyl acetate may be considered that the shift is taken place by the appearance of $\Delta\nu = 562$ cm.$^{-1}$, and that the latter shift seems to characterize the *o*-di-derivative, the former the monoderivative. The appearance of 586 and 616 cm.$^{-1}$ in *o*-kresyl benzoate, ($C_6H_5.CO.O.C_6H_4.CH_3$), gives the verification that the substance is a mono-derivative as well as di-derivative. This fact was confirmed by the studies of salicylates and phthalates, the report of which will be published soon.

The frequency of 1026 cm.$^{-1}$ in the benzoates which characterizes the mono-derivates of aromatic compounds shows a little decrease in phenyl acetate (1018) and in phenyl butyrate (1015), but increase in *o*-kresyl acetate (1040). The fact that the line in question, increases the frequencies and its intensity in the di-derivatives, which has been investigated by Kohlrausch(14) is confirmed also in this experiment. It is interesting that in the case of *o*-kresyl benzoate which is a mono-derivative as well as di-derivative, these relations appeared clearly, that is, $\Delta\nu = 1018$ and 1036 cm.$^{-1}$, have been observed.

2. Frequencies Associated with the C-H Linkage of Alkyl Radicals. The frequencies between 2850 and 2980 cm.$^{-1}$ which have been well known to be attributable to the aliphatic C-H linkage are almost in accord with those in the corresponding alkyl halides(15) and alcohols(16). The lines of this kind are difuse and broad.

In the first member of the series, viz., methyl benzoate, only a well defined line of $\Delta\nu = 2950$ cm.$^{-1}$ reveals in this region. In the case of ethyl benzoate the corresponding line is spalted into two lines, $\Delta\nu = 2930$ and 2980 cm.$^{-1}$, of the same intensity. On the other hand, in the case of *n*-propyl ester, the aggregation of many diffuse lines appears like a band. In the case of iso-propyl ester, however, three lines of $\Delta\nu = 2872$, 2930 and 2979 cm.$^{-1}$ reveal clearly, the middle one of which is the most intense and broad. As we proceed still higher up the series, viz., iso-butyl ester, the continuous spectrum between the two lines of $\Delta\nu = 2873$ and 2968 cm.$^{-1}$ appears like a band while in the case of iso-amyl ester the continuous part is quite homogeneous in the same position. These relations are shown in Diagram (1). In addition, it is found that iso-compounds show more intense and clear lines in this region, than those of the corresponding *n*-compounds.

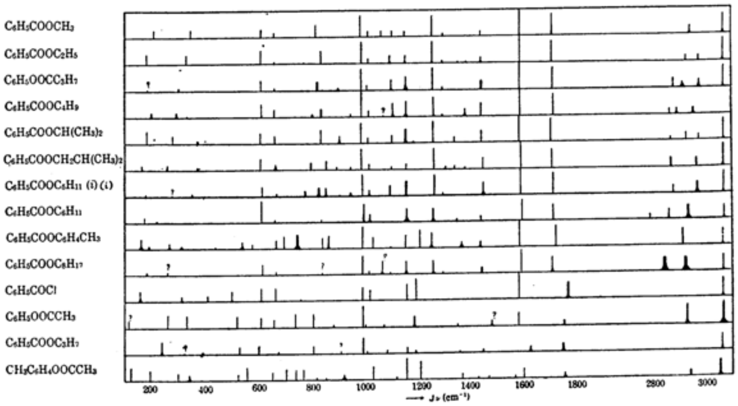
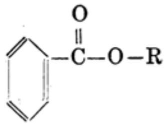


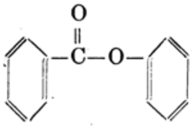
Diagram 1. Raman frequencies of esters of benzoic acid and fatty acids.

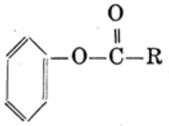
The frequency of 1452 appears in all the substances investigated except in the case of benzoyl chloride which does not contain the CH_2-group. The frequency has been known to be due to the transverse vibration of the hydrogen atoms in CH_2- group.

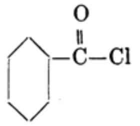
In the series of alkyl benzoates, the same line increases the intensity and its breadth as the carbon atoms increase.

3. Frequencies Possibly Associated with the $-\overset{O}{\overset{\|}{C}}-O-$ Group. The well-known frequency attributed to C:O linkage was observed also in good constance, practically, in all the benzoates. The shift of $\Delta\nu = 1720$ cm.$^{-1}$ in alkyl benzoates, $\Delta\nu = 1730$ cm.$^{-1}$ in *o*-kresyl benzoate, $\Delta\nu = 1760$ cm.$^{-1}$ in phenyl acetate and $\Delta\nu = 1768$ cm.$^{-1}$ in benzoyl chloride have been measured. It is found that there is a little increase of 10 cm.$^{-1}$, by substituting the $-C_nH_{2n+1}$ radical with the $-C_6H_4-CH_3$ radical, and a prominent increase of 50 cm.$^{-1}$, by exchanging the position of the benzene ring and alkyl radical or by substituting the -O.R group with Cl. The structure and the Raman frequencies in question are compared in the following:

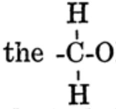

Δν=1720 cm.$^{-1}$


Δν=1730 cm.$^{-1}$


Δν=1761 cm.$^{-1}$


Δν=1768 cm.$^{-1}$

The frequencies of 1270 cm.$^{-1}$ was observed in good constance and in the strong intensity in all the benzoates. Benkateswaran and Bhagavantan⁽¹⁷⁾ have explained that it is attributed to the COH group from the results of alcohols and fatty acids. Wood and George Collins⁽¹⁸⁾

have explained that the same frequency is attributable to the transversal vibration of the hydrogen atoms of the  $-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{-OH}$ group, from the fact that methyl alcohol CH_3-OH and isopropyl alcohols $(CH_3)_2$-CHOH contain no CH_2OH and do not show the 1270 cm.$^{-1}$ frequency. The absence of the line in butyl and higher alcohols has been explained by the possibility that it exists in the higher alcohols and is simply too weak to be recorded.

Their explanations can not be applied, however, in the case of the benzoates which do not contain any COH or -CH_2OH group in the molecule.

The frequency at 670 cm.$^{-1}$ was observed also in all the benzoates independent of the numbers of the carbon atoms in the alkyl group. The fact that carbon dioxide(19) reveals a system of valency frequencies at 2295, 1280, 1223, and 673 cm.$^{-1}$ leads us to suggest that the frequencies at 1720, 1270 and 670 cm.$^{-1}$ in the benzoates may be possibly attributable to the valency frequencies of the carboxyl group, -CO-O-.

It is considered that the frequency at 1270 cm.$^{-1}$ in the benzoate corresponds to that at 1200 cm.$^{-1}$ in phenyl acetate, butyrate and *o*-kresyl acetate (CH_3-CO.O-$C_6H_4CH_3$). And the existence of the same frequency, in benzoyl chloride may be attributed to the -CO-Cl. It is also considered that the shift of $\Delta\nu = 1720$ cm.$^{-1}$ in the benzoates corresponds to 1760 cm.$^{-1}$ in phenol acetate and benzoyl chloride. And the existence of these frequencies in most of the fatty acids,(20) especially, in formic acid(21) which has not any alkyl radical, seems to given an other verifications of considerations above mentioned. The results have been compared:

$C_6H_5CO-O-R$	1720	1270	670
C_6H_5COCl	1776	1200	669
$C_6H_5-O-CO-CH_3$	1760	1193	661
$C_6H_5-O-CO-C_3H_7$	1753	1194	679
$CH_3-C_6H_4-O-CO-CH_3$	1764	1218 1261	656
$C_6H_5-CO.O-C_6H_4CH_3$	1730	1214	675
HCOOH	1724 1694	1200 1223	673(22) 187
CH_3COOH	1670	1280	623(23)
$CH_3-COOC_3H_7$	1740	1250	630(10)

Thus the consideration that the frequencies of $\Delta\nu = 1720$, 1270 and 670 cm.$^{-1}$ are attributed to the -CO-O- group in the compound of the type of C_6H_5-CO-O-X and 1776, 1194 and 661 cm.$^{-1}$ are attributed to that in the compound of the type of X-CO-O-C_6H_5 seems to be supported by the fact that in the case of *o*-kresyl benzoate, which has the both types of C_6H_5-CO-O-X and X-CO-O-C_6H_5, the both frequencies of $\Delta\nu = 1214$ and 1261 cm.$^{-1}$ reveal in the same intensity.

4. Inner and Outer Frequencies between Atoms or Atom Groups. Frequencies of the inner and outer vibration between two atoms or atom groups in a molecule are calculated by using the well-known equation(24)

$$\omega = \sqrt{\frac{f}{C\mu}}$$

where μ is the reduced mass; i.e., $\frac{1}{\mu}=\frac{1}{m_1}+\frac{1}{m_2}$. The constant C is known as $C=\frac{4x^2c^2}{L}=5.863\times10^{-2}$, where L is the Loschmidt numbers, 6.06×10^{23} and c is the velocity of light, 3×10^{10} cm./sec. More practically, by using the thermochemical data, work of dissociation, A (in Cal./Mol.), the wave numbers may be calculated from the formula(25)

$$\omega = 291.5\sqrt{A\cdot\frac{1}{\mu}}$$

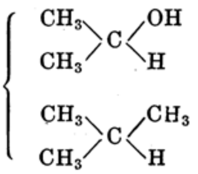
For the simplicity, the molecular formula, the bond, the force constant, f (in dynes/cm.) between the two atoms or atom groups taken from the table of Kohlrausch(26) or the „Aufspaltungsarbeit“ A (in Cal./Mol.) taken from the table of H. G. Grimm(27), the reduced mass, the wave numbers (in cm.$^{-1}$) calculated and that of observed have been tabulated as follows:

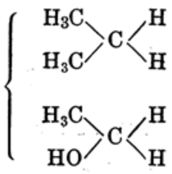
No.	Molecular formula	Bond	$f\times10^{-5}$	$\frac{1}{\mu}$	$\omega_{\text{cal.}}$	$\omega_{\text{abs.}}$
1.	$C_6H_5\cdot CO\cdot O\cdot R$	$O \leftrightarrow C$	4.99 (A=102)	0.1458	1114 (1124)	1110
2.	,,	$C \leftrightarrow C$	4.31	0.1667	1107	1110?
3.	$C_6H_5\cdot CO\cdot O\cdot CH_3$	$O \leftrightarrow CH_3$	4.99	0.1292	1088	1078
4.	$C_6H_5\cdot CO\cdot Cl$	$C \leftrightarrow Cl$	3.12 (A=70)	0.1115	770 (814)	769
5.	$C_6H_5\cdot O\cdot OC\cdot R$	$C_6H_5 \leftrightarrow O$	(A=101)	0.0755	804	810
6.	$C_6H_5\cdot CO\cdot O\cdot CH_3$	$C_6H_5COO \leftrightarrow CH_3$	4.99 (A=102)	0.0749	779 (806)	814
7.	$C_6H_5\cdot CO\cdot Cl$	$C_6H_5CO \leftrightarrow Cl$	3.12	0.03969	448	414
8.	$CH_3\cdot CO\cdot O\cdot C_6H_5$	$CH_3COO \leftrightarrow C_6H_5$	(A=101)	0.02994	507	525

The line of $\Delta\nu=1110$ cm.$^{-1}$ appears in all the benzoates and disappeared in benzoyl chlorides and phenyl acetate. It have been found also in alcohols and most of the esters of fatty acids observed by other authors.(28) These facts seem to make the confirmation of the estimation that it is attributed to the inner vibration of the O-C linkage.

The approximate calculation of the inner vibration of two atoms shows that the line at $\Delta\nu=1110$ cm.$^{-1}$ may be possibly attributed to the

C-C as well as to the O-C bond. Accidental as it may be, it seems to be not impossible. And the fact that the line of about $\varDelta\nu = 1110$ cm.$^{-1}$ has been found in some of the alkyl halides, such as, $(CH_3)_2CH.CH_2.Cl$, $(CH_3)_2CH.CH_2.Br$, etc.,⁽²⁹⁾ which have no O-C bonds, and the line has been found in $CH_3.OH$⁽³⁰⁾ and $C_6H_5.CO.O\text{-}CH_3$ which have no aliphatic C-C bond seems to give a verification about it. Kohlrausch and his co-worker⁽³¹⁾ have shown the fact that the OH and CH_3 groups exert the similar effect on the rest, that is, for example, the following pairs give the similar Raman lines related with the alkyl rest.





In the present case, we consider that the frequencies related with the $\text{-}CH_2\text{-}O\text{-}$ or $CH_3\text{-}O\text{-}$ may be possible similar to those related with the $\text{-}CH_2\text{-}CH_2\text{-}$ or $\text{-}CH_2\text{-}CH_3$ and that the two kinds of the frequencies are associated or united, which make an appearance of broad and diffuse line as the dispersion of the prism is not so large in our experiments. The fact seems to be more possible, especially, in the complex molecules.

The frequencies of $\varDelta\nu = 810$ cm.$^{-1}$ observed in phenyl acetate and butyrate are in good coincidence with the calculated value and the consideration is confirmed by the existence of the same line in phenol.

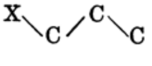
The same shift in methyl benzoate, however, is evidently different in its origin. The outer vibration or the valence frequency between the CH_3 group and the acid rest may be taken in this case, as shown in the above table.

Since the lengthening of the carbon chain exerted little effect on the benzene ring and on the -CO-O- group as mentioned above, it seems right to assume that only the $\text{-}CH_2\text{-}$ group attached to the rest relates with the valency frequencies as in the cases of alkyl halides studied by Harkins.⁽³²⁾ Thus, as one of the possible ways to explain the frequencies in the range of 800–900 cm.$^{-1}$ in the present investigation we may take the frequency shift of 846 cm.$^{-1}$ in ethyl benzoate as the valence frequency between the alkyl radical or the $\text{-}CH_2\text{-}$ group and the acid rest, corresponding to that of $\varDelta\nu = 814$ cm.$^{-1}$ in methyl benzoate.

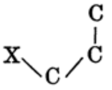
It is surprising, however, that in the case of *n*-propyl benzoate a shift of $\varDelta\nu = 811$ cm.$^{-1}$ and a very weak line of $\varDelta\nu = 845$ cm.$^{-1}$ were observed. In the case of *n*-butyl benzoate two broad and diffuse lines, corresponding $\varDelta\nu = 810$ and 843 cm.$^{-1}$ were observed in the same intensity. In iso-propyl benzoate only a intense line with the same frequency as that in the case of ethyl ester was observed clearly. In iso-butyl benzoate two broad lines corresponding to 804 and 863 cm.$^{-1}$ and in iso-amyl benzoate, 836 and 861 cm.$^{-1}$ of the same intensity were observed.

To explain these facts let us consider the " Free rotation " of the alkyl group, namely, that the chain and the ring form in the free space as considered by K.W.F. Kohlrausch and his co-workes in their studies of alkyl halides(33).

Thus in the case of *n*-propyl benzoate, the *n*-propyl radical takes two forms in the space against the rest of benzoic acid, viz.,



Chain form



Ring forms

where: X is the rest of benzoic acid.

With these two forms we can explain the two frequencies occurred, though one of which is very weak. And with the same principle, we can also explain the two frequencies observed in the other benzoates. The fact that iso-propyl benzoate which can not take two forms, and has only the frequency of 845 cm.$^{-1}$ as that in ethyl ester, seems to give a support of the principle. The frequencies of the benzoates are tabulated as follows:

	I	II
$X-CH_3$	$\omega_1 = 814$	
$X-CH_2-$	$\omega_2 = 846$	
$X-CH_2-CH_2-CH_3$	$\omega_2 = 845$	$\omega_3 = 811$
$X-CH_2-CH_2-CH_2-CH_3$	$\omega_2 = 843$	$\omega_3 = 810$
$X-CH<^{CH_3}_{CH_3}$	$\omega_4 = 845$	
$X-CH_2-CH<^{CH_3}_{CH_3}$	$\omega_2 = 863$	$\omega_3 = 804$
$X-(CH_2)_2-CH<^{CH_3}_{CH_3}$	$\omega_2 = 861$	$\omega_3 = 836$?

We may consider the relation between the forms and the frequencies as shown in following:

$X-CH_3$	ω_1
$\left\{ X-CH_2- \right.$	ω_2
$\left. X-CH_2- \right.$	ω_2 ω_3
$X-CH<$	ω_4

A remarkable deviation was found in iso-butyl and iso-amyl ester, which may attributable to the error of measurement, on account of the broad lines or a possible deviation due to the influence of the -CH$(CH_3)_2$ group.

The fact that $\Delta\nu = 845$ cm.$^{-1}$ in iso-propyl benzoate coincides with that of $\Delta\nu = 846$ in ethyl benzoate may be compare with the relation in iso-propyl iodide(34) ($\Delta\nu = 489$ cm.$^{-1}$) and ethyl iodide ($\Delta\nu = 497$ cm.$^{-1}$) and the weight of the molecular rests i.e. C_6H_5COO- $= 121$ and J $= 127$; though it is not only the weight that associated with the frequencies. And the fact that the frequency at $\Delta\nu = 814$ cm.$^{-1}$, in methyl benzoate, is less than the corresponding one (at $\Delta\nu = 846$ cm.$^{-1}$), in ethyl benzoate, seems to be possible when we compare it with the relation that in the case of alkyl chloride the difference between methyl ($\Delta\nu = 712$ cm.$^{-1}$) and ethyl derivative ($\Delta\nu = 655$ cm.$^{-1}$) is larger than that in the case of the corresponding iodide ($\Delta\nu = 522$ cm.$^{-1}$ in methyl and 497 cm.$^{-1}$ in ethyl iodide).

An Attempt of the Calculation of the Valency and Deformation Frequencies. If we make an assumption that the vibration of the system of three atoms or atom groups exerts the Raman lines, in the first order of approximation, independent of the other molecular rest, we may apply the theoretical calculations of Friedrich Lechner;(25) which are given in:

$$n_1^2+n_2^2+n_3^2 = \frac{f_{12}}{\mu_{12}}+\frac{f_{23}}{\mu_{23}}+\frac{d}{\mu_4}$$

$$\begin{aligned} n_1^2n_2^2+n_2^2n_3^2+n_1^2n_3^2 = {} & \frac{f_{12}}{\mu_{12}}\cdot\frac{f_{23}}{\mu_{23}}\left\{1-\frac{\mu_{12}\cdot\mu_{23}}{m_2^2}\cos^2\alpha\right\} \\ & +\frac{f_{12}}{\mu_{12}}\cdot\frac{d}{\mu_4}\left\{1-\frac{\mu_{12}\,\mu_4}{m_2^2}\left(\frac{s}{s_{23}}\right)^2\sin^2\alpha\right\} \\ & +\frac{f_{23}}{\mu_{23}}\cdot\frac{d}{\mu_4}\left\{1-\frac{\mu_{23}\,\mu_4}{m_2^2}\left(\frac{s}{s_{12}}\right)^2\sin^2\alpha\right\} \end{aligned}$$

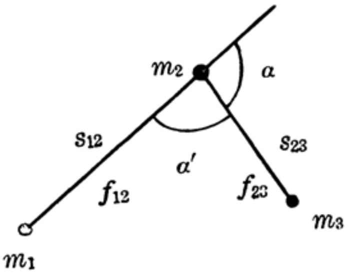
$$n_1^2\cdot n_2^2\cdot n_3^2 = \frac{f_{12}}{\mu_{12}}\cdot\frac{f_{23}}{\mu_{23}}\cdot\frac{d}{\mu_4}\left\{1-\frac{\mu_{12}\,\mu_{23}}{m_2^2}\right\}$$

where μ_{12}, μ_{23}; f_{12}, f_{23}; s_{12}, s_{23} are the reduced masses, the force constants and the distance between material particles, m_1 and m_2, m_2 and m_3 respectively, $\alpha' = (180^\circ-\alpha)$ is the valency angle and

$$\frac{1}{\mu_4} = \frac{1}{\mu_{12}}\cdot\frac{s^2}{s_{12}^2}+\frac{2}{m_2}\cdot\frac{s^2}{s_{12}\,s_{23}}\cos\alpha+\frac{1}{\mu_{23}}\cdot\frac{s^2}{s_{23}^2}$$

$$s_{12}^2 d_{12} = s_{23}^2 d_{23} = s^2 d$$

$$n^2 = 5.863 \times 10^{-2}\,\omega^2$$



When the three particles make an isosceles triangle, that is when $m_1 = m_3 = m$ and $m_2 = M$, $f_{12} = f_{23} = f$, $s_{12} = s_{23} = s$, the above equation can be simplified as following:

$$n_1^2 = \frac{f}{m} z$$

$$n_1^2 + n_2^2 + n_3^2 = \frac{f}{m}(1-p) + \frac{2d}{m} z \qquad (2)$$

$$n_2^2 n_3^2 = \frac{f}{m} \cdot \frac{2d}{m} \cdot p$$

where $$p = \frac{2m}{M} + 1, \qquad z = p + (1-p)\sin^2\frac{\alpha}{2} \qquad (3)$$

And the equations (2) have been rewritten in:

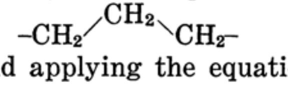
$$z^3 - az + b = 0 \qquad (4)$$

where $$a = \frac{n_1^2(n_1^2+n_2^2+n_3^2)p}{n_2^2 n_3^2}, \qquad b = \frac{n_1^4(p+1)p}{n_2^2 n_3^2} \qquad (5)$$

and the necessary conditions for the real solutions in the above equation are: $\frac{a^2}{27} > \frac{b^2}{4}$ and $1 < z \leqq p$.

Lechner has applied the above theory to the simple molecules, such as, CH_2Cl_2, CH_2Br_2, etc. for calculating the force constants and valency angles.

In the substances studied, the following assumptions have been made, since the molecules are very complicated. In the first, we assume that the theory can be applied to the system of three atom groups or an atom and two atom groups, and secondly, that it can be applied to a portion of the molecule, that is, the molecule is considered as some systems of three atoms or atom groups.

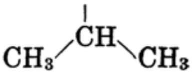
Under the assumptions above mentioned, we attempt to calculate the valency system by taking the part of  $-CH_2\overset{CH_2}{\diagup\;\diagdown}CH_2-$ in n-butyl radical as an isosceles triangle model and applying the equations of the valence system, mentioned above. In this case, if we take $m = M = 14$,

$\alpha' = 110^\circ$, the tetrahedral valence angle of the carbon atom, and the force constant $f = 4.3 \times 10^5$ dyne/cm., given by Kohlrausch,(36) the following values are obtained:

$$p = 3,\ z = 2.342,\ \omega_1 = 1108\ \text{cm.}^{-1}$$

And by assuming $\omega_3 = 298$ cm.$^{-1}$, the valence of $\omega_2 = 930$ cm.$^{-1}$ and $d = 0.21 \times 10^5$ dyne/cm. are obtained, which may compare with the set of the observed values, in *n*-butyl benzoate: $\omega_1 = 1110$, $\omega_2 = 957$, $\omega_3 = 298$ cm.$^{-1}$. And from these values, f, d and α in butyl benzoate has been calculated as shown below:

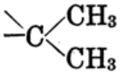
$$f = 4.28 \times 10^5,\ d = 0.21 \times 10^5,\ \alpha' = 109^\circ.40'.$$

An other calculation is carried out by taking the part of  $CH_3\diagup\overset{|}{CH}\diagdown CH_3$ as a system of an iso-sceles triangle. In this case if we take $m = 15$, $M = 13$, $\alpha' = 110$, $f = 4.3 \times 10^5$ dyne/cm. we obtain:

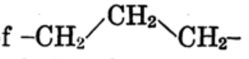
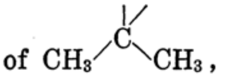
$$p = 3.3076,\ z = 2.5483,\ \alpha_1 = 1116.$$

Thus, when we assume $\omega_3 = 376$ cm.$^{-1}$ which seems to characterize the group in question, from the fact that it reveals in iso-propyl and iso-butyl benzoates but does not reveal in the normal benzoates, the following values are obtained:

$$\omega_2 = 963,\ d = 0.34 \times 10^5.$$

Comparing with the set of the observed frequencies $\omega_1 = 1110$, $\omega_2 = 916$, $\omega_3 = 378$ cm.$^{-1}$, the assumption seems to be possible. And if we take $m = 12$, $M = 15$ in  $-C\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$ group, we obtain, under the same assumption, $\omega_1 = 1143$, $\omega_2 = 959$ and $\omega_3 = 378$ cm.$^{-1}$

The facts that the frequencies of $\Delta\nu = 1110$, 916, 378 cm.$^{-1}$ in iso-propyl benzoate, 1110, 901, 378 cm.$^{-1}$ in iso-butyl benzoate and 1104, 915 (?), 356 (?), cm.$^{-1}$ in iso-amyl benzoate, are found, seem to confirm the above consideration, on one hand, and the facts that these frequencies have been found also in iso-propyl, iso-butyl and iso-amyl alcohols and halides, studied by other authors,(37) seem to give an other maintenance of our consideration, on the other hand.

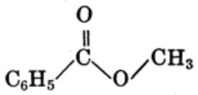
And since the frequencies calculated for the system of  $-CH_2\diagup CH_2\diagdown CH_2-$ are closed in their values with the frequencies calculated for the system of  $CH_3\diagup\overset{|\diagup}{C}\diagdown CH_3$, we may also be permitted to assume that the group of

$-CH_2\diagup^{CH_2}\diagdown CH_3$ in *n*-butyl and *n*-propyl benzoates, or $-CH_2-\overset{\diagup}{C}H-CH_3$ in iso-butyl and iso-amyl benzoates, have also the system of the frequencies closed with the above values, viz., $\varDelta\nu = 1117, 957, 289$ in *n*-butyl and *n*-propyl benzoates and 1110, 916, 378 cm.$^{-1}$ in iso-butyl and iso-amyl benzoates are compared.

Thus, we can explain the frequencies of $\varDelta\nu = 1110, 959, 910, 378$ cm.$^{-1}$ in iso-butyl benzoates and 1104, 955, 915, 356 (?) cm. iso-amyl benzoate, which have the system of $-CH\left\langle{}^{CH_3}_{CH_3}\right.$ as well as $-CH_2-CH_2-CH_2-$ group, that is, the combination of the two types. And since the frequencies of $\varDelta\nu = 1110$ cm.$^{-1}$ is so broad and diffuse that it may be suggested as the aggregation of the closed lines.

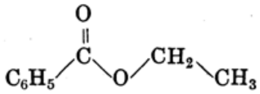
Unfortunately, these frequencies in question are so weak, especially in the case of iso-amyl benzoate, that we can not measure them exactly and the experiments are carried out by means of the spectroscope of lower dispersion, so that we have little right to advocate the consideration, but by comparing with the results of other derivatives which have the same type of alkyl groups, studied by other authors, as mentioned above, the estimation seems to be not impossible.

As regards to the vibration between alkyl radical and the complicated acid rest an other explanation has been done. Corresponding to the frequencies $\varDelta\nu = 1110, 916, 378$ for the system of $-CH_2\diagup^{CH_2}\diagdown CH_2-$, it seems to be possible to take $\varDelta\nu = 1108, 814, (845), 351$ m.$^{-1}$ as the frequencies for the system of $-\overset{\|}{C}\diagup^{O}\diagdown CH_3$ or $-\overset{\|}{C}\diagup^{O}\diagdown CH_2-$ in the benzoates. Thus we can explain the following frequencies in alkyl benzoates studied:



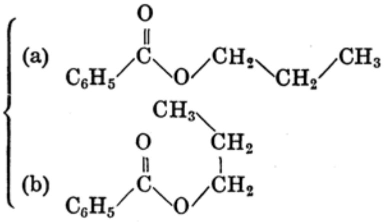
Methyl bezoate

Δν = 1108 814 351 cm.$^{-1}$



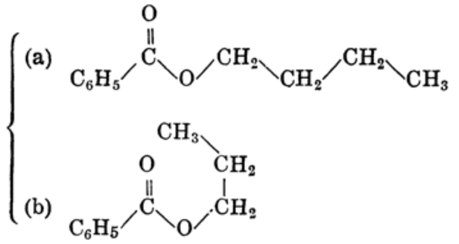
Ethyl benzoate

Δν = 1107 845 335 cm.$^{-1}$



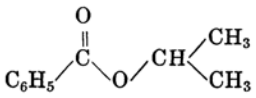
n-Propyl benzoate

Δν = 1110 $\left\{\begin{matrix}811\\845\end{matrix}\right.$ — cm.$^{-1}$



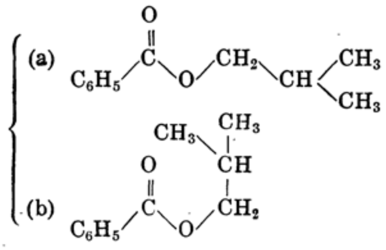
n-Butyl benzoate

$\Delta\nu = 1117$ $\left\{\begin{matrix}810\\843\end{matrix}\right.$ 338 cm.$^{-1}$



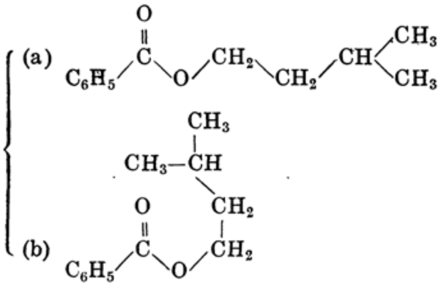
Iso-propyl benzoate

$\Delta\nu = 1110$ 845 284 cm.$^{-1}$



Iso-butyl benzoate

$\Delta\nu = 1110$ $\left\{\begin{matrix}804\\863\end{matrix}\right.$ 262 cm.$^{-1}$



Iso-amyl benzoate

$\Delta\nu = 1104$ $\left\{\begin{matrix}836\\861\end{matrix}\right.$ 282 ? cm.$^{-1}$

With the assumption that only the CH_2- group adjacent to the oxygen atom relates with the vibration of the system and the free rotation of the alkyl rest which has been mentioned in the foregoing article, we can explain these frequencies, as attributable to the system of $-\overset{\|}{C}\diagdown_{O}\diagup CH_2-$ in place of the frequencies between the alkyl radical and the complicated acid rest. The frequency of $\Delta\nu = 1110$ cm.$^{-1}$ may be explained by the accidental accordance of lines arising from the two origins, viz., from the systems of $-CH_2\diagup^{CH_2}\diagdown CH_2-$ and $-\overset{\|}{C}\diagup^{O}\diagdown CH_2-$.

In conclusion, the authors wish to express their thanks to Ass. Profs. T. Nozoe and Y. Ota for their advices and help and to Messrs. Y. Ishigaki and S. Murayama for their kind help. The authors express their indebtedness to the Taihoku High School which lent us the spectroscope during the present investigation.

Summary.

(1) The Raman spectra of the following substances have been measured: methyl, ethyl, *n*-propyl, *n*-butyl, iso-propyl, iso-butyl, iso-amyl, cyclo-hexyl, *o*-kresyl and *n*-octyl benzoates, benzoyl chloride, phenol esters of acetic acid and butyric acid and *o*-kresyl acetate.

(2) The constitutive influences exserted on the well-known frequencies of the benzene ring have been observed.

(3) The relation among the frequencies in the region between $\Delta\nu = 2860$ and 2980 cm.$^{-1}$ associated with the C-H linkage of alkyl radicals have been studied for the series of benzoates. It has been found that the intensity and the breadth of the line corresponding to the shift of $\Delta\nu = 1450$ cm.$^{-1}$, considered to be attributable to the transversal vibration of hydrogen atom in the CH_2- group, increases as the carbon atoms of the homologue are increased.

(4) The frequencies of $\Delta\nu = 1720, 1270, 670$ cm.$^{-1}$ in benzoates are estimated to be possibly attributed to the frequencies of the -CO-O- group.

(5) The following shifts corresponding to the inner vibrations between atoms or atom groups shown below have been established:

Molecular formula	Bond	$\omega_{Cal.}$	$\omega_{Obs.}$
$C_6H_5 \cdot CO \cdot O \cdot R$	$O \longleftrightarrow C$	1114	1110
$C_6H_5 \cdot CO \cdot O \cdot R$	$C \longleftrightarrow C$	1107	1110
$C_6H_5 \cdot CO \cdot O \cdot CH_3$	$O \longleftrightarrow CH_3$	1088	1078
$C_6H_5 \cdot CO \cdot Cl$	$C \longleftrightarrow Cl$	770	769
$C_6H_5 \cdot O \cdot CO \cdot R$	$(C_6H_5) \longleftrightarrow O$	804	810

(6) The frequency of $\Delta\nu = 814$ cm.$^{-1}$ in methyl benzoate has been estimated to be attributed to the bond between methyl group and the acid rest. The frequencies in the region between $\Delta\nu = 810$ and 863 cm.$^{-1}$ have been explained to be attributable to the valency frequencies between the acid rest and the adjacent -CH_2- group. The two frequencies in the region between $\Delta\nu = 810$ and 846 cm.$^{-1}$, in *n*-propyl, *n*-butyl, iso-butyl and iso-amyl benzoates have been explained by the consideration of the free rotation of the alkyl rest.

(7) The valency and the deformation frequencies have been thoretically calculated, assuming that the molecule is composed of some systems of three atoms or atom groups.

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