STUDIES OF THE RAMAN EFFECT. PART II. THE RAMAN EFFECT OF PHENYL-ACETATES, PHENYL-PROPIONATE, CINNAMATES, PHTHALATES, SALICYLATES AND PHENYLMETHYLCARBINOL.

By Kichimatsu MATSUNO and Kwan HAN.

Received December 5th, 1933. Published February 28th, 1934.

Introduction.

The Raman effects of a series of esters of benzoic acid and phenol esters of fatty acids have been recently studied.[1] In order to confirm the constitutive influences exerted on the frequencies attributable to the benzene ring, between mono- and diderivatives, and to study the influences exerted on the $-C=O$ linkage and the valency frequencies, of the $-\overset{\|}{C}-O-R$ system, the Raman spectra of the following nine kinds of alkyl esters of aromatic acids, viz., methyl phenyl acetate, ethyl phenyl acetate, ethyl phenyl propionate, ethyl cinnamate, iso-propyl cinnamate, dimethyl phthalate, diethyl phthalate, methyl salicylate and ethyl salycilate, and also for the comparison, methyl phenyl carbinol have been studied in the present investigation. Kohlrausch and Pongratz[2] have shortly published the Raman spectra of dimethyl-phthalate and ethyl cinnamate. Their results are good agreement with ours, though the experimental data of ethyl cinnamate have not been thoroughly reported.

(1) This Bulletin, **8** (1933), 333.
(2) *Ber.*, (B) **66** (1933), 1–12.

Experimental.

The experiments were carried out with the same apparatus as described in our previous paper.(1) All the substances used were prepared in our laboratory by the following processes, excepting methyl salicylate.

Methyl and ethyl phenyl-acetates(3) were made from the dehydrated alcohols and phenyl-acetic acid (made in Japan) by the action of conc. sulphuric acid.

Ethyl phenyl-propionate(4) was prepared from dehydrated ethyl alcohol and phenyl-propionic acid which was obtained by reducing the cinnamic acid with natrium amalgam.

Ethyl and iso-propyl cinnamate(5) were prepared from the corresponding alcohols and cinnamic acid (m.p. 133°C.), by the action of conc. sulphuric acid or dry hydrochloric acid gas.

Di-methyl and di-ethyl phthalates(6) were prepared by boiling the corresponding absolute alcohols and phthalic acid in the presence of conc. sulphuric acid.

Ethyl salicylate(7) was prepared from the absolute alcohol and the acid by the action of hydrochloric acid gas. As to methyl salicylate, Kahlbaum's was used.

Phenyl methyl carbinol(8) was prepared from benzaldehyde by the action of magnesium methyl iodide, that is, the Grignard reagent.

For the simplification, the name of the substance, the number of the table (Tb. No.), the numbers of the Raman lines (n), the number of the plate (Pl. No.) and the conditions under which the spectra were taken, viz., breadth of the slit (St), electric current (C) working the mercury vapour lamp, temperature of the sample during the experiment (T) and the time of exposure (t), are tabulated.

---

(3) *Ber.*, **2** (1869), 208.
(4) *Ann.*, **137** (1866), 334.
(5) *Ber.*, **28** (1896), 3254.
(6) *Monat. Chem.*, **25** (1904), 1204.
(7) *Ann.*, **197** (1879), 17.
(8) *Ber.*, **31** (1898), 1003.

Table A.

No.	Substance	Tl. No.	n	Pl. No.	St. 10^{-2}mm.	C (amp)	$T°$ (C)	t (hours)
1	Methyl phenylacetate	I	42	78	7	2.8	19	7
				79	6	3.2	19	13
2	Ethyl phenylacetate	II	35	80	7	3.2	20	8
				86	6	3.2	20	13
3	Ethyl phenylpropionate	III	30	92	7	3.2	20	13
				94	6	3.2	20	15
4	Ethyl cinnamate	IV	72	52	7	2.8	23	10
				54	7	3.2	19	2
				55	6	3.2	19	4
5	Isopropyl cinnamate	V	46	105	6	2.8	21	4
				106	6	3.2	21	3
6	Dimethyl phthalate	VI	37	46	7	2.8	23	8
				51	6	3.2	19	13
7	Diethyl phthalate	VII	42	41	8	2.8	22	7
				45	6	3.2	19	12
8	Methyl salicylate	VIII	34	56	10	3.2	23	2
				57	7	3.2	23	7
9	Ethyl salicylate	IX	35	59	7	2.8	23	7
				62	7	3.2	20	7
				84	6	3.2	19	10
10	Methyl phenyl carbinol	X	41	89	6	3.2	20	12
				90	6	3.2	20	9

A small quantity (3–10 c.c.) of methyl-, ethyl phenyl-acetates, ethyl phenyl-propionate, iso-propyl cinnamate and methyl phenyl carbinol was used for each experiment. From the fact of the coincidence of most of the Raman lines in ethyl phenyl propionate and ethyl cinnamate, it is considered that the small quantity of the cinnamate may be mixed with ethyl phenyl propionate due to the insufficient reduction.

The strong back grounds in the plates of methyl-, ethyl- and phenyl-acetates and methyl- and ethyl salicylates could not be removed even when the pure samples obtained by the repeated purifications were examined. The data of the Raman spectra are tabulated as follows.

Table I.

Methyl phenyl acetate $C_6H_5 \cdot CH_2CO \cdot O \cdot CH_3$.

No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0 - \Delta\nu$
1	24440	$^1/_2$(*b*)	*q*-2948	26	22169	3(*d*)	*e*- 769
2	24293	$^1/_2$(*b*)	*p*-3060	27	22120	3(*b*, *d*)	*e*- 818
3	24227	1(*b*, *d*)	*k*- 478	28	22047 ?	0	*e*- 891
4	24182	0	*k*- 523	29	22016 ?	0(*b*)	*e*- 922
5	24076	$^1/_2$(*bb*)	*k*- 629	30	21942	8	*e*- 996
6	24011	1(*b*)	*k*- 694	31	21913	3	*e*-1025
7	23952	2(*b*)	*k*- 753	32	21855	1(*d*)	*e*-1083
8	23894	0(*b*, *d*)	*k*- 811	33	21777	3	*e*-1161(*k*-2928)
9	23780	1(*d*)	*k*- 925	34	21754	5(*d*)	*e*-2951(*e*-1184)
10	23705	5	*k*-1000	35	21648	7(*b*, *d*)	*k*-3057
11	23681	2	*k*-1024	36	21562 ?	0	*i*-2954
12	23593	2(*b*, *d*)	*k*-1112	37	21502	$^1/_2$(*bb*, *dd*)	*e*-1436
13	23542	0(*b*)	*k*-1163	38	21338	6(*b*, *d*)	*e*-1600
14	23510	2(*b*)	*k*-1195(*i*-1006)	39	21196 ?	2(*bb*, *dd*)	*e*-1742
15	23434	0(*b*)	*k*-1271	40	20016	$^1/_2$	*e*-2922
16	23399 ?	0(*d*)	*k*-1306(*i*-1117)	41	19984	3(*b*)	*e*-2954
17	23311	$^1/_2$	*i*-1205	42	19881	2	*e*-3057
18	23274 ?	0	*k*-1431				
19	23103	2	*k*-1602				
20	22751	3(*d*)	*e*- 187				
21	22576	$^1/_2$(*b*, *d*)	*e*- 362				
22	22455	3(*b*, *d*)	*e*- 483				
23	22408	$^1/^2$(*d*)	*e*- 530				
24	22316	3(*b*)	*e*- 622				
25	22243	$^1/_2$(*d*)	*e*- 695				

$\overline{\Delta\nu}$: 187 (3 *d*); 362 ($^1/_2$ *b*, *d*); 481 (3 *b*, *d*); 527 ($^1/_2$ *d*); 622 (3 *b*); 695 ($^1/_2$ *b*, *d*); 761 (3 *d*); 818 (3 *d*); 924 (1 *d*); 998 (8); 1025 (3); 1083 (1 *b*); 1112 (3 *b*, *d*); 1162 (3 *b*); (1189) (5 *d*); (1271) ($^1/_2$ *b*, *d*) ?; 1306 ($^1/_2$ *b*); 1436 ($^1/_2$ *bb*, *dd*); 1601 (6 *b*, *d*); 1742 (2*b*, *d*); 2922 (3 *b*); 2953 (5 *d*); 3057 (7 *b*, *d*).

Table II.

Ethyl phenyl acetate $C_6H_5 \cdot CH_2 \cdot CO \cdot O \cdot CH_2 \cdot CH_3$.

No.	ν in cm.⁻¹	*I*	$\nu_0 - \Delta\nu$	No.	ν in cm.⁻¹	*I*	$\nu_0 - \Delta\nu$
1	24404	½(*d*)	*q*-2984	21	21969	½	*f*-1026
2	24302	½	*p*-3051	22	21944	8	*e*- 994
3	24238	1(*b*)	*o*-3055	23	21913	4	*e*-1025
4	24084	2(*b*)	*k*- 622	24	21823	1(*d*)	*e*-1115
5	23957	2	*k*- 749	25	21775	5(*dv*)	*e*-1163(*k*-2930)
6	23709	5	*k*- 996	26	21727	5(*b*, *d*)	*e*-1211
7	23683	3	*k*-1022	27	21623	2(*d*)	*k*-2978
8	23604	2(*d*)	*k*-1101	28	21650	7(*b*, *d*)	*k*-3055
9	23540	2(*d*)	*k*-1165	29	21543	½(*d*)	*e*-1395
10	23502	3(*d*)	*k*-1203	30	21483	1(*bb*, *dd*)	*e*-1455
11	23443 ?	½	*k*-1262	31	21338	7(*dv*)	*e*-1600
12	23312	½	*k*-1204	32	21201 ?	½(*dd*)	*e*-1737
13	23274	½(*b*, *d*)	*k*-1431	33	20016	2(*b*)	*e*-2922
14	23103	1(*d*)	*k*-1602	34	19953	2(*b*)	*e*-2985
15	22729 ?	½(*dd*)	*e*- 209	35	19884	2	*e*-3054
16	22316	3	*e*- 622				
17	22258	2(*B*)	*e*- 680				
18	22180		*e*- 758				
19	22150	2(*B*)	*e*- 788				
20	22080		*e*- 858				

$\overline{\Delta\nu}$: 209 (½ *dd*) ? ; 622 (3 *b*, *d*) ; 680 (2 *b*)—758 (2 *b*) ; 788 (2*b*)—858 (2 *b*) ; 997 (8) ; 1025 (4) ; 1108 (1 *d*) ; 1164 (5 *dv*) ; 1207 (5 *b*, *d*) ; (1265) (2 *d*) ? ; 1395 (½ *d*) ; 1455 (1 *bb*, *d*) ; 1601 (7 *dv*) ; 1737 (½ *dd*) ? ; 2922 (2 *b*) ; 2981 (2 *b*) ; 3055 (7 *b*, *d*).

Table III.

Ethyl phenyl-propionate $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot CH_2 \cdot CH_3$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0 - \Delta\nu$
1	23885	½(*b*)	*k*- 820	16	21945	7	*e*- 993
2	23708	4	*k*- 997	17	21915	3(*d*)	*e*-1023
3	23683	½(*d*)	*k*-1023	18	21833	2(*d*)	*e*-1105
4	23502	4(*b*)	*k*-1203	19	21791	6	*k*-2914
5	23443	½(*b*, *d*)	*k*-1262	20	21765	6	*e*-1173
6	23252	½(*d*)	*k*-1453	21	21742	6	*e*-1196
7	23213 ?	½(*d*)	*k*-1495	22	21681	6(*B*)	*e*-1257(*k*-3024)
8	23185	2(*d*)	*e*+ 247	23	21649		*k*-3056
9	23111	5	*k*-1594	24	21495	2(*b*, *d*)	*e*-1443
10	23076	5	*k*-1629	25	21447	0	*e*-1491
11	22766	1(*d*)	*e*- 178	26	21343	8	*e*-1595
12	22701	2(*dr*)	*e*- 237	27	21310	7	*e*-1628
13	22599	½(*d*)	*e*- 339	28	21277	½	*e*-1661
14	22320	2(*b*, *d*)	*e*- 618	29	21237	2	*e*-1701
15	22079	1(*b*)	*e*- 859	30	19885	1	*e*-3053

$\overline{\Delta\nu}$: 178 (1 *d*); 237 (2 *d*); 339 (½ *d*); 618 (2 *b*, *d*); (820) (½ *b*) ?; 859 (1 *b*); 995 (7); 1023 (2); (1105) (2 *d*); 1173 (6); 1196 (6); (1257) (5 *b*) ?; 1379 (½); 1448 (2*b*, *d*) ?; 1491 (½); 1595 (8); 1628 (7); 1661 (½); 1701 (2); 2914 (6); 2963 (6) ?; (3024) (5); 3055 (5 *b*).

Table IV.

Ethyl cinnamate $C_6H_5 \cdot CH{:}CH \cdot CO \cdot O \cdot CH_2\ CH_3$.

No.	ν in cm.$^{-1}$	*I*	$\nu_0 - \Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0 - \Delta\nu$
1	24433 ?	0(*d*)	*k*- 272	11	23709	6	*k*- 996
2	24297 ?	0	*k*- 408	12	23679	1	*k*-1026
3	24227	0	*k*- 478(*i*- 289)	13	23587	1(*d*, *b*)	*k*-1118
4	24119	1(*d*, *b*)	*i*- 397	14	23549	1(*d*)	*i*- 967(*k*-1156)
5	24088	2	*k*- 617	15	23527	8(*d*)	*k*-1178
6	24047	1	*i*- 469	16	23505	8(*d*)	*k*-1200
7	23989	1(*bb*)	*k*- 716	17	23446	6(*d*)	*k*-1259
8	23869	2	*k*- 836	18	23400	4	*k*-1305(*i*-1110)
9	23839	2(*d*)	*k*- 866	19	23375	1	*k*-1330
10	23729	1(*d*)	*k*- 976	20	23342	3(*d*)	*k*-1363(*i*-1174)

Table IV.—(*Concluded*)

No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	*I*	$\nu_0-\Delta\nu$
21	23315	3(*d*)	*k*-1390(*i*-1201)	51	21824	3(*b*, *d*)	*e*-1114
22	23258	5	*k*-1449	52	21782	3(*d*)	*k*-2923
23	23211	5	*k*-1494	53	21760	8(*s*)	*e*-1178
24	23172	2	*k*-1533(*i*-1339)(Hg)	54	21738	8(*s*)	*e*-1200(*k*-2980)
25	23154	$^1/_2$	*i*-1362	55	21679	6(*d*)	*e*-1259(*f*-1316)
26	23132	2	*k*-1573(*i*-1384)(Hg)	56	21638	5(*d*)	*e*-1300(*k*-3067)
27	23108	10	*k*-1597	57	21607	3	*e*-1331(*f*-1388)
28	23071	10	*k*-1634	58	21574	3	*e*-1364
29	23020	2	*i*-1496	59	21544	3	*e*-1994
30	22980	2	*i*-1536	60	21491	5	*e*-1447
31	22882	2	*i*-1634	61	21464	$^1/_2$	*f*-1531
32	22823	$^1/_2$(*b*, *d*)	*f*- 172	62	21445	5	*e*-1493(*i* -3071)
33	22761	2(*b*, *d*)	*e*- 177	63	21400	3	*f*-1595(*e*-1538)
34	22708	$^1/_2$(*d*)	*f*- 287(Hg)	64	21367	3	*e*-1571(*f*-1622)
35	22659	1(*b*, *d*)	*e*- 279	65	21341	10	*e*-1597
36	22591	$^1/_2$(*d*)	*f*- 404	66	21305	10	*e*-1633
37	22540	2(*d*)	*e*- 398	67	21296	1	*e*-1669
38	22466	0(*d*)	*e*- 472	68	21232	8(*d*)	*e*-1706
39	22367	4	*e*- 571	69	20073	2	*f*-2922
40	22323	6(*s*)	*e*- 615	70	20008	3	*e*-2920(*f*-2987)
41	22221	4(*b*, *d*)	*e*- 717	71	19957	3	*e*-2981
42	22163	3	*e*- 775	72	19874	5(*dv*)	*e*-3064
43	22126	0	*f*- 869				
44	22103	5	*e*- 835				
45	22071	5(*dr*)	*e*- 867				
46	22028	$^1/_2$?	*f*- 967				
47	21961	1(*d*)	*e*- 977(*f*-1034)				
48	21942	10(*s*)	*e*- 996				
49	21913	3(*s*)	*e*-1025				
50	21778	$^1/_2$(*d*)	*f*-1117				

$\overline{\Delta\nu}$: 177 (2 *b*, *d*) ? ; 279 (2 *bd*) ? ; 403 (2*d*) ; 475 (0) ? ; 571 (4) ; 616 (6 *s*) ; 717 (4 *b*, *d*) ? ; 836 (5) ; 867 (5 *d*) ; 977 (1 *d*) ; 996 (10 *s*) ; 1025 (3) ; 1116 (3 *b*, *d*) ; (1156) (3) ; 1178 (8) ; 1200 (8) ; 1259 (6 *d*) ; 1303 (5 *d*) ; 1331 (3) ; 1363 (3) ; 1392 (3) ; 1447 (5) ; 1494 (5) ; (1536) (3) ; 1572 (3) ; 1597 (10) ; 1634 (10) ; (1669) (1) ; 1706 (8 *d*) ; 2922 (3 *d*) ; 2981 (3) ; 3067 (5 *d*).

Table V.

Iso-propyl cinnamate $C_6H_5 \cdot CH:CH \cdot CO \cdot O \cdot CH(CH_3)_2$.

No.	ν in cm.⁻¹	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.⁻¹	*I*	$\nu_0-\Delta\nu$
1	24093	1/2	*k*- 612	26	21941	8	*e*- 997
2	23897	1/2	*k*- 808	27	21913	1(*d*)	*e*-1025
3	23710	4(*b*)	*k*- 995	28	21883	1(*d*)	*k*-2822
4	23681	1	*k*-1024	29	21825	1	*e*-1113(*k*-2880)
5	23592	1/2(*d*)	*k*-1113	30	21778	1	*k*-2927
6	23526	6(*d*)	*k*-1179	31	21761	7	*e*-1177
7	23505	6	*k*-1200	32	21739	7	*e*-1201
8	23445	4(*b*)	*k*-1260	33	21672	5(*d*)	*e*-1266
9	23401	1/2	*k*-1304(*i*-1115)	34	21632	4(*d*)	*e*-1305
10	23318	1	*k*-1387(*i*-1198)	35	21543	1/2	*e*-1395
11	23254	1	*k*-1451(*i*-1262)	36	21489	4	*e*-1449
12	23209	1	*k*-1496	37	21446	4	*e*-1492(*i*-3070)
13	23107	8	*k*-1598	38	21398	2	*f*-1597
14	23072	8	*k*-1633	39	21367	3	*e*-1571
15	22755	1(*bb*)	*e*- 183	40	21343	9	*e*-1595
16	22399	1/2	*e*- 399	41	21306	10	*e*-1631
17	22463	0	*e*- 475	42	21231	8	*e*-1707
18	22369	1(*d*)	*e*- 569	43	21116	1	*e*-2822
19	22322	4	*e*- 616	44	20016	1(*d*)	*e*-2922
20	22257	1	*e*- 681	45	19962	1/2(*d*)	*e*-2976
21	22211	2	*e*- 727	46	19872	1(*d*)	*e*-3066
22	22168	1	*e*- 770				
23	22122	5	*e*- 816				
24	22077	5	*e*- 861				
25	22047 ?	1/2	*e*- 891				

$\overline{\Delta\nu}$: 183 (1 *bb*); 399 (1/2); 475 (0); 569 (1 *d*); 616 (4); 681 (1); 727 (2); 770 (1); 814 (5); 861 (5); 891 (1/2); 996 (8); 1025 (2); 1113 (1); 1177 (7); 1201 (7); 1266 (5 *d*); 1305 (4 *d*); 1391 (1/2 *d*); 1450 (4); 1494 (4); 1597 (9); 1632 (10); 1707 (8); 2822 (1); 2925 (1 *d*); 2971 (1/2 *d*); 3070 (4 *d*).

Table VI.

Dimethyl phthalate $C_6H_4\cdot(CO\cdot O\cdot CH_3)_2$.

No.	ν in cm.⁻¹	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.⁻¹	*I*	$\nu_0-\Delta\nu$
1	24435	1/2	*q*-2953	21	22145	1/2	*e*- 793
2	24404	1/2	*p*-2949	22	21974	2(*b*, *d*)	*e*- 964
3	24319	1/2	*q*-3069(*k*- 386)	23	21899	6	*e*-1039
4	23885	2	*k*- 649	24	21856	1(*d*)	*k*-2849
5	23885	3	*k*- 820	25	21815	3(*d*)	*e*-1123
6	23741	1(*d*)	*k*- 964	26	21774	1	*e*-1163
7	23664	5	*k*-1041	27	21758	4	*e*-2947
8	23582	1(*b*, *d*)	*k*-1123	28	21666	5(*d*)	*e*-1272(*i*-2850)
9	23548	2(*d*)	*k*-1157(*i*- 968)	29	21633	7(*b*, *d*)	*k*-3072
10	23471	1/2	*i*-1045	30	21571	0	*i*-2945
11	23423	4(*b*, *d*)	*k*-1282	31	21492	1	*e*-1446
12	23265	1/2(*d*) ?	*k*-1440	32	21452	1	*e*-1486
13	23219	1/2	*k*-1486	33	21360	1/2	*e*-1578
14	23123	1	*k*-1582	34	21338	6	*e*-1600
15	23102	2	*k*-1603	35	21216	8	*e*-1722
16	22708	1(*d*)	*e*- 230	36	19988	4	*e*-2950
17	22641	0	*e*- 297	37	19868	3	*e*-3070
18	22539	1(*d*)	*e*- 399				
19	22287	3(*d*)	*e*- 651				
20	22120	6	*e*- 818				

$\overline{\Delta\nu}$: (230) (1 *d*) ? ; 297 (0) ; 393 (1 *d*) ; 650 (3 *d*) ; 793 (1/2) ; 819 (6) ; 964 (2 *b*, *d*) ; 1040 (6) ; 1123 (3 *d*) ; 1160 (1) ; 1277 (5 *d*) ; 1443 (1) ; 1486 (1) ; 1580 (2) ; 1602 (6) ; 1722 (8) ; 2849 (1 *d*) ; 2947 (4) ; 3071 (7 *b*, *d*).

Table VII.

Diethyl phthalate $C_6H_4(CO\cdot O\cdot CH_2\cdot CH_3)_2$.

No.	ν in cm.⁻¹	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.⁻¹	*I*	$\nu_0-\Delta\nu$
1	24416	1/2	*q*-2972	26	21836	4(*d*)	*f*-1159(*k*-2869)
2	24319	1(*d*)	*q*-3069	27	21816	2(*d*)	*e*-1122
3	24058	1(*d*)	*k*- 647	28	21779	7(*b*)	*e*-1159(*k*-2926)
4	23925 ?	0 ?	*k*- 780	29	21731	5(*b*)	*k*-2974(*f*-1264)
5	23860	1(*b*)	*k*- 845(*i*- 656)	30	21670	7(*d*)	*k*-1268
6	23670	5	*k*-1035(*i*- 846)	31	21632	8(*b*, *d*)	*k*-3073
7	23587	2(*b*, *d*)	*k*-1118	32	21577	2	*e*-1361(*i*-2939)
8	23544	2(*b*, *d*)	*k*-1161	33	21536	2	*i*-2978
9	23432	3(*b*, *d*)	*k*-1273	34	21489	3	*e*-1449
10	23334	1/2(*d*)	*k*-1371	35	21449	2	*e*-1489(*i*-3067)
11	23252	2	*k*-1453(*i*-1253)	36	21367	2	*e*-1571
12	23220	1/2	*k*-1485	37	21342	9(*s*)	*e*-1596
13	23172	0	*k*-1532	38	21220	8(*b*)	*e*-1718
14	23128	3	*k*-1577	39	20065	1	*f*-2930(*e*-2873)
15	23107	5	*k*-1598	40	20009	2	*e*-2929
16	22807	4(*b*, *d*)	*i*-1709	41	19965	2	*e*-2973
17	22592	1(*b*, *d*)	*e*- 346	42	19867	3	*e*-3071
18	22545	2	*e*- 393				
19	22294	5(*s*)	*e*- 644				
20	22159	2(*d*)	*e*- 779(*f*- 836)				
21	22096	5	*e*- 842				
22	22015 ?	1/2	*e*- 923				
23	21982	1/2	*f*-1013				
24	21922	1	*e*-1016				
25	21904	8(*s*)	*e*-1034				

$\overline{\Delta\nu}$: 346 (1 *b*, *d*); 393 (2); 644 (5 *s*); 779 (2 *d*); 843 (5); (923) (1/2); 1016 (1); 1034 (8 *s*); 1120 (2 *d*); 1160 (2 *b*); 1270 (7 *d*); 1362 (2); 1451 (3); 1487 (2); 1530 (1/2) ? ; 1574 (3); 1597 (9 *s*); 1718 (8 *b*); 2871 (5 *d*); 2928 (4 *b*); 2974 (3 *b*); 3070 (8 *b*).

Table VIII.

Methyl salicylate $C_6H_4\langle^{CO\cdot O\cdot CH_3}_{OH}$

No.	ν in cm.⁻¹	*I*	$\nu_0-\Delta\nu$	No.	ν in cm.⁻¹	*I*	$\nu_0-\Delta\nu$
1	24440 ?	1/2	*k*- 265	21	22134	6	*e*- 804
2	24282	1	*k*- 423	22	22093 ?	1/2	*e*- 845
3	24144	4	*k*- 561	23	21907	4	*e*-1031
4	23903	5	*k*- 802	24	21857	1	*e*-1081
5	23866	1/2(*b*)	*k*- 839	25	21808	3(*d*)	*e*-1130
6	23672	4	*k*-1033	26	21754	2	*k*-2951
7	23572	2(*b, d*)	*k*-1133	27	21695	5	*e*-1243
8	23460	5	*k*-1245	28	21614	5(*dd, b*)	*k*-3091(*e*-1324)
9	23377	5(*b*)	*k*-1328	29	21479	4(*d*)	*e*-1459
10	23270	1/2	*i*-1246	30	21364	1/2	*e*-1574
11	23240	3	*k*-1465	31	21335	1(*d*)	*e*-1603
12	23122	2(*d*)	*k*-1583	32	21266	5(*b, d*)	*e*-1672
13	23102 ?	1/2(*d*)	*k*-1603	33	19988	3	*e*-2950
14	22806 ?	1	*f*- 189	34	19861	3(*b, d*)	*e*-3077
15	22754	4	*e*- 184				
16	22677	1/2(*d*)	*e*- 261				
17	22582	2	*e*- 356				
18	22515	1	*e*- 423				
19	22424 ?	1/2	*e*- 514				
20	22380	4	*e*- 558				

$\overline{\Delta\nu}$: 184 (4); 264 (1/2 *d*) ?; (356) (2); 423 (1); (514) (1/2) ?; 560 (4); 804 (6); (845) (1/2) ?; 1032 (4); 1081 (1); 1132 (3 *d*); 1244 (5); 1326 (5 *b, d*); 1462 (4 *d*); 1578 (2 *d*); 1603 (1 *d*); 1672 (5 *b, d*); 2950 (3); 3084 (5 *bb, dd*).

Table IX.

Ethyl salicylate $C_6H_4\langle^{CO\cdot O\cdot CH_2\cdot CH_3}_{OH}$

No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$	No.	ν in cm.$^{-1}$	I	$\nu_0-\Delta\nu$
1	24402	½	*q*-2986	21	21901	4	*e*-1037
2	24253	2	*k*- 453	22	21830	1	*k*-2875
3	24143	4	*k*- 562	23	21773	1(*b*)	*k*-2932
4	23898	4	*k*- 807	24	21727	1	*k*-2978
5	23856	3	*k*- 849	25	21696	6(*b*)	*e*-1242
6	23674	4	*k*-1031	26	21621	5(*b, d*)	*k*-3084(*e*-1031)
7	23364	½(*d*) ?	*k*-1141	27	21575	½	*e*-1363
8	23462	5(*b*)	*k*-1243	28	21540	½	*e*-1398
9	23387	5(*b*)	*k*-1318	29	21479	4(*d*)	*e*-1459
10	23339	½ ?	*k*-1366	30	21327	½(*b, d*)?	*f*-1668
11	23312	½ ?	*k*-1393	31	21268	5(*d*)	*e*-1670
12	23238	4(*b, d*)	*k*-1467	32	20065	1(*d*)	*e*-2873
13	23119	1(*b, d*)	*i*-1396(*k*-1586)	33	20007	1(*d*)	*e*-2931(*f*-9288)
14	23102	1(*b, d*)	*k*-1603	34	19954	1(*d*)	*e*-2984
15	22771	3(*b, d*)	*e*- 167	35	19861	3(*b, d*)	*e*-3077
16	22693	2(*d*) ?	*e*- 245				
17	22481	½(*d*)	*e*- 457				
18	22381	4	*e*- 557				
19	22129	3	*e*- 809				
20	22090	2	*e*- 848				

$\overline{\Delta\nu}$: 167 (3 *b, d*); 245 (½ *d*) ? ; 452 (2) ? ; 559 (4); 808 (4); 848 (2); 1034 (4); 1141 (½ *b*); 1242 (6); 1318 (5 *b, d*); 1366 (½); 1395 (½); 1463 (4 *b, d*); (1586) (1 *b, d*) ? ; 1605 (½ *b, d*) ? ; 1670 (5 *d*); 2932 (1 *d*); 2980 (1 *d*); 3080 (5 *b, d*).

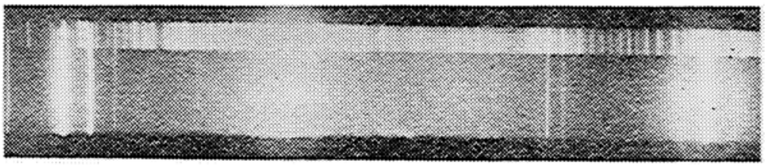
Table X.

Methyl phenyl carbinol $C_6H_5 \cdot CH(OH) - CH_3$.

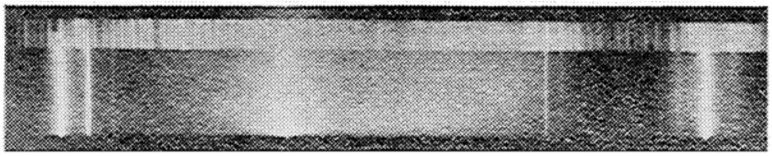
No.	ν in cm.⁻¹	I	ν₀—Δν	No.	ν in cm.⁻¹	I	ν₀—Δν
1	24219	½	k- 786	26	21865	½(b, d)	e-1073
2	23943	½(d)	k- 762	27	21835	½(d)	e-1103
3	23902	½(d)	i- 614	28	21783	5(dr)	k-2922(f-1212)
4	23711	5	k- 994	29	21740	7	e-1198(k-2965)
5	23684	2	k-1021	30	21674	1	e-1264
6	23500	½(d)	k-1205(i-1016)	31	21651	8(b, d)	k-3054
7	24437	½(d)	k-1268	32	21596	0(d)	i-2920
8	24311	0	k-1394(i-1205)	33	21543	1	e-1395(i-2973)
9	23257	½	k-1448	34	21494	2(d)	e-1444
10	23189	2(d)	k-1516(e- 251)	35	21458	3	i-3058
11	23108	5(d)	k-1597	36	21341	8	e-1597
12	22797	5(b, d)	e- 141	37	21261	4(b, d)	e-1678
13	22689	2(b, d)	e- 249	38	20081	1	f-2914
14	22619	1(d)	e- 319(f- 376)	39	20019	2	e-2919
15	22561	0(b, d)	e- 377	40	19964	½(d)	e-2974
16	22458	½(d)	e- 480(f- 531)	41	19886	5(b)	e-3052
17	22407	½	e- 531				
18	22324	4	e- 614				
19	22216	½	f- 779 ?				
20	22174	4(b)	e- 764				
21	22086	½(d)	e- 852 ?				
22	22039	2(b)	e- 899				
23	21980 ?	0	f-1015				
24	21947	10	e- 991				
25	21918	5	e-1020				

$\overline{\Delta\nu}$: 141 (5 *b*, *d*); 249 (2 *b*, *d*); (319) (1 *d*) ?; (377) (0 *d*) ?; 483 (½); (531) (½) ?; 614 (4); 763 (4 *b*); 852 (½ *d*); 899 (2 *b*); 993 (10); 1021 (½); 1073 (½ *b*, *d*); (1103) (½ *d*); (1161) (5 *d*) ?; 1201 (7); 1395 (1); 1446 (2 *d*); 1597 (8); 1678 (4 *b*, *d*); 2922 (5 *dr*); 2971 (7) ?; 3054 (8 *b*, *d*).

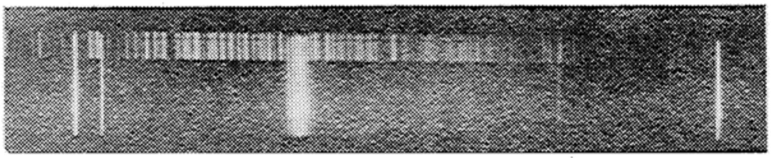
(1) Methyl phenyl acetate $C_6H_5 \cdot CH_2 \cdot CO \cdot O \cdot CH_3$



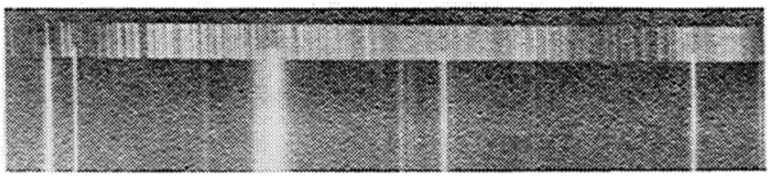
(2) Ethyl phenyl acetate $C_6H_5 \cdot CH_2 \cdot CO \cdot O \cdot CH_2CH_3$



(3) Ethyl phenyl propionate $C_6H_5 \cdot CH_2CH_2 \cdot CO \cdot O \cdot CH_2CH_3$

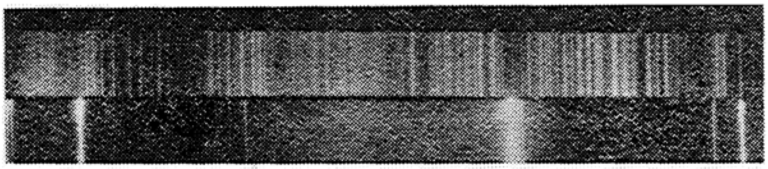


(4) Ethyl cinnamate $C_6H_5 \cdot CH:CH \cdot CO \cdot O \cdot CH_2CH_3$

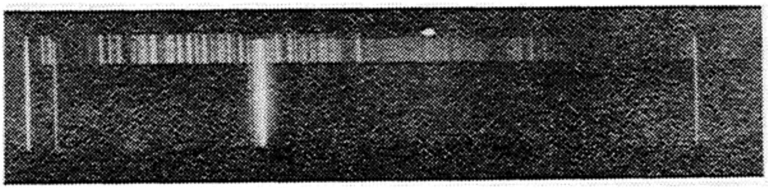


(5) Iso-propyl cinnamate $C_6H_5 \cdot CH:CH \cdot CO \cdot O \cdot CH(CH_3)_2$

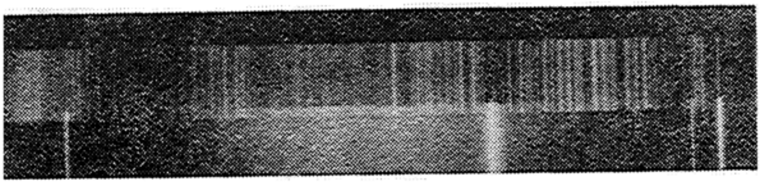
(6) Di-methyl phthalate $C_6H_4\cdot(CO\cdot O\cdot CH_3)_2$



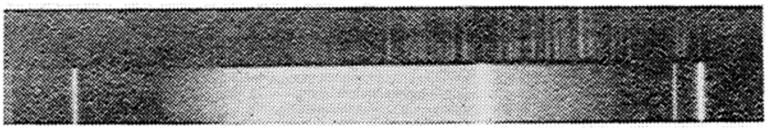
(7) Di-ethyl phthalate $C_6H_4\cdot(CO\cdot O\cdot CH_2CH_3)_2$



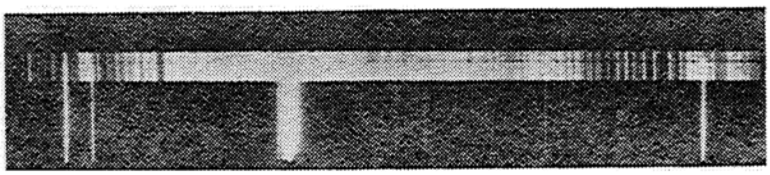
(8) Methyl salicylate $C_6H_4{<}^{CO\cdot O\cdot CH_3}_{OH}$



(9) Ethyl salicylate $C_6H_4{<}^{CO\cdot O\cdot CH_2CH_3}_{OH}$



(10) Methyl phenyl carbinol $C_6H_5\cdot CH{<}^{CH_3}_{OH}$



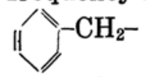
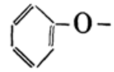
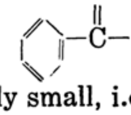
Discussion of the Results. As reported in this and the previous paper,[1] the frequency of $\Delta\nu = 3060$ cm.$^{-1}$ which has been known to be attributable to the C—H linkage in the benzene ring, was found as one of the most intense lines in the Raman spectra of the aromatic compounds investigated. For the comparison, the data observed are shown in the following :

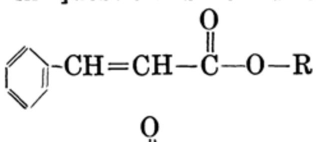
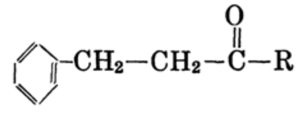
$C_6H_5 \cdot CO \cdot O \cdot R$	3070 cm.$^{-1}$	$C_6H_5 \cdot CO \cdot Cl$	3067 cm.$^{-1}$
$C_6H_5 \cdot CH_2 \cdot CO \cdot O \cdot R$	3057	$C_6H_5 \cdot O \cdot CO \cdot R$	3062
$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO \cdot O \cdot R$	3056	$CH_3 \cdot C_6H_4 \cdot O \cdot CO \cdot R$	3053
$C_6H_5 \cdot CH{:}CH \cdot CO \cdot O \cdot R$	3067	$HO \cdot C_6H_4 \cdot CO \cdot O \cdot R$	3080
$C_6H_5 \cdot CH(OH){-}CH_3$	3054	$C_6H_4 \cdot (CO \cdot O \cdot R)_2$	3070

The results of other authors[9] are ;

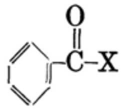
$C_5H_5 \cdot CH_3$	3054 cm.$^{-1}$	$C_6H_5 \cdot CH_2NO_2$	3059 cm.$^{-1}$
$C_6H_5 \cdot CH_2 \cdot Cl$	3054	$C_6H_5 \cdot CH_2 \cdot CH{:}CH_2$	3057
$C_6H_5 \cdot CH_2 \cdot NH_2$	3050	$C_6H_5 \cdot CH_2 \cdot CBr{:}CH_2$	3056
$C_6H_5 \cdot CH_2 \cdot OH$	3050	$C_6H_5 \cdot CO \cdot C_6H_5$	3052
$C_6H_5 \cdot CH_2 \cdot CN$	3057		

From these experimental data, we may suppose that in the aromatic compounds this frequency is influenced, to the first degree of approximation, only by the characteristics of the group or the atom adjacent to the carbon atom in the benzene ring.

It is observed that the frequency in question is found to be $\Delta\nu = 3055$ cm.$^{-1}$ in the compounds of  type, 3065 cm.$^{-1}$ in those of  type and 3070 cm.$^{-1}$ in those of  type. In the case of $C_6H_5 \cdot CO \cdot C_6H_5$[9] the shift is exceptionally small, i.e. is 3052 cm.$^{-1}$ which may be due to its symmetric form.

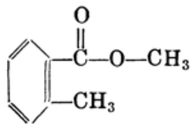
The fact that the frequency in question is found to be 3067 cm.$^{-1}$ in ethyl and iso-propyl cinnamates  and 3056 cm.$^{-1}$ in ethyl phenyl propionate  shows that the higher

(9) Kohlrausch, " Der Smekal-Raman Effect," 328–332.

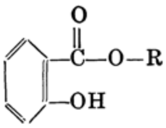
value of the frequency is due to the influence of the double bond of the carbon, $-\overset{\|}{C}-$, adjacent to the benzene ring, viz.,  .

Systematic studies[10] of the derivatives of benzene have shown that the benzene nucleus is characterized by a number of very constant frequencies, viz., $\Delta\nu = 616$, 1000, 1166 and 1595 cm.$^{-1}$, and the aromatic C—H frequency of 3060 cm.$^{-1}$ which has been just mentioned.

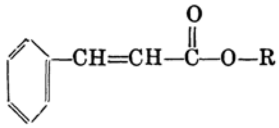
In the present experiment, it was observed that frequencies of $\Delta\nu = 615$ and 1000 cm.$^{-1}$ were shown in a good constancy in monoderivatives of benzene and they disappeared in the case of di-derivatives such as phthalates, salicylates and *o*-kresyl acetates. In place of 615 cm.$^{-1}$ in the di-derivatives (ortho), however, the frequency of $\Delta\nu = 562$ cm.$^{-1}$ in *o*-kresylacetate and 560 cm.$^{-1}$ in methyl and ethyl salicylate were observed with the same intensity. And both the frequencies of $\Delta\nu = 571$ and 616 cm.$^{-1}$ were observed in ethyl and iso-propyl cinnamates.



$\Delta\nu = 562$ cm.$^{-1}$



$\Delta\nu = 560$ cm.$^{-1}$



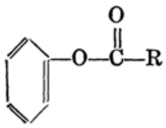
$\Delta\nu = 571$, 616 cm.$^{-1}$

Since all the substances studied contain the C=O group, the comparison of the influences on the frequency due to this linkage seems to be interesting. The lines associated with this linkage are broad, diffuse and intense. The constitutive influences of the substituents attached to the carbonyl group have been studied by Dadieu-Kohlrausch.[11] Considering the data we obtained in the previous and the present experiments the following facts are recognized.

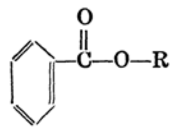
The C:O frequency is directly influenced by an atom or atom group attached directly to it, and independent of the group faraway from it. As shown below, in the cases of phenol esters of fatty acids and *o*-kresyl acetate, the shifts due to the C:O group are practically the same, i.e., 1760 and 1764 cm.$^{-1}$ So are the cases in the benzoates and the alkyl phthalates, the value of the shift in the latter esters decreases about 40 cm.$^{-1}$ from that of the former.

(10) *Monat. Chem.*, **60** (1932), 253; **61** (1932), 426; Kohlrausch, "Smekal-Raman Effect," 227.

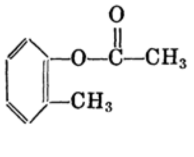
(11) *Ber.*, (B) **66** (1933), 1–12; Kohlrausch, "Smekal-Raman Effect," 157.



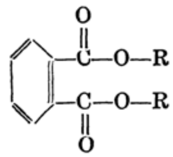
Δν = 1761 cm.$^{-1}$



Δν = 1720.

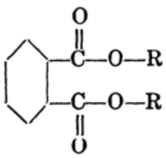


Δν = 1764 cm.$^{-1}$

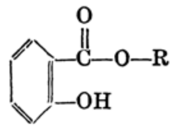


Δν = 1718 cm.$^{-1}$

In the case of salicylates, the OH group exerts a remarkable influence on the C : O linkage, even when the OH group is not directly attached to the same carbon atom of the C : O linkage. By the exchange of the -CO—O—R group of alkyl phthalates into OH, the shift decreases from 1718 cm.$^{-1}$ to 1672 cm.$^{-1}$

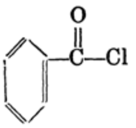


Δν = 1718 cm.$^{-1}$

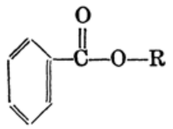


Δν = 1672 cm.$^{-1}$

On the other hand, the Cl atom seems to exert an opposite influence on the C : O group. Benzoyl chloride(1) and acetyl chloride(12) have the high values of 1768 and 1797 cm.$^{-1}$ respectively, compared with the low values of alkyl benzoates and acetyl acetate.



Δν = 1768 cm.$^{-1}$



Δν = 1720 cm.$^{-1}$

$CH_3 \cdot CO \cdot Cl$

Δν = 1797 cm.$^{-1}$

$CH_3 \cdot CO \cdot O \cdot CH_3$

Δν = 1737 cm.$^{-1}$

(12) Kohlrausch, "Smekal-Raman Effect," 318.

Thus the difference between the frequencies of C=O linkage in esters and the corresponding acid chlorides is about 50 cm.$^{-1}$

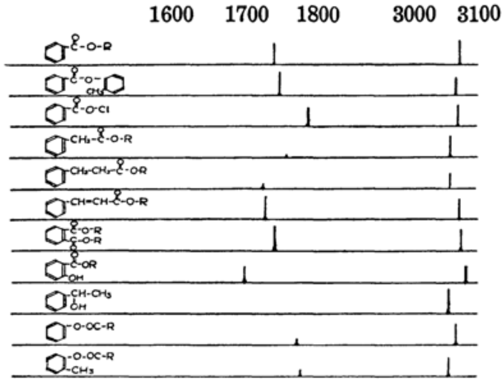


Fig. 1.

It was observed that the intensities of the frequencies due to the C=O linkage are strong in the case of esters of benzoic acid, cinnamic acid, phthalic acid, salicylic acid and benzoyl chloride, but weak in the case of phenol esters of fatty acids, alkyl esters of phenylacetic acid and ethyl ester of phenyl propionic acid. The difference of the intensities of these two kinds is so distinct that we can recognize it even under the visual measurement. It may be considered, in this case, that the –C=C– attached to the –C=O group strengthens the intensity of the latter linkage.

The frequency of $\Delta\nu$=804 in methyl salicylate and that of 814 cm.$^{-1}$ in dimethyl phthalate seems to be corresponded to that of 814 cm.$^{-1}$ in methyl benzoate(1) which may be attributable to the frequency of the system of $-\overset{\|}{C}-O-CH_3$. In ethyl salicylate and diethyl phthalate, the frequencies of 845 and 843 cm.$^{-1}$ have been observed, which may be attributable to the vibration of the system $-\overset{\|}{C}-O-CH_2-$ as in the case of ethyl benzoate.(1) A very weak line of $\Delta\nu$ = 845 in methyl salicylate observed may be considered as due to its impurity. These two kinds of frequencies were observed also in methyl- and ethyl-phenylacetates. They were, however, broad and

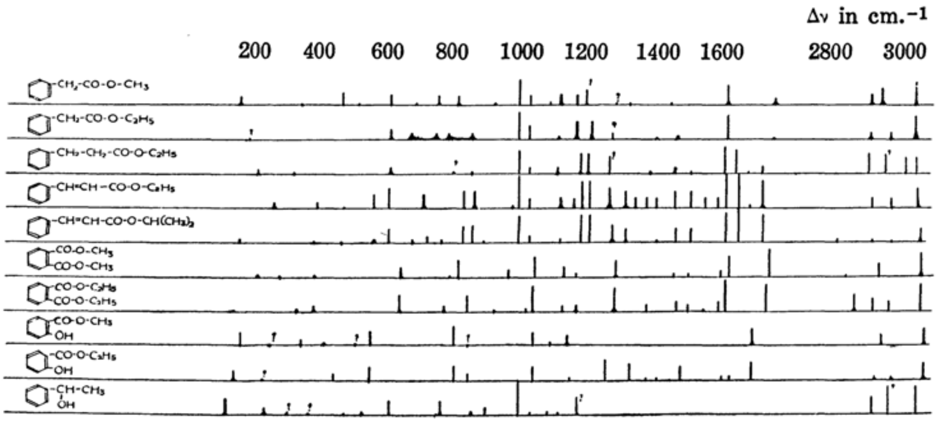
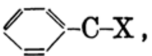
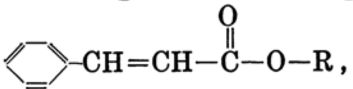
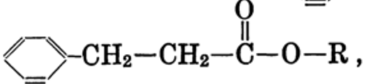
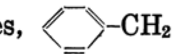
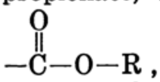
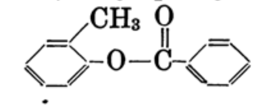
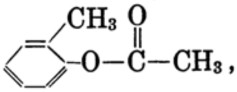


Fig. 2.

diffuse, moreover, on acount of the strong back ground appeared on the plates, the measurement could not be done exactly.

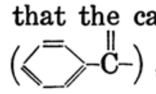
Two frequencies of 836, 867 cm.$^{-1}$ in ethyl cinnamate and 814, 867 cm.$^{-1}$ in iso-propyl cinnamate were clearly observed. It may be explained that the lower frequencies, viz., 836 in ethyl- and 814 cm.$^{-1}$ in iso-propyl cinnamates, are arising from the same origin mentioned above, namely that they are caused by the $-\overset{\|}{C}\diagup^{O}\diagdown CH_2-$ or $-\overset{\|}{C}\diagup^{O}\diagdown CH_3$ group, but the higher one, viz., 867 in both cases is caused by other linkage of the molecular rest. The confirmation on the facts however, will be made in near future, by studying the corresponding acid and other compounds.

The frequency of 763 cm.$^{-1}$ in methyl phenyl carbinol is estimated as the vibration between benzene ring and the carbon atom attached to it. The reason is this. The same frequency is observed in all the substances which have a vibration system, benzene ring and an attaching carbon like ;

, such as cinnamates, , ethyl phenyl propionate, , alkyl phenyl acetates,  , *o*-kresyl benzoate, , *o*-kresylacetate, , as shown in these experiments. Toluol, ethyl benzol and phenyl nitromethane[13] etc. have also the same shift in their Raman spectra.

Summary.

(1) The Raman spectra of methyl phenylacetate, ethyl phenylacetate, ethyl phenylpropionate, ethyl cinnamate, iso-propyl cinnamate, dimethyl phthalate, diethyl phthalate, methyl salicylate, ethyl salicylate and methyl phenyl carbinol were studied.

(2) The constitutive influences exerted on the C—H of the benzene ring were observed. It was found that the carbon with the double bond ($-\overset{\|}{C}-$) attached to the benzene ring , such as in the case of $C_6H_5 \cdot CO \cdot O \cdot R$ and $C_6H_5 \cdot CH=CH \cdot CO \cdot O \cdot R$ gave the higher frequency ($\Delta\nu =$ 3070) than that ($\Delta\nu = 3055$) in the case of $C_6H_5 \cdot CH_2 \cdot \overset{O}{\overset{\|}{C}}-O-R$ and other

(13) Kohlrausch, "Smekal-Raman Effect," 329–332.

compounds of the type, $C_6H_5 \cdot CH_2-X$ which have no carbon with double bond directly attached to the benzene ring.

(3) The constitutive influences exerted on the carbonyl group were observed.

(4) Disappearance of 615 cm.$^{-1}$ in diderivatives and appearance of 560 cm.$^{-1}$ in salicylates, *o*-kresyl acetate, *o*-kresyl benzoate and cinnamate were observed.

(5) Estimation of the valency frequencies of the $-\overset{\|}{C}\diagup^{O}\diagdown CH_2-$ linkage was confirmed.

Laboratory of Physical and Inorganic Chemistry,
Taihoku Imperial University, Taihoku.